All the plenary lectures speackers with the HOPV meeting organizers: From Left to Right (2nd row) : Prof. Laurie M. Peter, Prof. Arie Zaban, Mr. Gavin Tulloch, Prof. Craig Grimes, Prof. Michael Grätzel, *Dr. Emilio Palomares*, *Dr. Roberto Gómez, Prof. Juan Bisquert*. 1st row , Prof. Anders Hagfeldt, Prof. James R. Durrant, Prof. Taro Toyoda, Dr. Francisco Fabregat-Santiago, Prof. Prashant Kamat, Prof. Shozo Yanagida and Dr. Mortiz Riede

Report HOPV meeting

HOPV meeting committee.

The HOPV meeting was organised by : Professor Juan Bisquert (Universitat Jaume I, Castelló Spain), Dr. Emilio Palomares, ICREA research Professor at the Institute of Chemical Research of Catalonia (Tarragona, Spain), Dr. Roberto Gómez Senior Lecturer at the Unviversitat d'Alacant and Prof. Vasco Teixeira (University of Minho, Portugal).,

HOPV meeting abstract.

The meeting was organised from Sunday 10 to Wednesday 13 in May. During the 3 days all scientists stayed together at the Hotel Bali in Benidorm (Alicante , Spain).

The meeting was focussed on the advent of new molecular photovoltaic technologies. The key scientists on the different research areas namely (1) Dye Solar Cells, (2) Organic Bulk Heterojunction Solar Cells and (3) Organic Small Molecule Solar Cells. As an example, the list of plenary lectures included talks by Professor Michael Grätzel (EPFL, Laussane, Suitzeland), Professor James R. Durrant (ICL, Lond, UK), Professor Shozo Yanagida (Osaka University, Japan) and Dr. Moritz Reide (TUD, Dresden, Germany).

The discussions were focussed not only on the achievement of devices to convert light-to-energy conversion devices at low cost ,but also on the development of new materials and techniques to study and improve the existent technologies.

Every day, after the plenary lectures, an impressive panel of young speakers were delivering short communications (15 minutes) on the vanguard of each technology. Moreover, after these sessions, a poster session that allowed pre-doctoral and junior researchers to present their work was scheduled.

The meeting will be for sure the starting point for future EU research projects under the FP7 program not only at the Energy call but also in the nanomaterials area.

As a remarkable issue, we would like to stress that the HOPV meeting was on the Spanish newspapers and in local and regional television programs.

Public Program for the HOPV meeting.

Day	Time	Place		Included in registr.
	Day 0	10-May		
0	21:00-	Garden	Reception	Yes
	Day 1	11-May		
1	9:00-9:30		Opening	
1		Auditorium	Chairman, Director of Science Policy of Valencia, Major of Benidorm, Rector Universitat d'Alacant	
1	9:30-13:30		General session	
1	9:30-11:00	Auditorium	Keynote, OG1 (Invited sps.)	
1	11:00-11:30		Coffee break	Yes
1	11:30-13:30	Auditorium	Oral OG2-OG5 (Invited sps.)	
1	13:30-16:00		Lunch	Yes
1	16:00-17:30		Parallel sessions A and B	
1		Rooms 1 and 2	Oral OA1-OA4, OB1-OB4	
1	17:30-19:00	Auditorium	Break and exhibition	
	17:30-19:00	Auditorium	Coffe break and Exhibition	Yes
	17:30-19:00	Rooms ##	Project meetings (project representatives)	
1	19:00-20:30		Poster session A	
		Auditorium	Posters PA1-PA15	
1	22:00-		Night party	Optional
		Place to be announced	Party in honor of Dr. Carole K. Clark-Grätzel and Prof. Michael Grätzel	
	Day 2	12-May		
2	9:00-13:30		General Session	
2	9:00-11:00	Auditorium	Oral OG6-OG9 (Invited sps.)	
2	11:00-11:30		Coffee break	Yes
2	11:30-12:00	Auditorium	Oral OG10-OG13 (Invited sps.)	
2	13:30-16:00		Lunch	Yes
2	16:00-18:00		Parallel sessions C and D	
2		Room 1 and 2	Oral OC1-OC6, OD1-OD6	
2	18:00-19:00	Auditorium	Break and exhibition	Yes
2	19:00-20:00		Poster session B	
		Auditorium	Posters PB1-PB15	
	21:00-	Auditorium	Banquet	Yes
	Day 3	13 May		
3	9:00-13:20		Parallel sessions O and F	
3	9:00-11:00	Room 1 and 2	Oral OE1-OE6, OF1-OF6	
3	11:00-11:30		Coffee break	Yes
3	11:30-13:20	Room 1 and 2	Oral OE7-OE11, OF7-OF11	
3	13:20-13:30		Closing	
		Room 1	Closing and Announcement of HOPV10	

Description of the scientific content of and discussion at HOPV.

The research on carbon neutral renewable energy sources based upon the combination of supramolecular chemistry, nanostructured inorganic materials science and optoelectronic device physics is emerging as a powerful technology platform for the 21st Century. The particular interest of the HOPV meeting was the discussion on the development of light driven molecular devices where the limited functionalities of individual molecules and materials are enhanced by their organisation into larger hybrid self-organised systems, which can be used to convert light into different types of energy sources such as photovoltaic devices.

Semiconductor crystalline nanoparticles, organic molecules and molecular materials are well stabilised as attractive materials for the integration of molecules and supramolecular structures into photovoltaic devices as illustrated in **Figure 1.**

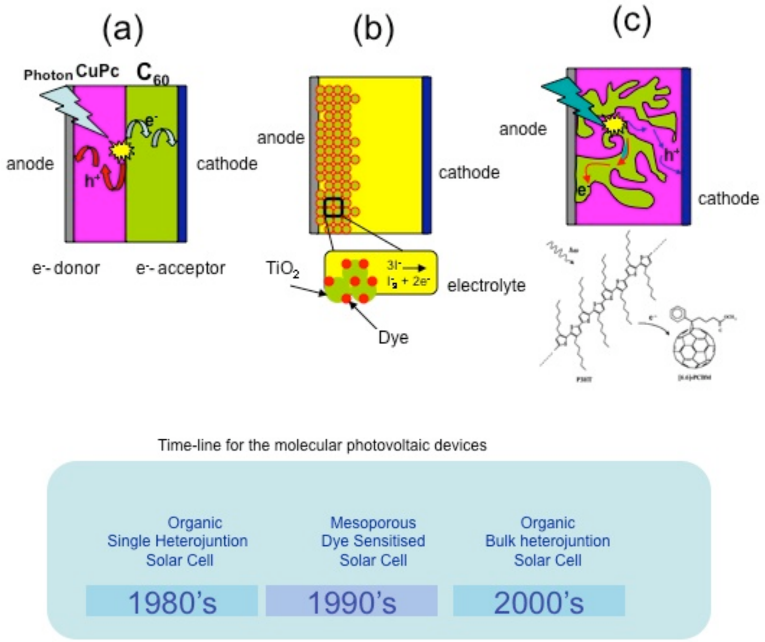


Figure 1. Several examples of molecular systems for photovoltaic devices currently investigated. (a) small organic molecule solar cell, (b) Gratzel cell and (c) organic bulk heterojunction solar cell.

At the HOPV meeting the 3 technologies, represented in **Figure 1**, were discussed.

The meeting contents are described below:

On Dye Solar Cells (DSC).

1. Device characterization
2. New materials for light harvesting.
3. New strategies for the achievement of efficient devices.
4. New strategies for long-term stability.
5. Latest advances on the Dye Solar Cell commercialization.

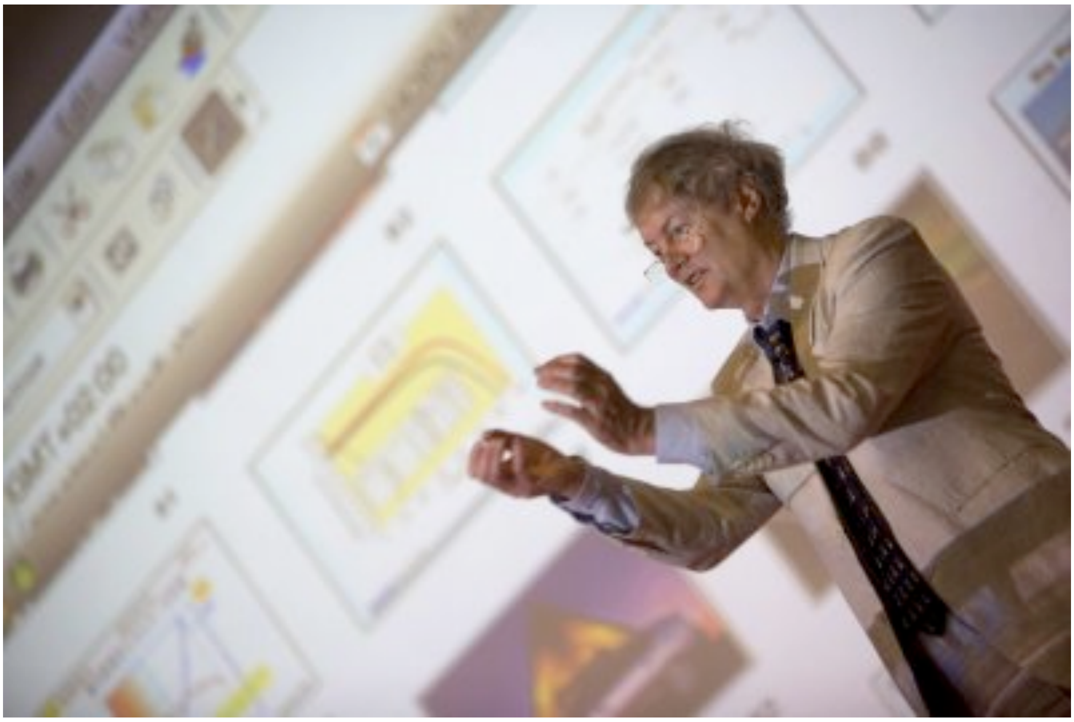
On Organic Bulk-Heterojuntion Solar Cells (OPV).

1. New events on the charge transfer characterization of the active materials.
2. New materials for light absorption on the near IR region of the solar spectrum.
3. New electron acceptors
4. New techniques to establish a device function-materials structure relationship.
5. The state-of-the art device efficiency and long term stability.

On Organic Small Molecule Solar Cells (OSMC).

1. State-of-the art on multi layer devices.
2. Record efficiencies and prospects for future materials
3. The effect of organic dopants on the device performance.
4. New tools to study charge transfer processes in OSMC.

The meting was organized to emphasize the discussion after the plenary lectures. We have included on this report several pictures tacking during the lectures and, later, on the discussion time..



Prof. Michael Grätzel (EPFL, Lausanne, Switzerland) during the keynote lecture on Dye Solar Cells.

Time for scientific discussion during the "coffee-break". In the picture (right) Prof. Craig Grimes listening the comments and suggestions after his lecture on quantum dot for photovoltaic's.

Young pre-doctoral and junior scientist attending the lectures.

A perspective of the audience during the lectures.

Prof. Juan Bisquert, HOPV coordinator, closing the meeting and thanking the ESF for their support through the ORGANISOLAR network.

Impact of HOPV on the future directions of the field.

The HOPV meeting has stablished a new paradigme of conferences in Europe by combining the lectures of world research leaders with starting tenure track researchers plus the vision of experinced of industrial leaders on the development of molecular photovoltaic devices.

At the HOPV meeting a key point was to stablish new collaborations with research institutions that have not been involved in joint research projects before. Thus, we expect that an increase on the FP7 proposals in the area of Energy and NMP should come from the HOPV interactions. Moreover, exchange of students between the research groups through national or european networks was also discussed.

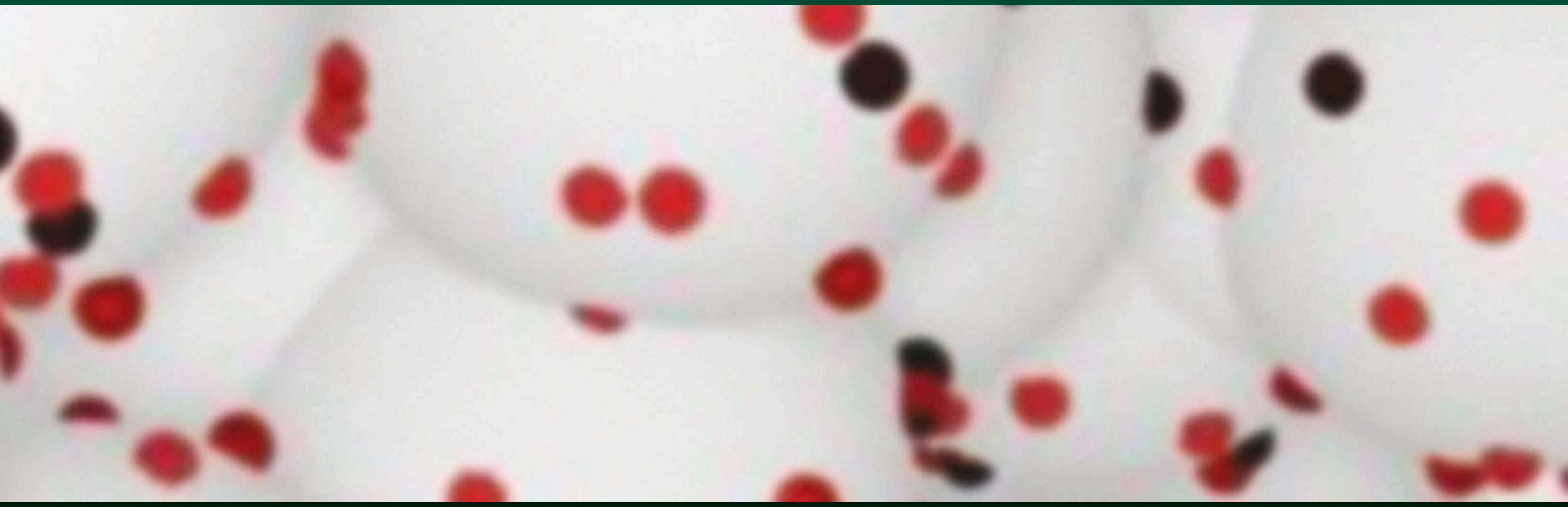
Finally, it was clear the success of HOPV and Prof. Filippo de Angelis (Isituto di Scienze e Technologie Molecolari del CNR, ISTM-CNT, Perugia, Italy) has proposed to continue the HOPV meeting next year 2009 in Italy .

From the technology transfer point of view, the attendance of the world leader industries on molecular photovoltaic (i.e. Dye Sol) allowed the groups to present their latest results on new dyes, electrolytes, and materials in general that may become part of the offer of Dye Sol in th near future.

HOPV09

Hybrid and Organic Photovoltaics Conference

BOOK OF ABSTRACTS



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BENIDORM

Sunday 10 - Wednesday 13 may 2009
Gran Hotel Bali
Benidorm, Spain

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ORAL PRESENTATIONS

KEYNOTE

K1	Michael Grätzel*	Power from the Sun: The Advent of Mesoscopic Solar Cells

INVITED

OG1	Oomman K. Varghese, Maggie Paulose, Xinjian Feng, Karthir Shankar, Gopal K. Mor, Craig A. Grimes*	Synthesis of Vertically Oriented TiO2 Nanotube/wire Arrays on FTO Coated Glass Substrates: Application to Hybrid, Organic and FRET Photovoltaics
OG2	Peng Wang*	Exotic organic optoelectronic materials in high-performance dye-sensitized solar cells
OG3	Prashant V. Kamat*	Solar Cell by Design. Harvesting Light Energy with Semiconductor Quantum Dots
OG4	Taro Toyoda*, Lina J. Diguna, and Qing Shen	Photovoltaic and Ultrafast Carrier Dynamic Properties of CdSe Quantum Dot-Sensitized Solar Cells Using Inverse Opal TiO2 Electrodes
OG5	G. Tulloch*, J. Desilvestro, P. Murray, R. Platts, R. Harikisun, A. Thein, M. Holding	Flexible Dye Solar Cells - stable performance in all light conditions
OG6	Shay Yahav, Sven Rühle, Arie Zaban*	Modification of Semiconductor-sensitized-electrolyte interface for efficient quantum-dot sensitized solar cell
OG7	Shozo Yanagida*, Yukyeong Kim, Youhai Yu, Kazuhiro Manseki	Nano-crystalline TiO2 Solar Cells fabricated using Aniline Oligomers as Hole Conductors
OG8	Anders Hagfeldt*	DSC tool-box – an integrated approach
OG9	Halina Dunn, James Jennings, Laurence Peter*, Alison Walker and Hongxia Wang	Studies of electron transport, trapping and electron transfer in dye-sensitized solar cells
OG10	Francisco Fabregat-Santiago*, Marcio Góes, Iván Mora-Seró, Eva M. Barea, Lourdes Marquez and Juan Bisquert	Transport and charge accumulation in nanotube based dye solar cells
OG11	James R. Durrant*	Charge photogeneration and recombination in dye sensitized and polymer / fullerene solar cells
OG12	Moritz Riede*	Optimizing Organic Solar Cells based on Small Molecules
OG13	L. Lutsen*, B. Campo, W. Oosterbaan, S. Bertho, A. Hadipour, D.Vanderzande	Stability problem of polymer based bulk heterojunction solar cells

PARALLEL SESSIONS

OA1	Shogo Mori*, Masanori Miyashita, Kenji Sunahara, Nagatoshi Koumura, Kohjiro Hara, Attila J. Mozer, Pawel Wagner, Wayne M. Campbell, David L. Officer, and Gordon G. Wallace	Factors influencing electron lifetime in dye-sensitized solar cells: Molecular structure of sensitizers, electrolytes and co-adsorbents
OA2	Tsukasa Yoshida* , Kazumasa Funabiki, Masaki Matsui, Hidetoshi Miura, and Yoshiya Fujishita	Plastic solar cells employing electrodeposited porous crystalline ZnO sensitized with organic dyes
OA3	F. De Angelis*, S. Fantacci	Ab initio simulation of Dye Sensitized Solar Cells
OA4	H. Choi, S. Kim, S. O. Kang, J. Ko, M. S. Kang, J. N. Clifford*, A. Forneli, M. K. Nazeeruddin, M. Grätzel and E. Palomares	Stepwise Co-Sensitization of Nanocrystalline TiO2 in DSSC
OA5	Zion Tachan*, Sven Rühle, Larissa Grinis, Arie Zaban	Dye Sensitized Solar Tube

OE7	E. Azaceta, R. Tena-Zaera*, R. Marcilla, D. Mecerreyes, J. Pomposo, H. Grande	Electrodeposition of ZnO in ionic liquids
OE8	M. Moya, M. Mollar and B. Marí*	Study of Eosin-Y/ZnO hybrid films electrodeposited in aqueous and organic solvents
OE9	J. A. Anta, C. Fernández-Lorenzo, R. Alcántara, J. Martín-Calleja, E. Guillén*	Solvent-free ZnO dye-sensitised solar cells
OE10	C. Prasittichai*,J. T. Hupp	Surface modification of nanoparticulate semiconductor by ALD
OF1	Christophe Defranoux*, J.P. Piel, A. Bourgeois.	Characterization of organic solar cells materials and structures by spectroscopic ellipsometric.
OF2	I. Etxeberria, U. Muñecas, M. Neophytou, J.Ajuria*, C. Waldauf, R. Pacios, J.C. Jimeno	Hybrid polymer: fullerene/silicon photovoltaic cells for maximizing the light harvesting
OF3	E. Cloutet*, M. Urien, H. Erothu, R.C. Hiorns, H. Cramail, L. Vignau	Photovoltaic solar cells based on Rod-Coil Block Copolymers Containing Poly(3-hexylthiophene) and Fullerene
OF4	R. García-Valverde*, N. Espinosa-Martínez, J. Padilla, J. Abad, J. Colchero and A. Urbina	Life Cycle Assessment of Organic Solar Cells
OF5	R. C. Hiorns*, E. Cloutet, E. Ibarboure, L. Vignaub, N. Lemaitre, S. Guillerez, H. Cramail	Main-chain fullerene polymers for photovoltaic devices
OF6	A. Ndobe*, C. Kitts, E. Margapoti, M. Muccini	Detail balance in morphology for efficient bulk heterojunction solar cell
OF7	Antonio Toffoletti, Lorenzo Franco, Lucia Bonoldi*, Luciano Montanari, Riccardo Po' , Giuliana Schimperna, Andrea Pellegrino , Maria Caldararo	LESR and TRESR characterization of fluorene-based polymer for organic photovoltaic cells
OF8	Roger Häusermann*, Nils A. Reinke, Evelyne Huber, Thomas Flatz, Michael Moos and Beat Ruhstaller	CT-State Dissociation and Charge Recombination in Organic Photovoltaic Cells
OF9	Youngsoo Kim, Tae-Kycong Lee and Kang-Jin Kim*	Enhanced performance of dyc-sensitized solar cells incorporated with functionalized Si nanoparticles as co-sensitizer

POSTER PRESENTATIONS

PA

PA1	Fabian Werner*, Renata Marczak, Jan-Frederik Gnichwitz, Andreas Hirsch, Wolfgang Peukert, Emilio Palomares and Dirk M. Guldi	ZnO – Porphyrin Dye Sensitized Solar Cells
PA2	I. Gonzalez-Valls*, M. Lira-Cantu	Vertically-Aligned Nanostructures of ZnO for Excitonic Solar Cells
PA3	Sophia Buhbut, Arie Zaban	ZnO nanorods based spectral splitting for efficient PV systems
PA4	T. C. Li*, M. S. Góes, F. Fabregat-Santiago, J. Bisquert, P. R. Bueno, C. Prasittichai, J. T. Hupp, and T. J. Marks	Slowing Charge Recombination in Solid-State Devices with ALD Deposited Barrier Layers
PA5	Sylvia Paul, Dieter Neher	Study of the Performance of Hybrid Solar Cells Incorporating Dense TiO2 Layers
PA6	Mi Yeong Park, Yeong-Tae Kim, Kyu Hwan Lee, Young Soo Jeong, Dong Chan Lim*	Low-Dimensional Nanostructures based hybrid Photovoltaic

PA7	I. Tacchini, A. Ansón-Casaos, E. M. Terrado, J. D. Nuñez, A. M. Benito, W. K. Maser, M. T Martínez	Templated synthesis and characterization of modified TiO2 nanotubes
PA8	M. Planells*, F. J. Céspedes-Guirao, A. Sastre-Santos, F. Fernández-Lázaro, E. Palomares	Supramolecular interactions in Dye Sensitized Solar Cells
PA9	S. M. Feldt*, G. Boschloo, A. Hagfeldt	Characterization of surface passivation for dye sensitized solar cells, using the ferrocene redox couple
PA10	E. L. T. Unger*, A. Hagfeldt, G. Boschloo	Exciton enhanced dye sensitized solar cells
PA11	L. Cavigli*, A. Vinattieri, V. Faso, G. Baldi, F. Bogani	Volume versus surface-mediated recombination in titania nanoparticles
PA12	Libby Gibson* , A. L. Smeigh, P. Qin, L. Li, J. Fortage, F. Odobel, L. Sun, L. Hammarström, G.Boschloo, A. Hagfeldt.	p-Type Dye Sensitized Solar Cells
PA13	R. A. Jensen*, H. Van Ryswyk, J. T. Hupp	Porphyrin Dyes and Unconventional Photoelectrodes in Dye-Sensitized Solar Cells
PA14	T. Marinado,* K. Nonomura, D. P. Hagberg, L. Sun, A. Hagfeldt	The effect of organic dyes on the redox electrolyte recombination in Dye-Sensitized Solar Cells
PA15	A. Alessi, P. Biagini, S. Fanutti, N. Perin, M. Salvalaggio*, S. Spera and A. Tacca	Lanthanide luminescent organic complexes: effect of N-based co-ligands on photophysical properties
PA16	K. C. D. Robson, P. G. Bomben, B. D. Koivisto, C. P. Berlinguette*	Utility of Cyclometalated Ru Chromophores in the Dye-Sensitized Solar Cell
PA17	A. Gertsin, G. Muradova, A. Shoka, D. Kim, S. Bereznev*, A. Tverjanovich, J. Kois, A. Öpik and Yu. Tveryanovich	Microwave Assisted Synthesis of CuInSe2 Nanopowder
PA18	Kee Eun Lee*, Cecile Charboneau, Guobin Shan, Raynald Gauvin, George P. Demopoulos, and Oumarou Savadogo	Preparation and characterization of TiO2 thin films by screen printing: Evaluation of material property and parameter effects
PA19	N. Gonzalez-Pech*, M. Lira-Cantu	Dye Sensitized Solar Cell fabrication at CIN2: Paste formulation for commercial (P25) and hydrothermal synthesized TiO2
PA20	David Gutiérrez-Tauste*, José A. Ayllónb, Laurent Aubouya, Gabrielle Nellesc, Yvonne Joseph	Low-temperature preparation route for nanocrystalline TiO2 in multigram scale using R2TiF6 (R=BetH+, Cho+) ionic liquid like precursor solutions: Application in Dye-Sensitized Solar Cells
PA21	Francisco Montilla, María Angeles Cotarelo	Electrochemical Fluorescence Spectroscopy applied to the study of Energy Transfer in Conjugated Polymer Blends
PA22	M. Ramos-Silva, A. Matos-Beja, P. Martín-Ramos*, P. Chamorro-Posada, L.M. Navas-Gracia, J. Martín-Gil	Er- and Yb-complexes with fluorinated ligands for photonic applications in Telecommunications
PA23	V. Senkovskyy, M. Stamm, S. A. Gevorgyan, F. C. Krebs, and Anton Kiriy*	Surface-initiated polycondensation: a new tool for the preparation of complex architectures of conjugated polymers for solar cells
PA24	Teresita Ruiz-Anchondo, Hazel Morales-Rodríguez, Alberto Flores-Hidalgo and Daniel Glossman-Mitnik *	Computational Determination of the Molecular Structure and Properties of Nanostructured Materials for Organic Photovoltaics
PA25	A. Forneli, E. Martínez-Ferrero, A. Sánchez-Díaz, A. Vidal Ferran, B. C. O'Regan, A. Reynal Verdú* , E. Palomares	Understanding the relationship between dye structure and device efficiency

PB

K1

Power from the Sun:
The Advent of Mesoscopic Solar Cells

Michael Graetzel,
Laboratory of Photonics and Interfaces, Ecole Polytechnique Fédérale de Lausanne
CH-1015 Lausanne Switzerland
michael.graetzel@epfl.ch

The field of photovoltaic cells has been dominated so far by solid state p-n junction devices made of crystalline or amorphous silicon, CdTe and copper indium gallium diselenide (CIGS) profiting from the experience and material availability of the semiconductor industry. However there is an increasing awareness of the possible advantages of devices based on mesoscopic inorganic or organic semiconductors commonly referred to as “bulk“ junctions due to their interconnected three-dimensional structure. The nanocrystalline morphology produces an interface with a huge area endowing these systems with intriguing optoelectronic properties. These cells offer the prospect of very low cost fabrication without expensive and energy intensive high temperature and high vacuum processes. They can feasibly be produced employing flexible substrates and are compatible with a variety of embodiments and appearances to facilitate market entry, both for use in domestic devices as well as in architectural or decorative applications. The prototype of this new PV family is the dye-sensitized solar cell (DSC). This cell accomplishes the separation of the optical absorption and the charge separation processes by the association of a sensitizer as light-absorbing material with a wide band gap semiconductor of nanocrystalline morphology [1-3]. The DSC has made phenomenal progress since its discovery was announced in the scientific literature only 15 years ago. Conversion efficiencies of over 12 percent and excellent stability have now been reached rendering it a credible alternative to conventional p-n junction photovoltaic devices. Mesoscopic solar cells have become viable contenders for large-scale future solar energy conversion systems on the bases of cost, efficiency, stability and availability as well as environmental compatibility.

References

1.B.O'Regan and M.Grätzel, “*Nature* 335, 1991, 7377.
2.U.Bach, D.Lupo, P.Comte, J.E.Moser, F.Weissörtel, J.Salbeck, H.Spreitzert and M.Grätzel, *Nature*,395, 1998, 550.
3.M. Grätzel *Nature*, 414 , 2001, 338.

Acknowledgement: This work was supported by the Swiss National Science Foundation, the Swiss Federal Energy Offfce, the Swiss Commission of Technology and Research the “Robust DSC, EU Joule 7 Project, The Stanford KAUST Center on Advanced Molecular Photovoltics (CAMP), the European Research Office of the United States Air Force. Financial contributions by industrial partners are also gratefully acknowledged.

OG1

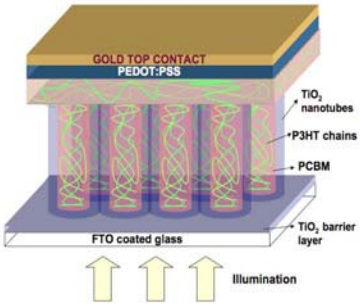
Synthesis of Vertically Oriented TiO2 Nanotube/wire Arrays on FTO Coated Glass Substrates: Application to Hybrid and Organic Photovoltaics

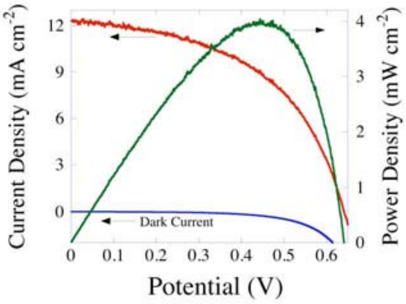
Oomman K. Varghese, Maggie Paulose, Xinjian Feng, Gopal K. Mor, Craig A. Grimes*
Department of Electrical Engineering The Pennsylvania State University, University Park, PA 16802

Synthesis of vertically oriented TiO2 (anatase) nanotube arrays, by anodic oxidation of a starting metal film sputtered on the FTO coated glass1, and (rutile) nanowire arrays on FTO coated glass substrates by a low temperature hydrothermal route2,are considered with application to heterojunction solar cells.

A depiction of a nanotube array based device is shown in **Figure 1**. In initial work we choose a nanotube length of 270 nm, and pore size of 50 nm which is large enough to allow the subsequent polymeric layer to infiltrate the nanotubes and allow the polymer to form a crystal structure similar to that in the bulk. The polymer used is a blend of an electron donor (P3HT) and an electron acceptor (PCBM); a 10 mg/ml solution of P3HT in chlorobenzene and 8 mg/ml solution of PCBM in chlorobenzene were mixed in a 1:1 ratio using the procedure outlined by Heeger and colleagues and infiltrated into the nanotubes. Subsequently a layer of hole injecting polymer Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) known more commonly as PEDOT:PSS was deposited by spin-coating an aqueous suspension of the polymer at 5000 rpm. The samples were then placed on a hot plate at 170°C for fifteen minutes to drive away residual water and to drive the polymer into the TiO2 nanotube arrays. All spincoating and baking steps were carried out in a nitrogen glovebox. A 50 nm film of gold was evaporated onto the devices though a shadow mask to form the top contact.

Charge separation in our device occurs at both the n-type TiO2-P3HT interface as well as the n-type PCBM-P3HT interface. The barrier layer of compact TiO2 at the bottom of the nanotube array prevents holes in the polymer from reaching the TCO contact. A key advantage of the TiO2 nanotube array electron accepting network is that it prevents the electron donating material (P3HT) and electron accepting materials (TiO2 and PCBM) from both being in contact with the anode and the cathode of the solar cell at the same time as is the case with the conventional bulk heterojunction device geometry. The resulting solid state solar cells show a short-circuit current density of 12.4 mA/cm2, 641 mV open circuit potential and a 0.51 fill factor yielding power conversion efficiencies of 4.1 % under AM 1.5 sun3.





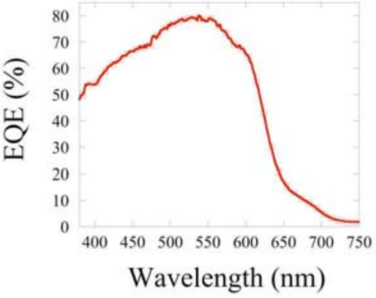


Figure 1 Illustration showing the device configuration, materials used and the direction of illumination.
Figure 3 J-V Characteristics of TiO2 nanotube array-polymer double heterojunction solar cells showing the dark current density (blue), photocurrent density (red) and power density (green) of described double heterojunction solar cells under 1 sun AM 1.5 illumination.
Figure 4 External Quantum Efficiency (EQE) of nanotube array-polymer double heterojunction solar cells.

1 X. J. Feng, K. Shankar, O. K. Varghese, M. Paulose, T. J. LaTempa, C. A. Grimes, Vertically Aligned Single Crystal TiO2 Nanowire Arrays Grown Directly on Transparent Conducting Oxide Coated Glass: Synthesis Details and Applications. Nano Letters 8, 3781-3786 (2008)

2 G. K. Mor, O. K. Varghese, M. Paulose, C. A. Grimes, Transparent Highly-ordered TiO2 Nanotube-arrays via Anodization of Titanium Thin Films, Advanced Functional Materials 15 (2005) 1291-1296.

3 G. K. Mor, K. Shankar, M. Paulose, O. K. Varghese, C. A. Grimes. High Efficiency Double Heterojunction Polymer Photovoltaic Cells using Highly Ordered TiO2 Nanotube Arrays. Appl. Physics Letters 91 (2007) 152111.

OG2

Exotic organic optoelectronic materials in high-performance dye-sensitized solar cells

Peng Wang*
State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences.

In view of the limited availability of fossil fuels and the disastrous environmental issues concomitant with their combustion, it is imperative to develop renewable energy resources for the increasing global energy demand. Affluent solar energy has a widely recognized capacity to become a major sustainable energy supply. Incontrovertibly, the performance/price ratio will play a pivotal role in the eventual selection of various photovoltaic devices. The dye-sensitized solar cell (DSC) has attracted considerable attention as a promising technology for low-cost photovoltaic cells in the past two decades owing to its high efficiency of over 11% and its high performance under the prolonged light and thermal dual stress. The DSC efficiency could be further improved by the design of new sensitizers showing a good spectral overlap with the solar irradiance and by exploration of multi-junction tandem device architectures. Here I will present our recent progress on rational design of some exotic organic optoelectronic materials in high-performance DSCs as well as related studies on device physics.

OG3

Solar Cell by Design.
Harvesting Light Energy with Semiconductor Quantum Dots

Prashant V. Kamat*
Department of Chemistry and Biochemistry, Department of Chemical and Biomolecular Engineering,
University of Notre Dame, Notre Dame, IN 46556
http://www.nd.edu/~pkamat

Renewable energy resources are needed to meet our clean energy demand. Semiconductor nanoparticle and nanotube assemblies provide new ways to develop next generation solar cells.[1-4]. Of particular interest is the nanowire/nanotube architecture which can significantly improve the efficiency of nanostructure based solar cells. Quantum dot solar cells have been constructed by assembling different size CdSe quantum dots on TiO_2 films composed of particle and nanotube morphologies. Upon bandgap excitation, CdSe quantum dots inject electrons into TiO_2 nanoparticles and nanotubes, thus enabling the generation of photocurrent in a photoelectrochemical solar cell (Figure 1). These composite semiconductor nanostructures can be tailored to tune the photoelectrochemical response via size control of CdSe quantum dots and improve the photoconversion efficiency by facilitating the charge transport through TiO_2 nanotube architecture. Ways to improve power conversion efficiency and maximize the light harvesting capability through the construction of a rainbow solar cell will be presented.

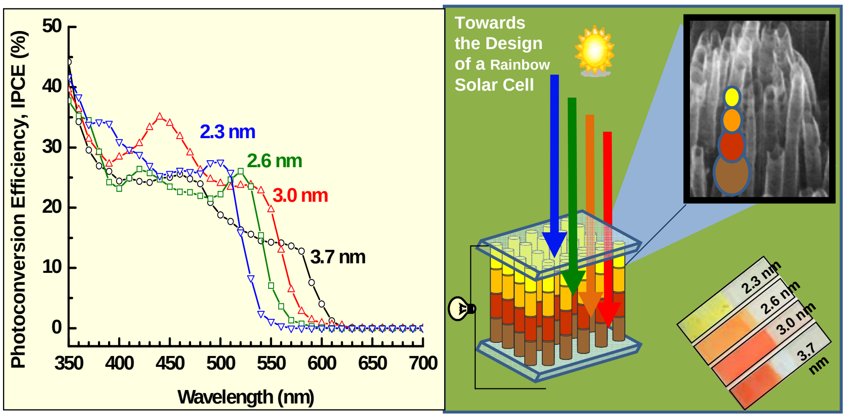


Figure 1 CdSe quantum dot based solar cell performance. The photoresponse can be tuned by varying particle size of CdSe quantum dots. Picture on the right shows a schematic design for the construction of a rainbow solar cell.

References:

1. Kamat, P. V., *Meeting the Clean Energy Demand: Nanostructure Architectures for Solar Energy Conversion.* **J. Phys. Chem. C, 2007**, *111,* 2834 - 2860.
2. Kamat, P. V., *Quantum Dot Solar Cells. Semiconductor Nanocrystals as Light Harvesters.* **J. Phys. Chem. C, 2008**, *112,*.
3. Kongkanand, A.; Domínguez, R. M.;Kamat, P. V., *Single Wall Carbon Nanotube Scaffolds for Photoelectrochemical Solar Cells. Capture and Transport of Photogenerated Electrons.* **Nano Lett., 2007**, *7,* 676-680.
4. Robel, I.; Subramanian, V.; Kuno, M.;Kamat, P. V., *Quantum Dot Solar Cells. Harvesting Light Energy with CdSe Nanocrystals Molecularly Linked to Mesoscopic* TiO_2 *Films.* **J. Am. Chem. Soc., 2006**, *128,* 2385-2393.18737-1873.

OG4

Photovoltaic and Ultrafast Carrier Dynamic Properties of CdSe Quantum Dot-Sensitized Solar Cells Using Inverse Opal TiO_2 Electrodes

Taro Toyoda*, Lina J. Diguna, and Qing Shen
Department of Applied Physics and Chemistry, The University of Electro-Communications,
1-5-1 Chofugaoka, Chofu, Tokyo 182-8585, Japan

Dye-sensitized solar cells (DSSCs) have been the focus of much attention as a promising alternative to conventional Si solar cells due to high conversion efficiency, simple fabrication, low cost, and good long term stability.[1,2] However, the expensive and using special organic dyes has encouraged the pursuit of alternative light harvesters. Narrow band-gap semiconductor quantum dots (QDs) could provide the solutions due to its tunable energy gap, large intrinsic dipole moments leading to rapid charge separation, and large extinction coefficient. Also, the QD-sensitized solar cells have capability of producing multiple electron-hole pairs (exitons) per photon with impact ionization.[3] We demonstrate a novel approach to sensitized solar cells, based on TiO_2 inverse opal electrodes and the use of CdSe QDs as sensitizers. The photovoltaic performance was significantly improved by surface modification with ZnS and fluorine ions.[4,5] An photovoltaic conversion efficiency of about 3.1% has been attained under solar illumination of 100 mW/cm^2. This value is relatively high for TiO_2 solar cells sensitized with the QDs. Ultrafast carrier dynamics measured with transient grating (TG) technique[6] show a fast (hole) decay process and a slow (electron) decay one with lifetimes of a few picoseconds and a few tens to hundred picoseconds, respectively.[7] The vales of these lifetimes are smaller than those obtained on conventional nanocrystalline TiO_2 electrodes, indicating the importance of the interfaces between CdSe QDs and TiO_2 electrodes in carrier relaxation.

References

1. B. O'Regan and M. Grätzel, *Nature,* 1991, **353**, 737.
2. Y. Chiba, A. Islam, Y. Watanabe, R. Komiya, N. Koide, and L. Han, *Jpn. J. Appl. Phys*., 2006, **45**, L638.
3. A. J. Nozik, *Physica E*, 2002, **14**, 115.
4. L. J. Diguna, Q. Shen, J. Kobayashi, and T. Toyoda, *Appl. Phys. Lett*., 2007, **91**, 023116.
5. Q. Shen, J. Kobayashi, L. J. Diguna, and T. Toyoda, *J. Appl. Phys*., 2008, **103**, 084304.
6. K. Katayama, M. Yamaguchi, and T. Sawada, *Appl. Phys. Lett*., 2003, **82**, 2775.
7. L. J. Diguna, Q. Shen, A. Sato, K. Katayama, T. Sawada, and T. Toyoda, *Mater. Sci. Eng. C*, 2007, **27**, 1514.

GO5

Flexible Dye Solar Cells – stable performance in all light conditions

J Desilvestro, G E Tulloch*, P Murray, R Harikisun, R Platts, A Thein, M Holding
Dyesol Limited, 3 Dominion Place, Queanbeyan, NSW, Australia.

Security forces worldwide seek solar charging units that can provide power under all light conditions for a variety of applications including remote sensing and battery charging to reduce the usage of primary batteries. Existing technological solutions that are sufficiently light weight utilize thin film technologies such as amorphous silicon and CIGS. However these products lose power dramatically under shaded or variable light – data will be shown of real life testing of some commercial devices.

Dyesol accepted the challenge from the Australian Defence Department to develop a durable flexible DSC panel to produce 8W and to be able to produce usable power over the full light spectrum, including dappled light and in all potential operating environments. An added complexity involved the panel having camouflage characteristics in the visible and IR regions.

In this paper we present the electrical and materials design utilized to achieve a successful outcome. Results of performance and durability testing will be provided and camouflage capability will be shown. Comparison of the Dyesol panel with competitor products demonstrates the superiority of this technology in real-life conditions.

OG6

Modification of the Semiconductor-Sensitizer-Electrolyte Interfaces for Efficient Quantum-Dot sensitized solar cell

Shay Yahav, Sven Rühle, Arie Zaban*,
Chemistry Department, Institute for Nanotechnology and Advanced Materials
Bar-Ilan University, Ramat-Gan 52900, Israel.
Email: zabana@mail.biu.ac.il

Dye sensitized solar cell (DSSC) is a low cost alternative for clean energy generation. DSSCs are based on the photoinjection of electrons from dye molecules into an inorganic semiconductor and holes transport by a redox mediator. The high light to energy conversion efficiencies achieved with DSSCs may be attributed to the nanoporous semiconductor electrodes. These electrodes consist of nanosize, low-doped crystals of wide band gap semiconductors that are sintered on a transparent conducting substrate. The electrodes have a porous geometry and a very large surface area. The porosity allows the redox mediator to contact each of the nanocrystals present in the electrode while the large surface area enhances surface effects related to the single nanocrystals by orders of magnitude.

In recent years we developed methods for the modification of the electronic characteristics of the nanoporous electrodes, utilizing organic and inorganic materials in core shell configurations. These methods are now used to replace the organometallic sensitizers by thin inorganic layers or quantum dots, aiming at better utilization of the solar spectrum and long term stability. Inorganic sensitization of the wide bandgap semiconductor requires alignment of the energy levels at the sensitizer-semiconductor interface as well as catalysis of the hole transfer to the redox mediator. We found that deposition of thin functional layers at the semiconductor-sensitizermediator interfaces leads to efficient and stable solar cells that can be tuned to the solar spectrum.

We will discuss the mechanism, synthesis, characterization and application of DSSCs as standalone systems and as components in multi-bandgap photovoltaics.

OG7

Nano-crystalline TiO_2 Solar Cells fabricated using Aniline Oligomers as Hole Conductors

Shozo Yanagida*, Yukyeong Kim, Youhai Yu, Kazuhiro Manseki
Osaka University, Center for Advanced Science and Innovation,
Yamada-oka, Suita, Osaka Japan 565-0871

Dye-free nano-crystalline TiO_2 (nc-TiO_2) solar cells composed of aniline oligomers as hole conductor and PEDOT as catalyst on cathode FTO were fabricated and evaluated. The pore of the nano-porous nc-TiO_2 anode was filled with the aniline oligomer through *in-situ* photo-electrochemical oxidative polymerization of aniline under photo-excitation of nc-TiO_2 layers in aqueous solution. The resulting transparent sole TiO_2 solar cells gave 30% IPCE at □=350 nm, being regarded as so-called "Honda-Fujishima-effect" solar cells. We optimized the short circuit photocurrent (Jsc=0.71mA/cm^2), increasing conversion efficiency up to 0.36% with high open circuit voltage 0.83 V and respectable fill factor, 0.62 under simulated 1- sun conditions.
The application to dyed TiO_2 solar cells will be also presented as far as time allows.

References

1. Y. Kim, J. Lim†, Y. Sung, J. Xia‡, N. Masaki, S. Yanagida, Journal of Photochemistry and Photobiology A: Chemistry, in contribution..

OG8

DSC tool-box – an integrated approach

Anders Hagfeldt*
Department of Physical and Analytical Chemistry, Uppsala University, Box 259, 751 05 Uppsala, Sweden.
Center of Molecular Devices, School of Chemical Science and Engineering, Royal Institute of Technology, Teknikringen 30, 100 44 Stockholm, Sweden.

The talk will summarize our research and development activities of dye-sensitized solar cells (DSC), focusing on the development of characterisation techniques of complete DSC devices - what we call the 'tool-box'.

The scientific challenge of DSC is to handle the complex molecular interactions and the inherent multi-scaling properties, both in time and length. We have approached this scientific challenge by developing 'tool-box' techniques. These techniques make it possible to extract information at the molecular level on complete DSC devices operating under normal working conditions. The methods provide information on for example energetics, charge transport and electron transfer processes. Some examples will be given at the meeting including Photoinduced Absorption Spectroscopy as a suitable method to study for example the quality of pore filling in case of solid hole conductors.

Some of our materials research will be presented. We have developed series of organic dye molecules with the general structure donor – conjugated linker – acceptor. Best efficiencies, above 7%, were obtained with polyene-diphenylaniline type dyes, using an iodide/triodide based redox electrolyte. The influences of substitutions of the donor group (a diphenylaniline moiety), the length of the conjugated linker chain and different acceptor/anchoring groups are presently being studied and will be discussed at the meeting.

The majority of studies in this field are based on the sensitization of a n-type semiconductor. However, DSCs in which the cathode is photoactive are also possible and the development of a photocathode can provide an entry to the preparation of a tandem solar cell, in which both electrodes are photoactive. Until now there have been few studies on the sensitization of p-type semiconductors. We will report on new organic dyes, designed for a p-type DSC, and its performance in a photovoltaic device based on NiO as the photocathode and a passive anode. The external quantum yield of this system has a maximum of above 40% which is among the highest values recorded so far for p-type DSCs.

OG9

Studies of electron transport, trapping and electron transfer in dye-sensitized solar cells

Halina Dunn[a], James Jennings[a], Laurence Peter[a*], Alison Walker[b] and Hongxia Wang[a]
a. Department of Chemistry, University of Bath, Bath BA2 7AY, United Kingdom.
b. Department of Chemistry, University of Bath, Bath BA2 7AY, United Kingdom.

Optimization of dye-sensitized nanocrystalline solar cells (DSCs) requires detailed understanding of the loss mechanisms in the cell. Reliable methods to determine the efficiencies for light harvesting, electron injection and electron collection are also essential, as are methods to characterize the factors that determine the open circuit voltage and fill factors. Electron transport and electron transfer (back reaction) in DSCs are normally studied using pulsed or modulated illumination, but interpretation of the results is complicated by electron trapping. In our recent work we have used infrared transmittance measurements to probe the density of electrons in DSCs under stationary and dynamic conditions. These IR measurements have been combined with a range of other techniques in an attempt to build up a consistent theoretical framework to describe cell operation. In parallel with the refinement of experimental techniques, we have developed a numerical model to describe electron transport, trapping and transfer in the DSC. The predictions of this model have been compared with analytical approaches based on different approximations in order to test their validity. This talk will highlight some of our most recent results and discuss some of the problems that we have encountered in achieving a clearer understanding of the DSC.

* corresponding author. l.m.peter@bath.ac.uk

OG10

Transport and charge accumulation in nanotube based dye solar cells

Márcio Góes,[a] **Francisco Fabregat-Santiago,**[*b] **Ivan Mora,**[b] **Eva Barea,**[b] **Juan Bisquert,**[b]
a Departmentde Física, Universitat Jaume I, Castelló, 12071, Spain.
b Departamento de Física-Química, Instituto de Química de Araraquara, Universidade Estadual Paulista, Araraquara SP, 14800-900, Brazil

Dye-sensitized solar cells (DSCs) are being increasingly investigated as viable as a source of energy. The standard DSC configuration uses a porous TiO_2 film consisting of a disordered network of colloidal nanoparticles about 10 nm in diameter.[1] Efficiencies up to an 11% [2] have been obtenied with this architecture. DSCs comprised of ordered nanoarchitectures such as nanowires and nanotubes, grown from the substrate, have raised considerable interest. The ordered material architecture offers the benefits of (i) a better transport, avoiding inter-particle connections, (ii) the possibility to form surface electrical fields that should reduce recombination by confining the injected electrons in the central zone of the tubes;[3] and (iii) superior void penetration for the hole conductor in solid-state DSCs, due to the less intricate shape of the nanostructure.[4]

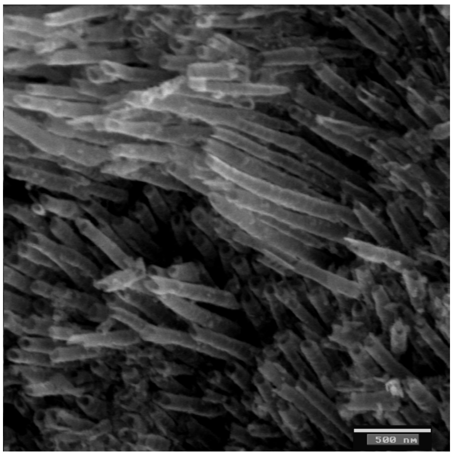


Fig. 1 TiO_2 nanotubes

The crucial properties determining the photovoltaic performance of nanotubes and nanowires are electronic conductivity and recombination. Carrier density, which is in turn dependent on the doping level, plays a key role in determining both properties.

In this work we will describe the electrical properties of TiO_2 and ZnO nanotubes as in Fig. 1, their performance in DSC's and the changes that processes such as doping may cause on them.[5]

Acknowledgements

The authors want to acknowledge Prof. Hupp and Prof. C. Grimes and Dr, Ramón Tena for useful samples and discussions. financial support from Ministerio de Educacion y Ciencia under project HOPE CSD2007-00007 (Consolider-Ingenio 2010).

References

1 O' Regan, B.; Grätzel, M. *Nature*, ***353***, 737 (1991).
2 Wang, Q.; Ito, S.; Grätzel, M.; Fabregat-Santiago, F.; Mora-Seró, I.; Bisquert, J.; Bosshoa, T.; Imaic, H. *J. Phys. Chem. B*, ***110***, 19406 (2006).
3 Mora-Seró, I.; Fabregat-Santiago, F.; Denier, B.; Bisquert, J.; Tena-Zaera, R.; Elias, J.; Lévy-Clement, C. *Appl. Phys. Lett.*, ***89***, 203117 (2006).
4 Snaith, H. J.; Schmidt-Mende, L. *Adv. Mat.*, ***19***, 3187 (2007).
5 F. Fabregat-Santiago, E. M. Barea, J. Bisquert, G. K. Mor, K. Shankar, C. A. Grimes, J. *American Chem. Soc.,* **130**, 11312–11316 (2008).

OG11

Charge photogeneration and recombination in dye sensitized and polymer / fullerene solar cells

James Durrant*
Department of Chemistry, Imperial College London, Exhibition Road,
London SW7 2AZ, U.K. E-mail: j.durrant@imperial.ac.uk

My lecture will focus on charge separation and recombination in excitonic solar cells - comparing and contrasting dye sensitized solar cells with polymer / fullerene bulk heterojunctions. I will start of considering the energetics and kinetics of charge photogeneration. Concerning charge photogeneration, I will focus on the energetic cost of charge photogeneration, and its impact upon device efficiency. Topics I intend to address include triplet versus singlet injection, overcoming the coulomb attraction of photogenerated charges, the minimization of kinetic redundancy and a comparison of charge separation limitations upon device performance between different sensitiser dyes and polymers. I will then go on to consider recombination losses in such devices - including quantification of bimolecular recombination losses, transport issues and interface engineering approaches to reduce recombination losses.

OG12

Optimizing Organic Solar Cells based on Small Molecules

Moritz Riede[a*]
a,Institut fuer Angewandte Photophysik, Technische Universitaet Dresden, George-Baehr-Str. 1, 01069 Dresden, Germany

In recent years organic solar cells have attracted much interest and their development has reached a stage at which several companies are preparing to make them commercially available. Yet, there are still a number of open questions on the fundamental physics, e.g. the process of free charge carrier generation, and challenges like device life time and proving the power conversion efficiency. One very promising approach for organic solar cells uses thermal evaporation of small molecules in vacuum to created an organic stack in the p-i-n concept, i.e. an intrinsic absorber layer sandwiched between p- and n-doped wide gap transport layers[1]. The vacuum deposition of the layers in the solar cell enables an easy stacking of many layers, e.g. for tandem and triple solar cells. The controlled doping allows for an active control of the Fermi level in the doped layers, makes transport materials highly conductive, and creates ohmic contacts to the electrodes.

Based on the p-i-n structure, approaches for the optimisation of small molecule solar cells will be presented: Through the choice of suitable doped hole transport materials, single heterojunction solar cells based on dicyanovinyl-quinquethiophene:C60 have lead to efficient solar cells with an optimised open circuit voltages of 1V[2]. Additionally, utilising the freedom of the p-i-n stack to position the intrinsic absorbing layer at different distances from the highly reflective Al-cathode by varying the thickness of the transport layers the effects of the thin film optics become clearly evident already in single heterojunction solar cells. However, such an optical optimisation becomes even more important for tandem solar cells, because the currents of the subcells have additionally to match for efficient devices. This is demonstrated through a study in which the optical spacer between the two identical zincphthalocyanine:C60 based subcells is systematically varied from 10nm to 150nm with significant consequences on the short circuit current confirming our optical simulations[3]. To harvest a wide range of the solar spectrum to next the goal is to use different absorbing materials in each subcell. Again current matching is an issue and for the exact characterisation the spectrum of the light source plays an important role. Based on the optical simulation and a systematic screening and characterisation optimised devices are realised by combining oligothiophene:C60 heterojunctions with standard zincphthalocyanine:C60 ones, achieving more than 4% power conversion efficiency.

References

1. B. Maennig, J. Drechsel, D. Gebeyehu, P. Simon, F. Kozlowski, A. Werner, F. Li, S. Grundmann, S. Sonntag, M. Koch, K. Leo, M. Pfeiffer, H. Hoppe, D. Meissner, N.S. Saricifci, I. Riedel, J. Parisi, *Appl. Phys. A - Mat. Sci. Process*., 2004, **79**, 1-14.
2. K. Schulze, C. Uhrich, R. Schueppel, K. Leo, M. Pfeiffer, E. Brier, E. Reinold, P. Bäuerle, *Adv. Mater*., 2006, **18**, 2872-2875.
3. R. Schueppel et al. *in preparation*

OG13

Stability problem of polymer based bulk heterojunction solar cells

L.Lutsen[1*], B. Campo[3], W. Oosterbaan[3], S. Bertho[3], A. Hadipour[2], D.Vanderzande[1, 3]
[1]*IMEC/ IMOMEC, Wetenschapspark 1, B-3590 Diepenbeek, Belgium*
[2]*IMEC vzw, Kapeldreef 75, B-3001 Leuven, Belgium*
[3]*Hasselt University, Campus Diepenbeek, Agoralaan, building D, B-3590 Diepenbeek, Belgium*

Nowadays a continuous progress in the efficiency of polymer based solar cells is observed mainly due to progress in material development in combination with progress in device engineering. This combined efforts result in single cell efficiencies of about 6% for several different donor materials in combination with PCBM-C61 or PCBM-C71 as acceptor material. Recent theoretical models have given rise to design rules toward potential high performance materials and lead to consistent predictions of maximal single cell efficiencies between 10 and 15%. However still at this moment the stability of said type of solar cells is quite limited, well below a lifetime necessary for real applications. It is generally understood that this issue is tightly linked to the stability of the nano-structured morphology of the active layer, which is mostly mere the result of a kinetically frozen phase separation process of donor and acceptor materials. In this way lifetimes of such devices are limited to about 1000 hours at 65°C and 1 sun illumination. In this contribution the stability problem of polymer based bulk heterojunction solar cells will be discussed. Possible approaches to improve stability will be presented. Specifically the performance of co-polymers of P3HT in solar cells with PCBM as acceptor will be reported leading to a stability improvement of at least a factor ten.

OA1

Factors influencing electron lifetime in dye-sensitized solar cells: Molecular structure of sensitizers, electrolytes and co-adsorbents

Shogo Mori[a]*, Masanori Miyashita[a], Kenji Sunahara[a], Nagatoshi Koumura[b], Kohjiro Hara[b], Attila J. Mozer[c], Pawel Wagner[c], Wayne M. Campbell[d], David L. Officer[c], and Gordon G. Wallace[c]
a, Division of Chemistry and Materials, Faculty of Textile Science and Technology, Shinshu University, 3-15-1 Tokida, Ueda, Nagano 386-8567, Japan
b, National Institute of Advanced Industrial Science and Technology, 1–1–1 Higashi, Tsukuba, Ibaraki 305-8565, Japan
c, ARC Centre of Excellence for Electromaterials Science, University of Wollongong, Wollongong NSW 2522, Australia.
d, Nanomaterials Research Centre, IFS-Chemistry, Massey Universit, New Zealand,

The highest energy conversion efficiency of dye-sensitized solar cells (DSCs) has been held with Ru complex sensitizer dyes. On the other hand, recent papers have shown new dyes having high charge injection efficiency for wide absorption spectrum. Thus, the short-circuit currents with the new dyes are becoming comparable with the best Ru complex dye. On the other hand, most of the dyes give lower open-circuit voltage (Voc) than the Ru dye. It has been attributed that the low Voc is mostly due to faster charge recombination rate in the solar cells, while the Voc varies depending on the dye structure. Thus, it is important to understand how the structure influences the recombination rate.

We have measured various dyes; series of coumarine dyes, indoline dyes, carbazole dyes, porphyrin dyes, and Ru complex dyes. Among the metal-free organic dyes, we observed tendency that the charge recombination rate was decreased with the increase of molecular size. In comparison to Ru complex dyes, most metal free-organic dyes and Zn-porphyrin dyes showed faster recombination rate [1,2]. It was attributed that these dyes increased local concentration of I_3^- at the vicinity of TiO_2 surface. On the other hand, series of oligoene dyes have shown a decrease of Voc with an increase of molecular size [3]. In this presentation, the results of the recombination rate of such small molecule dyes will be presented, and compared with larger molecular size dyes.

Typically, *tert*-butylpyridine is added to electrolyte and chenodeoxycholic acid is added to dye solution. These materials influence the charge recombination rate and the rate depends on not only the cell fabrication conditions but also the structure of dyes. The mechanism of the dependency will be also discussed.

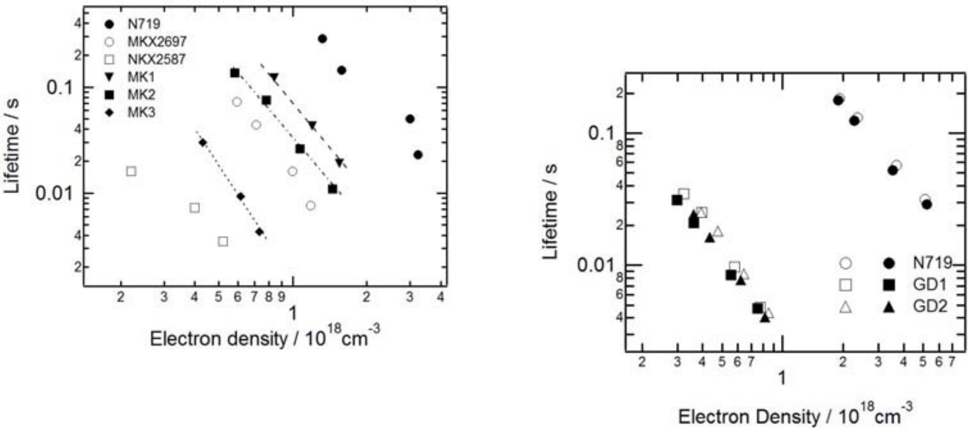


Figure Electron lifetim in DSCs emplying Ru dye (N719), coumarin dyes (NKX), carbazole dyes (MK), and porphyrin dyes (GD).

References

1. M. Miyashita, K. Sunahara, T. Nishikawa, U. Uemura, N. Koumura, K. Hara, A. Mori, T. Abe, E. Suzuki, S. Mori, *Journal of the American Chemical* Society ASAP 2008.
2. A. J. Mozer, P. Wagner, D. L. Officer, G. G. Wallace, W. M. Campbell, M. Miyashita, K. Sunahara, S. Mori, *Chemical Communications* 2008, 4741.
3. T. Kitamura, M. Ikeda, K. Shigaki, T. Inoue, N. A. Anderson, X. Ai, T. Lian, S. Yanagida, *Chemistry of Materials* 16, 2004, 1806

OA2

Plastic solar cells employing electrodeposited porous crystalline ZnO sensitized with organic dyes

Tsukasa Yoshida,[a*] Kazumasa Funabiki,[a] Masaki Matsui,[a] Hidetoshi Miura,[b] and Yoshiya Fujishita[c]
a, Center of Innovative Photovoltaic Systems, Gifu University, Yanagido 1-1, Gifu 501-1193, Japan.
b, Chemicrea Inc., Quattro Muromachi Bldg. 9F, 4-16 Nihonbashi Muromachi Chuoh-ku, Tokyo 103-0022, Japan.
c, Sekisui Jushi Corp., Kagami 731-1, Ryuoh-cho, Gamoh-gun, Shiga 520-2596, Japan.

We are challenging to achieve efficient plastic solar cells for versatile applications by combination of originally developed materials and method of preparation, i.e., electrodeposition of ZnO in a porous crystalline structure and organic dyes suited to ZnO [1]. Cathodic electrodeposition of ZnO from O_2 saturated $ZnCl_2$ aqueous solution in the presence of eosinY yields three dimensionally interconnected nanowire ZnO that preserves perfectly crystalline structure. Such a “porous crystalline” structure is ideal as the electrode for dye-sensitized solar cells (DSSCs) because of the high surface area for dye adsorption and high crystallinity for electron transport in one body. As the process requires neither high temperature nor aggressive chemicals, it is perfectly compatible with soft electrode material such as ITO coated plastic film.

Owing to the electron diffusion length longer enough than the film thickness, DSSCs employing the electrodeposited ZnO promises high IPCE up to 90% when it is combined with suitable photosensitizer dyes. As it is well known, Ru(II) complexes with carboxylated polypyridine ligands are not suitable to ZnO as they dissolve ZnO and form randomly structured aggregates. Those complexes which are the best for TiO_2 can only achieve disappointingly low efficiencies. However, indoline dyes free of precious metals were found to match with ZnO. Efficiencies close to 6% (AM 1.5) were achieved in combination with D149 dye. The new indoline dye DN98 having an octyl group attached to one of the nitrogen atoms of the double rhodanine moiety have exhibited an increased voltage due to suppression of back reaction and pushed the efficiency up to 6.24% by the measurement in Gifu University. Sekisui Jushi have further improved the efficiency beyond 6.4% and TDK 7.9%, both of them developing the cells with the same principle.

Extension of the sensitivity towards the near infrared (NIR) region is essential for higher efficiencies, because D149 and DN98 absorbs only up to 670 nm when they are adsorbed on ZnO. New indoline dyes with modified donor/linker/acceptor groups have achieved extended absorption to the NIR region, although many of them suffered from the decreased efficiency of charge separation. Among them, dyes with triple rhodanine acceptor having positively shifted LUMO level achieved relatively high IPCE. Besides broadening of the sensitivity, NIR dyes to add on the existing indoline dyes were also developed. Asymmetric squarilium (SQ) dyes with enhanced push-pull character achieved over 3% efficiency in the NIR region (peak around 670 nm). Even longer sensitivity up to 870 nm was achieved by heptamethine cyanine (HMC) dyes. The best HMC dye has achieved 1.2% efficiency despite of the fact that the cell is not colored to human eyes because it absorbs only in the NIR and not in the visible. The HMC dye is therefore perfect for applications as power generating window and white wall.

Scaling up of the technology to a 10 cm square sub-module leads to an only small decrease of the efficiency. A full plastic module of such geometry achieved over 4% efficiency when a volatile solvent is used. Modules with non-volatile solvent goes below 2% efficiency but can survive photostability and thermo/humidity cycle tests of JIS C8938 conditions, while the heat/humidity test (85˚C/85%) destroys the module by the exposure of the module to such an environment beyond 500 h. Even though such tests required for roof-top applications are being still too tough in the moment, the modules can be stable enough for applications under milder environments. Such application studies are also under their way.

References

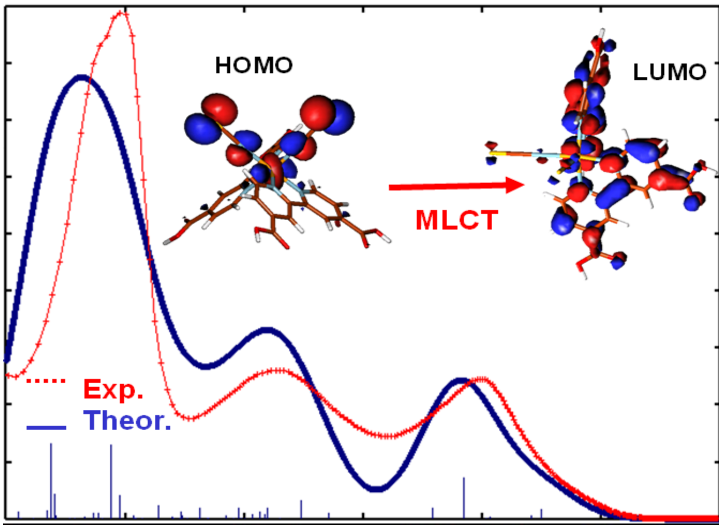
1. T. Yoshida, J. Zhang, D. Komatsu, S. Sawatani, H. Minoura, T. Pauporté, D. Lincot, T. Oekermann, D. Schlettwein, H. Tada, D. Wöhrle, K. Funabiki, M. Matsui, H. Miura and H. Yanagi, Adv. Func. Mater., 2009, **19**, 17-43.

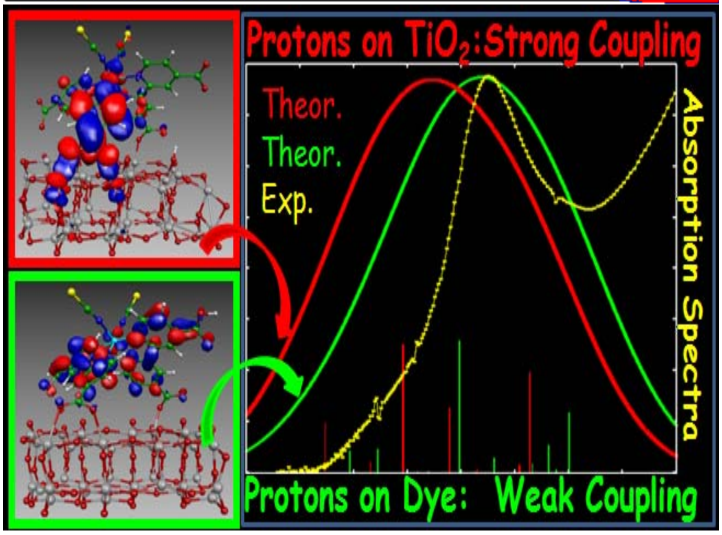
OA3

Ab initio simulation of Dye-Sensitized Solar Cells

<u>Filippo De Angelis*</u>, Simona Fantacci
Istituto di Scienze e Tecnologie Molecolari (ISTM-CNR) and Dipartimento di Chimica, Università di Perugia, 06123, Perugia, Italy. E-mail: filippo@thch.unipg.it

We present the potential of computer simulations based on ab initio methods applied to the investigation of the structural, electronic and spectroscopic properties of Ru(II) and organic dyes of interest in the field of Dye-Sensitized Solar Cells. We devised over time a computational strategy based on DFT and its Time Dependent extension (TDDFT) which allows the accurate calculation of excited state properties of large systems in solution. The ingredients of our computational strategy are presented and the main results are discussed in direct connection to available experimental data. Due to the implemented methodological advances, theory is today a predictive tool, allowing us to scrutinize and screen in silico the properties of organic and inorganic dyes even before their synthesis. This procedure is based on the calculation of the ground and excited state redox potentials. Realistic models of DSSC devices, obtained by adsorbing different dyes on TiO2 nanoparticles are discussed, simulating the fundamental processes of light-harvesting and charge injection in DSSCs. The factors affecting the cell efficiency are discussed as a function of the sensitizer characteristics. In particular, we find a substantial influence of the dye adsorption mode on the DSSC open potential, which we ascribe to the sensitizer dipole shifting the TiO_2 conduction band energy.





References

1 P. Giannozzi, F. De Angelis, R. Car *J. Chem. Phys.* **2004**, *120*, 5903.
2 F. De Angelis, S. Fantacci, A. Sgamellotti *Theor. Chem. Acc.* **2007**, *117*, 1093.
3 F. De Angelis, S. Fantacci, M. Grätzel et al. *Inorg. Chem.*, **2007**, *46*, 5989.
4 S. Fantacci, F. De Angelis, A. Selloni. *J. Am. Chem. Soc.* **2003**, *125*, 4381.
5 F. De Angelis, S. Fantacci, M. Grätzel et al. *J. Am. Chem. Soc.* **2005**, *127*, 16835.
6 S. Fantacci, F. De Angelis, M. Grätzel et al. *J. Am. Chem. Soc.* **2006**, *128*, 16701.
7 J-H. Yum, F. De Angelis, M. Grätzel et al. *J. Am. Chem. Soc.* **2007**, *129,* 10320.
8 F. De Angelis, A. Tilocca, A. Selloni *J. Am. Chem. Soc.* **2004**, *126*, 15024.
9 F. De Angelis, S. Fantacci, A. Selloni, M. Grätzel et al. *Nano Lett.* **2007**, *7,* 3189.
10 F. De Angelis, S. Fantacci, M. Grätzel al. *J .Am. Chem. Soc.* **2007**, *129,* 14156.
11 F. De Angelis, S. Fantacci, A. Selloni *Nanotechnology* **2008**, *19*, 424002.

OA4

Stepwise Co-Sensitization of Nanocrystalline TiO_2 in DSSC

H. Choi,[a] S. Kim,[a] S. O. Kang,[a] J. Ko,[a] M. S. Kang,[b] J. N. Clifford,[c] A. Forneli,[c] M. K. Nazeeruddin,[d] M. Grätzel[d] and E. Palomares[c]

a. Department of New Material Chemistry, Korea University Jochiwon, Chungnam 339-700 (Korea)
b. Energy & Environment Lab., Samsung Advanced Institute of Technology (SAIT) Yongin, 446-712 (Korea)
c. Institute of Chemical Research of Catalonia (ICIQ) Avenguda Països Catalans, 16, Tarragona 43007 (Spain)
d. Laboratory of Photonics and Interfaces, École Polytechnique Fédérale de Lausanne, 1015 Lausanne (Switzerland)

The Grätzel cell offers one solution to the problem of meeting the worlds future energy needs in a green and renewable way. It consists of a working electrode of dye-sensitized nanocrystalline semiconductor film (usually TiO_2) that is deposited onto a conducting support. A platinum counter electrode and hole-conducting medium (usually I^-/I_3^- redox couple) that connects the working and counter electrodes completes the cell. Such devices have shown promising efficiencies hitherto with a maximum of 11.3% recorded.[1] Efforts to improve upon this efficiency are manifold ranging from modifications to the nanocrystalline film, dye sensitizer and redox couple. One of the many approaches we are investigating involves improving the spectral response of the sensitized film by the co-sensitization of 2 different dye sensitizers onto the TiO_2, improving the current and voltage of the cell.[2]

References

1. M. Grätzel. *Prog. Photovolt: Res. Appl,* 2006, 14, 429

2. H. Choi, S. Kim, S. O. Kang, J. Ko, M. S. Kang, J. N. Clifford, A. Forneli, M. K. Nazeeruddin, M. Grätzel and E. Palomares. *Angew. Chem. Int. Ed,* 2008, 47, 1

OA5

Dye Sensitized Solar Tube

Zion Tachan, Sven Rühle, Larissa Grinis, Arie Zaban
Bar-Ilan Institute of Nanotechnology and Advanced Materials
Bar-Ilan University, Ramat-Gan 52900, Israel

In this work we present a new Dye Sensitized Solar Cells (DSSC) structure intending to capture sun light from all directions, without the need for sun tracking devices.

To achieve this we have developed a DSSC which was deposited onto the inner walls of a glass tube to form a so called dye sensitized solar tube (DSST). We developed the synthesis of Fluorine doped Tin oxide (FTO), which was deposited inside a glass tube by the spray pyrolysis. The FTO was produced using HF and tin chloride salt dissolved in ethanol. The properties of the FTO such as conductivity, thickness and morphology were controlled by adjustment of the substrate temperature, precursor concentration and flow rates. The mesoporous TiO_2 film was deposit by Electrophoretic Deposition (EPD) inside the glass tube. This DSST was sensitized with a Ru-dye (N3) before it was immersed into an iodide/iodine redox electrolyte while the electrical circuit was closed by a graphite rode as a counter electrode. Compared to the conventional flat dye sensitized solar cell the new design reduces signifclly the sealing problems. It also offers simple and efficeant current collection based on sheding of the bottom part of the tube which is not important for total light harvesting. Panels consisting of DSSTs allow air flow in between the tubes, thus decreasing the wind resistivity while diffuse light is collected more effectively due to the cylindrical shape of the DSST.

OB1

Analysis of photocurrent transients in polymer solar cells

Chris McNeill,* Inchan Hwang and Neil Greenham
Cavendish Laboratory, University of Cambridge, J J Thomson Ave, Cambridge, CB3 0HE, United Kingdom.

We present a simple, yet powerful technique for investigating the charge generation, transport and recombination dynamics in polymer solar cells. The technique measures the photocurrent response of a polymer solar cell to a square pulse of light with pulse duration of 500 nanoseconds to 100 microseconds. By varying the light intensity of the pulse, and by also applying a constant background illumination with variable intensity, we are able to separate the signatures of charge transport, charge trapping, geminate and bimolecular recombination. Analysis is assisted by the application of a time-dependent drift-diffusion model incorporating the Onsager-Braun model for charge pair dissociation. For efficient all-polymer devices based on blends of P3HT with the red polyfluorene F8TBT,[1] we show that while free charges are swept out of the device within a microsecond or two of generation, the short-circuit photocurrent takes tens of microseconds to equilibrate due to the trapping and detrapping of electrons. In particular, at high intensities the build-up of trapped charge in the device causes a reduction in the electric field strength near the anode that enhances recombination not only through bimolecular recombination but also through a turning off of the electric-field dependent charge separation process. Applications of this approach to study aging mechanisms in organic solar cells will also be discussed.

References

1. C.R. McNeill, A. Abrusci, J. Zaumseil, R. Wilson, M.J. McKiernan, J.J.M. Halls, N.C. Greenham, R.H. Friend, *Appl. Phys. Lett.* 2007, **90**, 193506.

OB2

Fullerene bisadducts for enhanced open circuit voltage and efficiency in polymer solar cells

Martijn Lenes[ab], GertJan A.H. Wetzelaer[a], Floris B. Kooistra[a], Jan C. Hummelen[a], Paul W. M. Blom[a]

a, Molecular Electronics, Zernike Institute for Advanced Materials, University of Groningen, the Netherlands.

b, Currently at Instituto de Cienca Molecular, Universidad de Valencia, Valencia, Spain.

The polymer:fullerene bulk heterojunction (BHJ) solar cell is considered to be a promising candidate for a large area, flexible, and more importantly, low cost renewable energy source. A significant part of the effort made in this field has been optimizing the fabrication of solar cells based on poly(3-hexylthiophene) (P3HT) as the donor and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) as the acceptor. Especially the improvements made by thermal and solvent annealing have led to external quantum efficiencies peaking around 80% and internal quantum efficiencies surpassing 90%. From the observed quantum efficiencies it is clear there is not much room for improvement for this combination of donor and acceptor. When analyzing the electronic levels of the P3HT:PCBM system a significant loss mechanism can be identified;[1] for electron transfer from donor to acceptor to occur, the lowest unoccupied molecular orbital (LUMO) of the donor needs to be 0.3 to 0.5 eV higher than the LUMO of the acceptor. In the case of P3HT however, this energy difference is much higher, namely 1.1 eV. This results in a less then optimal open circuit voltage Voc, since the open-circuit voltage is ultimately limited by the difference between the HOMO of the donor and the LUMO of the acceptor.

The fullerene bisadduct, bisPCBM, is presented with a significant lower electron affinity as compared to the standard acceptor PCBM.[2] By this raise of the LUMO level we increase the open circuit voltage of polymer:fullerene bulk heterojunction solar cells based on P3HT by 0.15 V(see Figure 1. As a result the energy loss in the electron transfer from donor to acceptor material is reduced. Maintaining high currents and fill factor an externally verified power conversion efficiency of 4.5% is reported for a P3HT solar cell, 20% larger as compared to the efficiencies of our best P3HT:PCBM cells, clearly showing bisPCBM to be superior acceptors compared to standard PCBM. Furthermore, other fullerene types with higher lying LUMO levels are discussed.

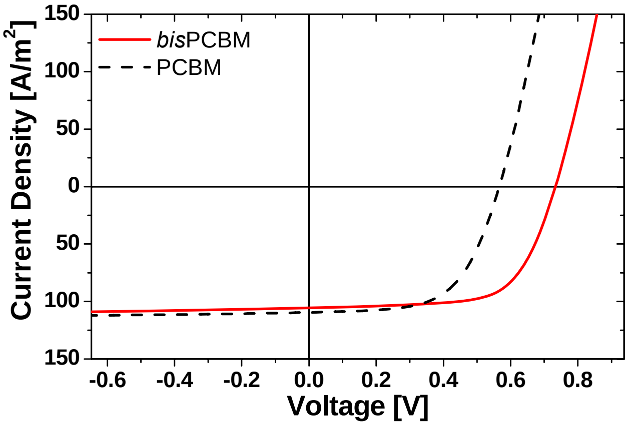


Figure 1. J-V characteristics of a P3HT:PCBM and P3HT:bisPCBM solar cell.

References

1 R. Kroon, M. Lenes, J. C. Hummelen, P. W. M. Blom, B. de Boer, *Polymer Review*, 2008, **48**, 531.

2 M. Lenes, G. A. H. Wetzelaer, F. B. Kooistra, S. C. Veenstra, J. C. Hummelen, P. W. M. Blom, *Adv. Mater*. 2008, **20**, 2116.

OB3

Fully Coupled Opto-electronic Modelling of Organic Photovoltaic Cells

Nils A. Reinke[a,*], Roger Häusermann[a], Evelyne Huber[a], Michael Moos[b], Thomas Flatz[b], Beat Ruhstaller[a, b],
a, Institute of Computational Physics, ZHAW, 8401 Winterthur, Switzerland.
b, Fluxim AG, Switzerland.

Record solar power conversion efficiencies of up to 5.5 % for single junction organic photovoltaic cells (OPVs) are encouraging but still inferior to values of inorganic solar cells. For further progress, a detailed analysis of the mechanisms that limit the external quantum efficiency is crucial. It is widely believed that the device physics of OPVs can be reduced to the processes, which take place at the donor/acceptor-interface. Neglecting transport, trapping and ejection of charge carriers at the electrodes raises the question of the universality of such a simplification. In this study we present a fully coupled opto-electronic simulator, which calculates the spatial and spectral photon flux density inside the OPV, the formation of the charge transfer state and its dissociation into free charge carriers.

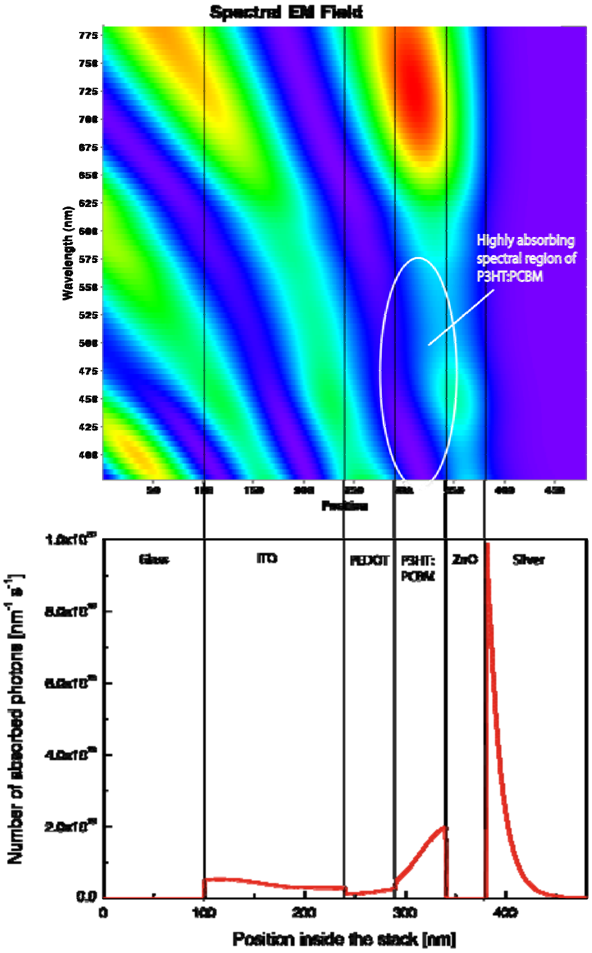


Figure 1. Optical field penetration and charge generation profile inside the organic photovoltaic cell.

Our simulator solves the drift-diffusion equations for the generated charge carriers as well as their ejection at the electrodes. Our results help to interpret both the steady state and transient characteristics of polymeric bulk hetero-junction (BHJ) cells. We address the influence of physical quantities such as the optical properties, film-thicknesses, the recombination rate and charge carrier mobilities on performance figures. Our simulations lead to rules of thumb, which help to optimise a given OPV structure.

OB4

Surface-initiated polycondensation: a new tool for the preparation of complex architectures of conjugated polymers for solar cells

Volodymyr Senkovskyy[a], Manfred Stamm[a], Suren A. Gevorgyan[b], Frederik C. Krebs[b], and Anton Kiriy[a]*

a Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Straße 6, 01069 Dresden, Germany

b Risø National Laboratory for Sustainable Energy, Technical University of Denmark, Frederiksborgvej 399, DK-4000 Roskilde, Denmark

Improper morphology of active layers in polymer bulk heterojunction solar cells is one of the bottle-neck problems limiting the performance of solar cells. To solve the problem, a new generation of polymeric materials able to self-assemble into desired morphologies are needed. A propensity of complex architectures of polymers, such as block copolymers, graft copolymers, stars, polymer brushes, etc., to form variety of well-defined morphologies via self-assembly was nicely exemplified in the case of non-conjugated and non-conductive polymers, however, their pi-conjugated counterparts are much less available. This is because the synthesis of CPs usually involves polycondensation reactions that proceed through a step growth mechanism. McCullough[1] and Yokozawa[2] groups have made an important discovery that Ni-catalyzed Kumada-polycondensation of 2-bromo-5-chloromagnesio-3-alkylthiophene (1) into regioregular poly(3-hexylthiophene) (P3HT) involves not the step growth mechanism, as it was believed for decades, but instead, follows the chain growth scheme. We made a step further developing surface initiated polycondensation process allowing one to grow P3HT from photo-cross-linked poly(-4-bromostyrene) (PS-Br) [3], or from block copolymer films.[4] The process involves catalyst-transfer polycondensation (CTP) of 1 selectively from the sites on the surface where $Ni(PPh_3)_4$ catalyst was covalently immobilized. In principle, the chain growth nature of the CTP might provide the access to other architectures of CPs, including block copolymers and stars. However, the great potential of this reaction was not yet explored. We will highlight our recent achievements in the development of CTPs utilizing different catalytic systems. In the present contribution we wish to report our recent results along these lines and discuss photovoltaic properties of new architectures of polythiophenes prepared by the surface-initiated polycondensation route.

References

1. McCullough, R. et al. *Macromolecules* **2005**, *38*, 8649
2. Yokozawa, T. et al. *J. Am. Chem. Soc.* **2005**, *127*, 17542
3. Senkovskyy, V.; Khanduyeva, N.; Komber, H.; Oertel, U.; Stamm, M.; Kuckling, D.; Kiriy, A. *J. Am. Chem. Soc.* **2007**, *129*, 6626.
4. Khanduyeva N, Senkovskyy V, Beryozkina T, Horecha M, Stamm M, Uhrich C, Riede M, Leo K, Kiriy A. *J. Am. Chem. Soc.* **2009**; *131*; 153-61.

OC1

Influence of Cations on Electron Accumulation in Dye-sensitized Solar Cells

Hongxia Wang,[*] **Laurence M. Peter**
Department of Chemistry, University of Bath, Bath, BA2 7AY, UK

The effect of cations with different ratio of charge/radius on the performance of dye-sensitized solar cells (DSC) was characterized comprehensively. It has been found that significant charge accumulation occurs for small cations such Li^+ based DSC. For some large cations, the electron density is even more than two orders of magnitude lower. For the same charge density n_t, the difference in the position of the quasi-Fermi level $_nE_F$ relative to the redox Fermi level, $E_{F,redox}$, gives information the shift of the conduction band E_{cb} because the broadening parameter of the trap distribution of the DSC is comparable for small cations. Investigation of the dependence of the electron lifetime, τ_n, on $_nE_F - E_{F,redox}$ confirmed the relative shifts of the conduction band E_{cb} in the presence of different cations. The dependence of the electron injection efficiency on conduction band position was also derived. Measurements of the electron diffusion length L_n gave values in the range 30 - 170 μm, depending on the nature of the cation.

OC2

Thin film transparent electrodes of ITO and AL:ZNO Deposited by sputtering at room Temperature and subsequently HEATED in vacuum

C. Guillén[a] and J. Herrero[b]
Departamento de Energía (CIEMAT) Avda. Complutense 22, Madrid-28040 (Spain).
a) phone: +34 91 346 6669, fax: +34 91 346 6037, e-mail: c.guillen@ciemat.es
b) phone: +34 91 346 6670, fax: +34 91 346 6037, e-mail: jose.herrero@ciemat.es

Nowadays, tin-doped indium oxide ($Sn:In_2O_3$ or ITO) thin films are commonly used as transparent conductive electrodes for optoelectronic devices due to its high electrical and optical quality. The high demand and the limited indium resources have resulted in a considerable price increase in the last years, and alternative electrodes that contain a reduced amount or no indium have attracted much attention, between which aluminum-doped zinc oxide (Al:ZnO or AZO) layers have emerged as an interesting option. The highest ITO and AZO quality is usually obtained on glass substrates heated at high temperatures (> 300 ºC). For the growth of the metal oxide films onto flexible plastic substrates or onto photoactive polymers, however, it is necessary to reduce the preparation temperature due to the poor thermal endurance of many of such organic materials.

We have prepared ITO and AZO thin films onto conventional soda lime glass substrates, by sputtering of the corresponding ceramic targets, at room temperature. Several deposition parameters as the sputtering power, the deposition time and the oxygen content in the sputtering atmosphere were adjusted for each material in order to obtain thin films with similar optical and electrical characteristics. After the deposition process, annealing of the sputtered layers has been performed in vacuum by heating with halogen lamps. In this work, the relationships between the electro-optical properties of the layers and their dependence on the annealing temperature are studied comparatively for the ITO and AZO samples. Average visible transmittance around 85 % has been achieved with both AZO and ITO materials as-grown at room temperature, with sheet resistance in the 20-30 Ω/sq range, that prove their capability to be applied as transparent electrodes on low temperature organic substrates and devices. Besides, significant improvement of the electro-optical quality has been obtained by subsequent heating in vacuum, which gives a maximum increment in the average visible transmittance of ~ 5 % and reduces the electrical resistance until to half of the as-grown value.

OC3

TCO-less-dye-sensitized solar cells consisting of hybrid and tandem structures

Y. Kashiwa[1], Y. Ogomi[1], J. Usakawa[1], M. Kono[2], Y. Yamaguchi[2], and S. Hayase*
Kyushu Institute of Technology1, Nippon Steel Chemical Co. Ltd.2

Efficiency of dye sensitized solar cells (DSC) [1] has reached 11%. In order to increase the efficiency, we propose 3D DSCs (Figures 1-3) consisting of dye-double layer structures and hybrid Ti electrodes to cover wide ranges of wavelengths and collect electrons effectively.

1) **Improvement of charge collections by surface state passivation of nano-porous TiO_2 layers** [2]: We found that surface states of nano-porous TiO_2 layers can be passivated with organic dye molecules which stained titania surfaces under a pressurized CO_2 condition. This process realized long electron life time, high electron diffusion coefficient and suppression of unfavorable dye aggregations. 10.4 % efficiency is reported.

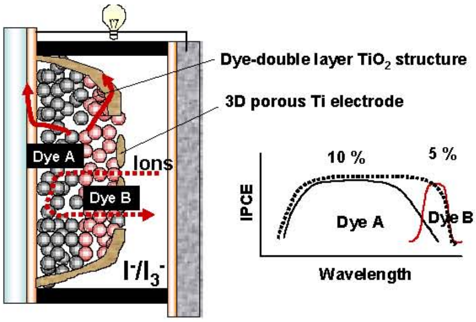


Figure 1. 3D-DSC consisting of dye double layer structure and porous Ti electrode

2) **Light harvesting covering wider range of wavelengths [3]:** 3D structures consisting of a dye-double layer titania structure and a 3D-porous Ti electrode are reported. The former enable to harvest light with wide range of wavelength, and the latter can help collect electrons from the back-side of the titania layer. The dye-double layer was realized by dye staining under a pressurized CO_2 process. The porous 3D-Ti electrode was fabricated by using nano ZnO crystals as the sacrifice materials. It was proved that these structures have a potential to be high efficiency cells. The advantages of the dye-double layer cell over a dye cocktail type DSC and the staining mechanism under the CO_2 condition are discussed.

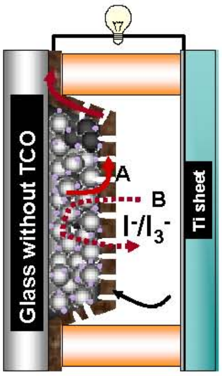


Figure 2. TCO-less-all-metal-DSC having 8% efficiency

3) **Transparent conductive layer less-DSC (TCO-less-DSC)-All metal electrode type DSC-** [4]: We report TCO-less-DSCs with all-metal electrodes. We focuse on nano-porous Ti electrodes prepared by use of nano-materials. 8% efficiency is reported for the all-metal-DSC.
4) **Tandem DSC consisting of floating electrode;** New tandem type solar cells shown in Figure 3 were fabricated. The fabrication process and the tandem performance are reported.

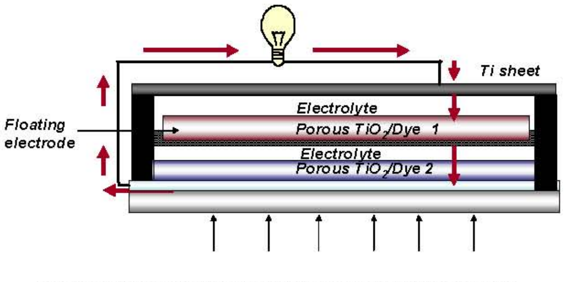


Figure 3. 3D-tandem DSC consisting of floating electrode

References

[1] B. O'Regan, M. Grätzel, Nature, 353, 737 (1991). [2] Y. Ogomi, S. Hayase, et.al., J.Electrochem. Soc., 153, A2294 (2006). [3] F. Inakazu, Y. Noma, Y. Ogomi and S. Hayase, Appl. Phys. Lett., (2008), in press. [4] Y. Kashiwa, S. Hayase et al., Appl. Phys. Lett., 92, 033308 (2008).

OC4

Degradation chemistry of N719 and Z-907 dyes at elevated temperatures.

Torben Lund[a*], Phuong Tuyet Nguyen[a] and Hoang Thai Nguyen[b]

[a] *Department of Science, Systems and Models, Roskilde University, DK-4000, Denmark*

[b] *Department of Chemistry, University of Sciences, HoChiMinh City, Vietnam*

The popular dye sensitized solar cell dyes N719 and Z-907 are in general accepted to be very stable under solar cell conditions below 45 ºC.[1] The dyes, however, may undergo thiocyanate ligand substitution reactions with the DSC solvent and additive molecules at elevated temperatures (80-100 ºC).

Recently we have established the mechanism and kinetics of these thiocyanate exchange reactions in both homogeneous solutions and colloidal mixtures with the dyes attached to TiO_2 particles.[2,3] The half life's at 85 ºC of the N719 and Z-907 bound to TiO_2 particles in colloidal solutions of 3-methoxypropionitrile and 4-*tert*-butylpyridine (0.5M) were 120h and 150h respectively. These results indicate that the N719 and Z-907 dyes will not be able to survive a 1000h solar cell thermal stress test [4] at 85 ºC. Strategies to reduce the dye degradation at elevated temperatures will be presented.

References

1) A. Hinsch, J. M. Kroon, I. Uhlendorf, J. Holzbock, A. Meyer, J. Feber, Prog. Photovolt. Res. Appl. 2001, **9**, 425.

2) H.T. Nguyen, H. M. Ta, and T. Lund, *Solar Energy Materials & Solar Cells* 2007**, 91**, 1934.

3) P. T. Nguyen, R. Degn, H. T. Nguyen, and T. Lund, *Submitted to Inorganic Chemistry.*

4) 1215, I., Crystalline Silicon Terrestrial Photo Voltaic (PV) Moduls Design. Qualification and Type Approval. International Electrotechnical commission **1993**.

OC5

W and Z Series Interconnections for Dye Solar Cell Modules

F. Giordano*, E. Petrolati, S. Mastroianni, T. M. Brown, A. Reale, A. Di Carlo
*CHOSE - Centre for Hybrid and Organic Solar Energy, University of Rome "Tor Vergata", Electronic Engineering Department, via del Politecnico 1, 00133 Rome, Italy *fabrizio.giordano@uniroma2.it*

Dye Solar Cells (DSCs) are interesting as a promising low cost PV technology. In order to increase the voltages, cells have to be connected in series. DSC technology allows the fabrication of series interconnected cells on a single substrate simultaneously in a variety of ways. Constraints in the geometrical design of cells and modules are given by the increasing series resistance with area due to the significant resistivity of Transparent Conductive Oxides (TCOs). It is also necessary to ensure full isolation between cell electrolyte chambers and between any electrical connection and the corrosive electrolyte.

Here we will consider DSC modules fabricated using the Z and W interconnection schemes (see Fig 1).

Series connection can be made by adding vertical connections or conductive fingers between cells (Z connection, Figure 1a). These conductive lines and the additional encapsulant necessary to isolate the connections from the electrolyte occupy useful space on the on the total area.

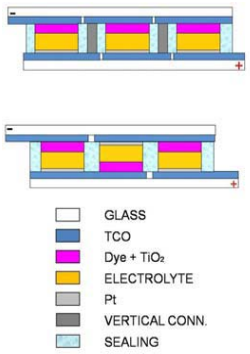
By contrast the W connection (Figure 1b) does not require vertical interconnects as the connection is made using the TCO, via the alternation of counter electrodes (CE) and working electrodes (WE). In this case, the inactive area consists of the sealant between cells only. The disadvantage of this configuration is that half of the cells are illuminated from the counter electrode side: a signficant fraction of light is absorbed by the electrolyte reducing the current significantly for roughly half the cells of the module. In order to match the currents for all the cells on each module [1], CE-illuminated cells need to be made larger than the WEilluminated cells.

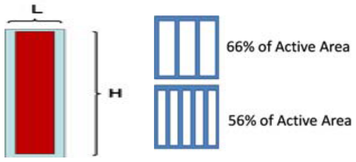
Here we present optimization of the geometric characteristics for both the W and Z architectures Ander AM1.5, 1000W/m2 illumination. We have prepared a series of single cells that differ only by their width (L). Increasing the width of the cell (L, Figure 2) results in a significant decrease in Fill Factor (and thus of efficiency) as shown in Figure 3 due to a higher TCO series resistance.

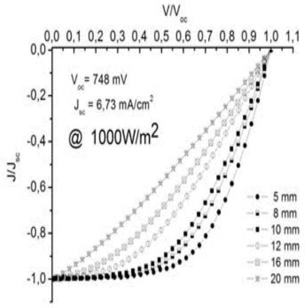
Making very narrow cells is not however a viable option as the ratio of active area over total module area decreases with L since the non-active area occupied by the sealants and interconnects is fixed by fabrication constraints. We find that the optimal length, weighing these two aspects, depends on cell efficiency, illumination conditions and module architectures. For the case of cells with efficiency of between 3%-4%, sealant space of 4mm illumination conditions of 1000 W/m$_2$ the optimum L is 10 mm.

For optimization of the W interconnected module we diluted the concentration of I_{3-} species of the electrolyte used of the Z module (R-150, Solaronix), thereby making the electrolyte more transparent. In this way it was possible to reduce the area of CE- illuminated cells by 50% leading to an overall increase of module efficiency.In conclusion it is exposed a quantitative comparison of performancesprovided by these two types of module schemes after our optimization,to evince advantages and disadvantage of both configurations.

(a)







(b) **(a)** **(b)**

Figure 1: *Z connection scheme (a) and W connection scheme (b).*

Figure 2: *Cell geometry (a), Module design (b): the percent of active area over total module area.*

Figure 3: *Normalized IV curves of cells with different widths (L).*

Referentes

[1] R. Sastrawan , J. Renz, et al., *Journal of Photochemistry and Photobiology A: Chemistry,* 2006, **178**, 33–40

OC6

Optimization of monolithically connected OPV devices with respect to first applications.

I. Etxebarria[a, b, *], M. Neophytou[a], U. Muñecas[a], J. Ajuria[a], M. Gomez[a], C. Waldauf[a] and R. Pacios[a]
a, Dpt. of Microsystems, Ikerlan S.Coop, Paseo J.M. Arizmendiarrieta 2, 20500, Spain.
b Dpt. of Chemical engineering,Universidad del País Vasco(Facultad de Ciencia y Tecnología) ,Barrio Sarriena , 48940, Spain.
**, ietxebarria@ikerlan.es*

Lifetime, efficiency and production costs of state-of-the-art organic photovoltaic devices are already very close to fulfill the demanded targets for daily life applications such as portable electronics. The easiest way for a market breakthrough would be as a potential replacement of standard 1.5V-batteries that are currently used to power most devices of this kind.

Consequently we would like to present design and production techniques for monolithically connected OPV devices which provide 1.5V under indoor lighting conditions. Processes are optimized in terms of yield and efficiency. Moreover, the resulting devices are designed with AA-batteries dimensions to prove their potential to presumably power small portable electronic devices of our daily life such as remote controls, mp3 players, calculators etc.

OD1

Novel Concepts in Solid-state dye-sensitized solar cells

K. Willinger, J. Brendel, Y. Lu, M. Thelakkat *
Applied Functional Polymers, Department of Macromolecular Chemistry I, University of Bayreuth, 95440 Bayreuth, Germany

We present two major concepts to improve the performance of solid-state dye-sensitized solar cells (SDSC). In concept I, we design and synthesize novel heteroleptic Ru(II)bis(bipyridyl)(NCS)2 dyes carrying a variety of donor-antenna groups. These dyes typically comprise of an efficient anchoring group to guarantee a proper connection between the dye and the mesoporous TiO2 surface, two NCS-groups to cause a bathochromic shift of the absorption spectra and novel donor-antenna groups. These groups effect very high extinction coefficients and as a consequence of this a distinctive light harvesting behaviour. To prove the performance of this new dyes they were applied in SDSCs consisting of FTO coated glass, mesoporous TiO2 and for regeneration of the dyes Spiro-OMeTAD as hole transport layer. In concept II, we developed novel porous TiO2 network using spherical polymer electrolyte brushes (SPB) as templates to control the morphology of the network and thus to provide best conditions for a sufficient pore filling and an effective electron transport. The facile tuning of the brush length as well as core size of the precursor and defined amounts of TiO_2 hydrolysed within the brushes finally provide exact control on the resulting morphology of the porous network.

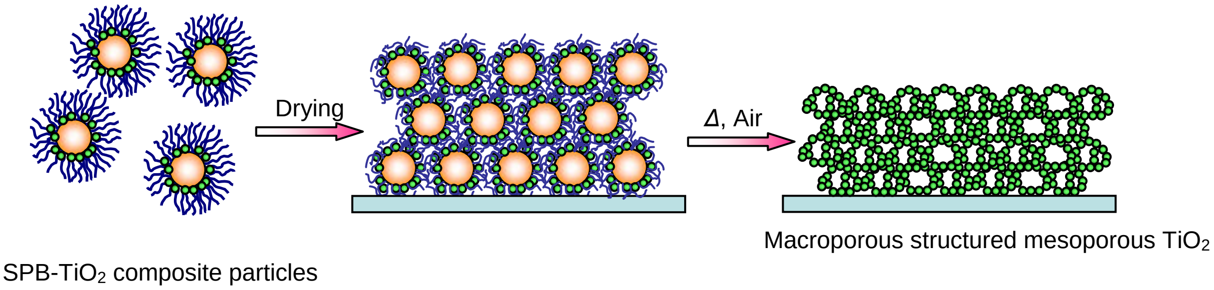


Figure 1: *Schematic representation of a novel method for the preparation of mesoporous network of TiO_2 with controlled pore sizes using spherical polymer brush (SPB) template*

References:

1. K. Shankar, J. Bandara, M. Paulose, H. Wietasch, O. K.Varghese, G..K. Mor, T. J. LaTempa, M. Thelakkat, and C. A. Grimes, Highly Efficient Solar Cells using TiO2 Nanotube Arrays Sensitized with a Donor-Antenna Dye, *Nano Letters 8, 1654-1659, (2008).*

2. C. S. Karthikeyan, M. Thelakkat, Key aspects of individual layers in solid-state dye-sensitized solar cells and novel concepts to improve their performance
Inorganica Chimica Acta 361 635–655 (2008).

3. S. Handa, H. Wietasch, J. R. Durrant, M. Thelakkat, S. A. Haque, Reducing charge recombination losses in solid state dye sensitized solar cells: the use of donor-acceptor sensitizer dyes
Chem Commun. **17**, 1725-1727 (2007)

OD2

Interface modification after TiO_2 electrode being dye-sensitized in quasi-solid state dye-sensitized solar cells

Y. T. Shi*, L. D. Wang*, B. B. Ma, R. Gao, F. Luo and Y. Qiu
Key Lab of Organic Optoelectronics & Molecular Engineering of Ministry of Education, Department of Chemistry, Tsinghua University, Beijing 100084, China

In our study, some interface modification work have been done in recent years. Firstly, interface modification was carried out with alumina after the TiO_2 films being sensitized with dye. The interaction between the dye and the resulting Al_2O_3 overlayer was investigated by ultraviolet–visible (UV–vis) spectrum, Fourier transform infrared (FTIR) spectrum and X-ray photoelectron spectrum (XPS). The Al_2O_3 overlayer at the dye/electrolyte interface resulted in a 28% improvement in overall photo-to-electrical conversion efficiency. Dark current measurements showed that Al_2O_3 acted as an insulator barrier to retard recombination between the TiO_2 and dye/quasi-solid-state electrolyte interface.

Secondly, N3 dye and Al_2O_3 was used to form an alternating assembly structure in dye-sensitized solar cell. The alternating assembly could increase the adsorption of dye sensitizer, prohibit the aggregation of the dye, and retard the recombination reaction. These effects were investigated by ultraviolet–visible spectrum, Fourier transform infrared spectrum, transient photovoltages, current density-voltage characteristics and dark current measurements. The photon–electron conversion efficiency of the cell with alternating assembly structure was improved. And the stability of the cell was also improved.

Finally, The electrically conductive function of high–molecular weight poly(ethylene oxide) (PEO) ($M_w = 2\times10^6$ g/mol) was investigated in polymer gel electrolytes. Based on the results of diffusion coefficient of I_3^-/I^- and the conductivity of polymer gel electrolyte, it was revealed that the mobility of Li^+ was enhanced by PEO. It was also found that the enhanced mobility of Li^+ could facilitate the diffusion of injected electrons within TiO_2 electrode through ambipolar mechanism at the TiO_2 electrode/electrolyte interface, then internal resistance of DSC was reduced and the device's photovoltaic performance was improved. Assembled with a polymer gel electrolyte in which the PEO weight ratio was 10.0%, a quasi-solid state DSC showed considerable conversion efficiency of 6.12% under 100mW/cm^2 light illumination.

OD3

Reliable Electron-Only Devices: Electron Transport in n-type Polymers and Hybrid TiO_2-Polymer Structures

Robert Steyrleuthner, Sebastian Bange, Silvia Paul, Steve Albrecht and Dieter Neher*
Institut für Physik und Astronomie, Universität Potsdam, Karl-Liebknecht-Straße 24-25, 14476 Potsdam-Golm, Germany

Charge transport properties of conjugated polymers have received increasing attention during the last years as a possibly limiting factor for solar cell performance. In addition, layers of inorganic metal oxides such as TiO_2 und ZnO have been used in the past as the electron-transporting layer in combination with suitable polymers. While hole transport properties have been extensively studied using single-carrier current-voltage measurements, only few reports can be found where this was applied to electron transport. Here, we summarize the experimental difficulties associated with electron-only single-carrier devices. The role of leakage currents and nonlinear differential resistance is discussed and the physical origin of these effects analyzed. We present a preparation technique for the metal electrodes which significantly improves the reliablity of electron-only devices. Using this method, electron transport was studied for two representative n-type polymers over a wide range of layer thickness and temperature. The results are explained in terms of established trapping models with exponential trap distribution. We used the same approach to study electron transport through thin films made from TiO_2 nanoparticles. These studies revealed significant effects of the preparation conditions and of the surface states on the electron transport perpendicular to layer plane.

OD4

Integration and effect of nanoparticle-based one dimensional photonic crystals in dye sensitised solar cells

Silvia Colodrero,1 Mauricio E. Calvo,1 Agustín Mihi,2 Manuel Ocaña,1 Gerrit Boschloo,2 Leif Häggman,2 Juan A. Anta,3 Anders Hagfeldt,2 Hernán Míguez1,*
1 Instituto de Ciencia de Materiales de Sevilla (CSIC), Américo Vespucio, 49, 41092 Sevilla, Spain
2 Department of Chemistry, Center of Molecular Devices, The Royal Institute of Technology, Teknikringen 30, S-100 44 Stockholm, Sweden
3 Depto. de Sistemas Físicos, Químicos y Naturales, Universidad Pablo de Olavide, 41013 Sevilla, Spain
hernan@icmse.csic.es

A novel nanoparticle-based-one dimensional photonic crystais implemented in dye sensitised solar cells (DSSC) to enhance the solar to electric power conversion efficiency. The employed photonic crystals are highly reflecting and porous to allow the flow of the electrolyte through it. The experimental analysis of the photogenerated current of very thin and uniform dye-sensitised nanocrytalline titanium oxide (nc-TiO2) electrodes coupled to these high quality one-dimensional photonic crystals confirm that photon resonances within absorbing electrodes are responsible for the light harvesting enhancement, in good agreement with previously been reported theoretical predictions for photonic crystal based solar cells. With a thickness of just half-micron, the photonic crystal is able to efficiently localize incident light within the nc-dyed TiO2 electrode in a targeted wavelength range. Average power conversion efficiencies are improved between 15% and 30% with respect to the reference value attained for standard electrodes. Besides, the transparency of the cell remains intact contrarily to what happens when other scattering layers are employed to improve light harvesting. Also, photoconducting Bragg mirrors can be attained using a single type of material (TiO2) through a precise control of the porosity in each deposited layer. The resulting material combines photogenerated electron transport with photonic crystal properties, which allows the tuning of the photoelectric response with the photonic crystal lattice parameter.

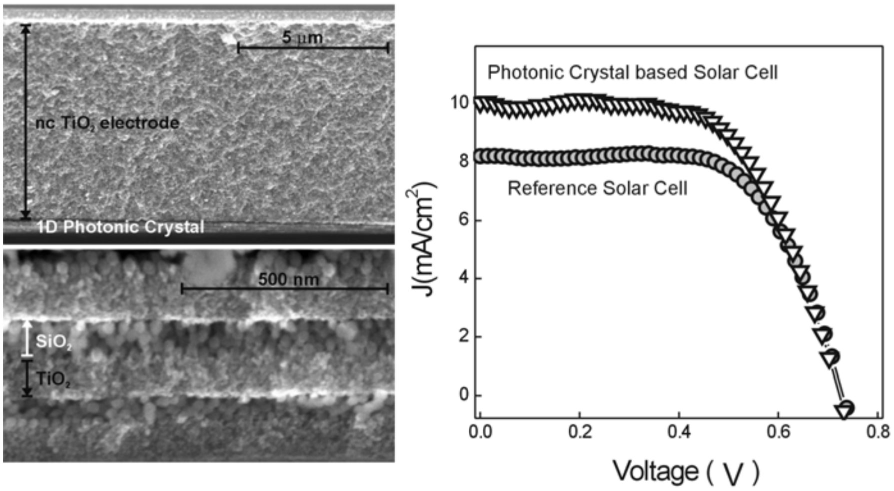


Figure. *Left*: FESEM images showing a cross-section of a dye sensitised nc-TiO$_2$ electrode onto which a nanoparticle multilayer has been deposited (top) and a magnified view of the nanoparticle layers composing the 1D photonic crystal (bottom). *Right:* Current-Voltage characteristics for both a standard electrode made of titanium dioxide nanoparticles and the same electrode coupled to a 1D photonic crystal.

[1] Colodrero, S., Mihi, A., Anta, J.A., Ocaña, M., Míguez, H. *J. Phys. Chem. C,* 2009, published online on January 5th 2009. DOI: 10.1021/jp809789s

[1] Mihi, A.; Míguez, H. *J. Phys. Chem. B,* 2005, **33**, 15968.

[1] Colodrero, S., Mihi, A., Häggman, L., Ocaña, M., Boschloo, G., Hagfeldt, A., Míguez, H. *Advanced Materials,* 2008, published online on December 16th 2008. DOI: 10.1002/adma.200703115.

[1] Calvo, M. E., Colodrero, S., Rojas, C.T., Ocaña, M., Anta, J.A., Míguez, H. *Adv. Func. Mater,* 2008, **18**, 2708.

OD5

Characteristics of iodide / triiodide electrolytes used in dye-sensitized solar cells

Gerrit Boschloo* **and Anders Hagfeldt**
Department of Physical and AnalyticalChemistry, Uppsala University, Box 259, 75101 Uppsala, Sweden.

The iodide / triiodide redox couple is by far the most used mediator in dye-sensitized solar cells. It is also the most successful in terms of solar cell efficiency. Nevertheless, there are several issues related to this redox couple:

- It is highly corrosive. Imperfect sealing of the cell may lead to attack of metal current collectors and destroy the module.
- Triiodide is colored and absorbs a significant amount of light, up to ca. 500 nm. This leads to a filter effect that can be significant in case of ionic liquid electrolytes that have higher I_3^- concentrations, and in case of illumination through the counter electrode (leading to a longer pathlength of the light through the electrolyte). Furthermore, reactive species are formed upon excitation of triiodide that may be detrimental to the long term stability of the solar cell.
- There is an internal loss of potential in the solar cells due to intermediate redox reactions. Specifically, the dye regeneration reaction may be written as follows:

  $$D^+ + 2\,I^- \rightarrow D + I_2^{-\cdot}$$

  The formal redox potential of the I_2^- / I^- couple is estimated to be about 0.3 V positive of the I_3^-/ I^- redox potential. This potential is lost in the cell, because the I_2^- radical is short-lived and disproportionates to I_3^- and I^-.

This paper will focus on the latter two issues. Photoinduced absorption spectroscopy and photomodulated voltammetry experiments on I_3^-/ I^- electrolytes and complete solar cells are described and used to obtain information on the intermediate redox species that are present in dye-sensitized solar cells under operation conditions.

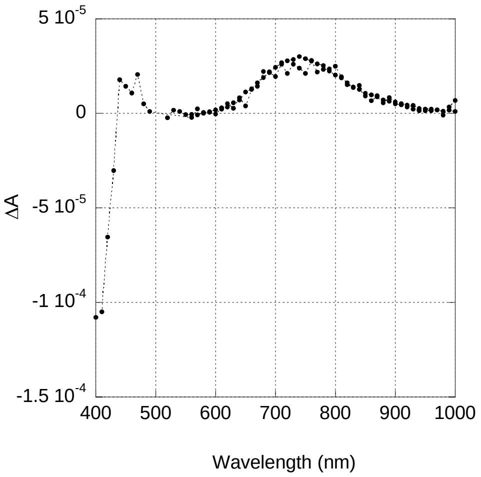


Figure 1. Photoinduced absorption spectrum of 0.5 M NaI and 0.05 M I_2 in propylene carbonate. A characteristic peak at 740 nm due to I_2^- formation is clearly visible.

OD6

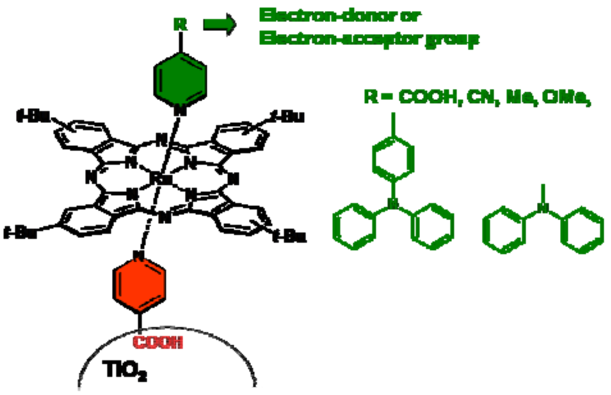
Ruthenium(II)phthalocyanines for Dye-Sensitized Solar Cells

Ismael López-Duarte[a]*, M. Victoria Martínez-Díaz[a], Ana Morandeira[c], Brian O´Regan[c], Amparo Forneli[b], Emilio Palomares[b], James Durrant[c] and Tomás Torres[a]

[a]Departamento de Química Orgánica, Facultad de Ciencias, Universidad Autónoma de Madrid, 28049
Cantoblanco, Spain.
[b]Institute of Chemical Research of Catalonia (ICIQ), Avda. Paisos Catalans 16,
Tarragona 43007, Spain.
[c]Department of Chemistry, Imperial College London, Exhibition Road, London SW7 2AZ, U.K

Considering their strong absorption in the red-near IR region of the spectrum and their good chemical, electrochemical and photochemical stability, phthalocyanines are among the most appealing dyes for the sensitization of nanocrystalline metal oxide films[1]. For many years, phthalocyanines have been incorporated in dye-sensitized solar cells (DSSCs) and the general conclusion raised is that the low efficiency of the devices may be related to strong tendency of phthalocyanine to form aggregates leading to deactivation of the excited state of the dye. Therefore, many efforts have been made towards the preparation of phthalocyanine with low tendency for aggregation and/or the use of aggregation inhibitors such as Cheno. Indeed, the introduction of axial ligands strongly bound to the central metals is by far the best strategy to avoid phthalocyanine aggregation. Moreover, it can be also a way to tune the electronic properties of phthalocyanine and an easy route to introduce anchoring functional groups such as carboxylic acids.

We have synthesized a new family of ruthenium(II)phthalocyanine complexes[2] bearing two similar or different pyridine axial ligands. Our goal was firstly to avoid pthhalocyanine aggregation, and secondly to evaluate the role of the substitutes both at the periphery and the pyridine axial ligand and to understand the influence of the macrocycle orientation at the metal oxide surface on the device´s performance.



References

1. G. de la Torre, C.G. Claessens, T. Torres, *Chem. Commun*. **2007**, 2000.
2. A. Morandeira, I. Lopez-Duarte, M.V. Martinez-Diaz, B. O´Reagan, C. Shuttle, N.A. Haji-Zainulabidin, T. Torres, E. Palomares, J.R. Durrant, *J. Am. Chem. Soc.* **2007**, 129, 9250

OE1

CdTe Quantum Dots: From Colloids to Photoanodes

G.P. Kissling,[a] E. Aslan,[b] C. Bünzli,[a] L. Asprey,[a] E. Arici-Bogner[c] and D.J. Fermín[a]*
[a]*School of Chemistry, University of Bristol, Cantocks Close, Bristol BS8 1TS, UK.*
[b]*Department of Chemistry and Biochemistry, University of Berne, Freiestr. 3, Berne 3012, Switzerland.*
[c]*Linz Institute for Organic Solar Cells, Johannes Kepler Universitaet Linz, Altenberger Strasse 69, Linz A-4040, Austria.*

Quantum dots (QDs) have been identified as key materials in the development of excitonic solar cells.[1] State-of-the-art chemical synthesis provides fine control over the size and shape of the QDs, in particular II-VI materials.[2] The strong *quantum confinement* behaviour exhibited by these materials has stimulated intense research on their use as sensitisers for wide band gap photoanodes and in photoactive bulk QD-polymer heterojunctions.[1] Despite recent progress in the design of excitonic solar cells, fundamental aspects connected to the dynamics of charge transfer as a function of the QD energy levels remains little explored.[3] In the present contribution, we shall discuss the charge transfer reponses involving CdTe QDs assembled at metal and metal oxide surfaces in relation to the position of the band edges as probed by electrochemical measurements.

Mercaptopropionic acid (MPA) stabilised CdTe QDs were prepared by an established two-step synthesis protocol.[3] Tuning growth conditions allows control of the average dot radius in the range of 1.7 to 2.5 nm. The position of the *valence band edge of the dots*, with respect to the Ag/AgCl reference electrode, was estimated from current-potential measurements of colloidal solutions using a rotating disc electrode. The electrochemical data was rationalised from values associated with bulk semiconductor electrodes employing semiquantitative models for quantum confinement. These studies suggest that MPA binding shifts the band edges towards higher energies with respect to the values expected for “clean” particles. Binding of MPA to the CdTe QDs was also investigated by high resolution XPS measurements.

The position of the valence band edge strongly influences the dynamics of electron transfer mediated by a QD monolayer. The assembly of a QD monolayer at thiol modified Au electrodes generates an increase in the kinetics of electron transfer to species in solution, in particular towards the reduction step. This unusual *faradaic current rectification* is dependent on the QD radius. This behaviour is substantially different to the enhancement in the charge transfer rate observed in 2D arrays of metallic nanostructures.[4] Finally, the photovoltaic responses of CdTe assemblies at mesoporous TiO_2 photoanodes will be briefly presented. The polymer poly [2-methyl, 5-(3*,7** dimethyl-octyloxy]-p- para-phenylene vinylene) (MDMO-PPV) is employed as hole-transporting layer in these devices.

Acknowledgements. The authors gratefully acknowledge the contributions to this work by Prof. N.S. Sariciftci (Johannes Kepler Universitaet Linz), Dr. Annette Foelske (Paul Scherer Institute) and Dr. Ruediger Koetz (Paul Scherer Institute). E.A. and D.J.F. are also grateful to the Swiss National Science Foundation (PP002-116898/1) and the European Science Foundation for the financial support.

References

1. P. Kamat, *J. Phys. Chem. C*, 2008, **112**, 18737.
2. Z.A. Peng and X. Peng, *J. Am. Chem. Soc.*, 2002, **124**, 3344
3. A. Kongkanand et al., *J. Am. Chem. Soc.*, 2008, **130**, 4007
4. C.R. Bradbury, J. Zhao and D.J. Fermín, *J. Phys. Chem. C.*, **112** (2008) 10153

OE2

Quantum Dot sensitized Solar Cells: on the different ways of attaching quantum dots to the titanium dioxide nanoporous electrode

Néstor Guijarro, Teresa Lana-Villarreal, Roberto Gómez*
Institut Universitari d´Electroquímica i Departament de Química Física, Universitat d´Alacant, Apartat 99. E-03080 Alacant, Spain; e-mail: Roberto.Gomez@ua.es

Semiconductor quantum dots (QDs) are being employed to harvest light in photovoltaic devices. Up to now, one of the more important hurdles is the difficulty of assembling QDs into the nanoporous TiO_2 as to obtain a full monolayer and an effective electron injection. Interestingly, the mode of attachment of QDs to the oxide matrix plays an important role in the performance of the solar cell[1].

Different approaches have been employed to sensitize nanoporous TiO_2 electrodes with CdSe QDs. On the one hand, the QDs have been grown directly onto the oxide by Successive Ionic Layer Adsorption and Reaction (SILAR). This method allows direct contact between QDs and TiO_2, but unfortunately there is no separate control of QD size and coverage. On the other, the TiO_2 surface has been modified by using presynthesized and well-characterized QDs capped with TOP. In the latter, CdSe QDs have been attached either by direct adsorption or through a linker, a bifunctional molecule that acts as a molecular cable (such as mercaptopropionic acid –MPA-, cysteine, cisteamine and 4-mercaptobenzoic acid). In all cases, QD coverage has been controlled by changing adsorption time. IPCE and electrochemical measurements have been done in an aqueous Na_2SO_3 solution.

From the results obtained with the corresponding electrodes, the effect of the linker cannot be interpreted solely on the basis of the average distance between QD and oxide, but other chemical, more specific effects seem to concur. In any case, for equivalent presynthesized QD loading, direct adsorption leads, in general, to higher IPCE values than linker-mediated adsorption. It seems that reducing the distance between QD and TiO_2 enhances vectorial electron injection. On the other hand, the IPCE-QD loading dependence shows a maximum for direct adsorption, while a monotonous increase up to a constant saturation value occurs in the case of adsorption through a linker. As shown in **figure 1**, AFM images of sensitized TiO_2 single crystal electrodes reveal that, in contrast with linker-mediated adsorption, direct adsorption leads to a high degree of aggregation, particularly for long adsorption times. This aggregation hinders the electron injection from QD to TiO_2 and, even more importantly, blocks the nanopores of the electrode, making the charge transport more difficult. A remarkable observation is that the maximum coverage obtained for direct adsorption of 3.4-nm CdSe QDs is only 14% of TiO_2 real surface area (5 µm-thick P25 film). Probably, a large part of the inner TiO_2 surface remains inaccessible for QDs (bottle necks, tortuous channels). Finally, the efficiency in the case of direct adsorption is compared with that obtained with the SILAR method, which has been optimized for CdSe in our laboratory.

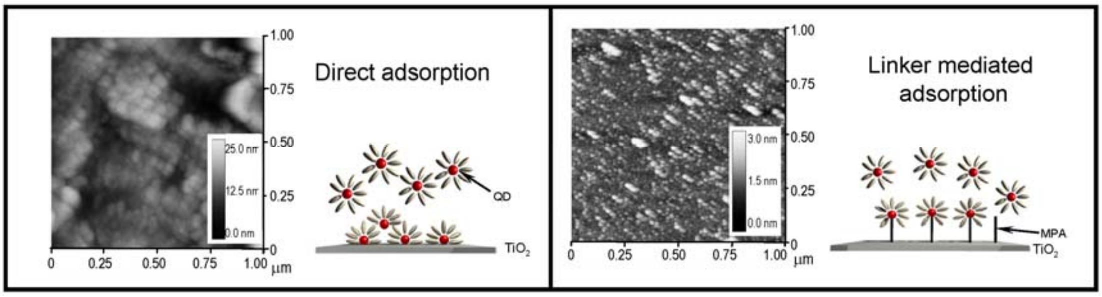


Figure 1

References

1. N. Guijarro, T. Lana-Villarreal, I. Mora-Seró, J. Bisquert, R. Gómez, *J.Phys. Chem. C*, ***In Press***

OE3

Pushing up the performance of colloidal quantum dot sensitized solar cells

Iván Mora-Seró[1,*], Sixto Giménez[1], Lorena Macor[1], Nestor Guijarro[2], Teresa Lana-Villareal[2], Roberto Gómez[2], Lina J. Diguna[3], Qing Shen[3], Taro Toyoda[3,*] and Juan Bisquert[1]

[1] *Photovoltaic and Optoelectronic Devices Group, Departament de Física, Universitat Jaume I, 12071 Castelló, Spain*

[2] *Departament de Química-Física i Institut Universitari d'Electroquímica, Universitat d'Alacant, Ap. 99, E-03080 Alacant, Spain,*

[3] *Department of Applied Physics and Chemistry, The University of Electro-Comunnications, 1-5-1 Chofugaoka, Chofu, Tokyo 182-8585, Japan*

[*]***Corresponding author:** sero@fca.uji.es, toyoda@pc.uec.ac.jp*

Solar cells on a mesoporous structure of TiO_2 with polysulfide redox electrolyte were prepared by direct absortion of colloidal CdSe quantum dot light absorbers without any special linkers. Several factors cooperate to improve the performance of quantum dot sensitized solar cells: i) we show a new strategy for adsorbing presynthesized colloidal QDs without the aid of any molecular linker, which increases significantly the obtained photocurrents; ii) an open structure of the wide bandgap electron collector that allows higher covering of the internal surface with the sensitizer; iii) surface passivation of TiO_2 to reduce recombination, and iv) enhanced counter electrode materials. As a result solar cells of 1.83% efficiency under full 1 sun illumination intensity have been obtained. This is to the best of our knowledge the highest efficiency ever reported for solar cells employing presynthesized colloidal CdSe quantum dots. Despite relatively large short circuit current (J_{sc}=7.13 mA/cm^2) and open-circuit voltage (V_{oc}=0.53 V), the colloidal quantum dot solar cell performance is still limited by a low fill factor of 0.50, which is believed to arise from charge transfer of photogenerated electrons to aqueous electrolyte.

OE4

Effect of atmospheres on the photovoltaic performance of Excitonic Solar Cells (XSCs) based on semiconductor oxides

Dr. Monica Lira-Cantu*

a. Centre de Investigaciò en Nanociencia i Nanotecnologia. Campus UAB, Edifici ETSE 2nd Floor. Bellaterra (Barcelona) Spain E-08193. monica.lira@cin2.es

Excitonic solar cells (organic, hybrid and dye sensitized) are the best examples of efficient and environmental friendly energy conversion devices. Recently, XSCs based on semiconductor oxides and conducting organic polymers (better known as Hybrid Solar Cells, HSC), have shown to depend on atmosphere conditions.[1] Long-term irradiation tests show that inert atmospheres (e.g. argon, vacuum) decrease photovoltaic performance, while air (oxygen) improves their photovoltaic response.[1,2] The later has been attributed to the oxygen release and exchange mechanism observed from the semiconductor oxide as already reported.[3] In this work, we will show our fist studies carried out on the modification of different XSCs components (hole or electron transport materials) and the photovoltaic effect observed when properties are tuned (e.g. cristallinity, conductivity, etc). We will show how the photovoltaic response, analyzed under long-term irradiation conditions, is affected when different testing parameters are applied (e.g. temperature, atmosphere, relative humidity, etc), as shown in Figure 1.

We will briefly present the initial results obtained in our laboratory on the application of other XSCs like Dye Sensitized Solar Cells (DSC) or solid-state Dye Sensitized Solar Cells (ss-DSC).[4,5]

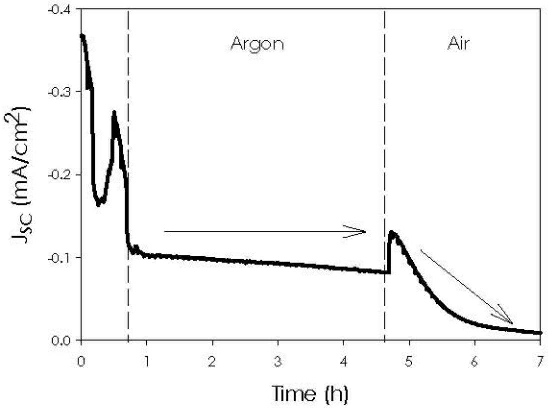


Figure 1. Photovoltaic response observed for semiconductor oxide –based excitonic solar cell under continuous illumination (A.M.1.5, 1000 W/m$_2$) applying different atmospheres. Measurements carried out at 77 ºC with a fixed gas flux, active area 0.6 cm$_2$. Analyses performed at the photovoltaics laboratory at CIN2 (CSIC-ICN).

References

1. M. Lira-Cantu, K. Norrman, J.W. Andreasen, N. Casan-Pastor, and F.C. Krebs. J. Electrochem. Soc., 2007. **154**(6), B508-B513.
2. M. Lira-Cantu and F.C. Krebs. Sol. Enegr. Mater. Sol. Cells, 2006. **90**(14), 2076-2086.
3. M. Lira-Cantu, M., K. Norrman, J.W. Andreasen, and F.C. Krebs. Chem. Mater. 2006. **18**(24), 5684-5690.
4. Gonzalez-Valls and M. Lira-Cantu. *Energy Environ. Sci*., 2009. In Press DOI:10.1039/b811536b. Published on-line November 25, 2008.
5. D. Muñoz-Rojas, M. K. Siddiki, R. Amade, J, Oro and M. Lira-Cantu. Submitted.

OE5

Single Molecule Spectroscopy of a Proton Transfer Dye Encapsulated in Mesosoporous Nanochannels

Boiko Cohen, Juan Angel Organero, Abderrazzak Douhal*
Departamento de Química Física, Sección de Químicas, Facultad del Medio Ambiente, UCLM, 45071 Toledo, Spain
Corresponding Author: abderrazzak.douhal@uclm.es

Studies by our group on the excited state dynamics of guest molecules encapsulated in various nanohosts have contributed to the characterization of the confinement effect.[1-3] Of these the interactions within the zeolite nanocavities are least characterized. Mesoporous silicate networks have many applications ranging from medicine[4] and photonics[5-6] to catalysis. It is of great importance to gather knowledge regarding the behavior of a chromophore encapsulated in zeolite nanocavity on single molecule level. In this presentation, we report on the results of single molecule confocal microscopy studies of fluorescence lifetime and emission spectra of a proton transfer dye absorbed to the inner surface of amorphous silica and mesoporous structured silicate. A representative image, the photobleach fluorescence trace and the derived monoexponential decay of such complex is presented in Figure 1. From the presented results it is clear that the preparation methods of molecular zeolite complexes are of great importance and often don't yield the same outcome. Figure 2 shows the dramatic change in spectral and time-resolved behavior of the single molecule-zeolite complexes depending on the mode of encapsulation. This indicates that special care needs to be taken during the preparation process to prevent formation of unwanted complexes. The results also support the conclusion that the electronic confinement concept is valid even at single molecule level. We demonstrate that chemical modifications to the zeolite framework can influence the guest molecule behavior. In general the SMS can provide valuable insight information regarding the behavior single molecule-zeolite complexes. In addition we show that proton transfer chromophores can be used as single molecule reporters for changes in the molecular environment.

Acknowledgements: This work was supported by the MEC and JCCM through the projects: CTQ-2005-00114/BQU, UNCM05-23-025 and PCI08-0037-5868. BC acknowledges MEC for the Ramon y Cajal fellowship.

References:

[1] A. Douhal, *Chem. Rev.* 2004, 104, 1955.
[2] A. Douhal, *Acc. Chem. Res.* 2004, 6, 349
[3] A. Douhal, Editor, "Cyclodextrin Materials Photochemistry, Photophysics, and Photobiology", Elsevier, Amsterdam, 2006,ISBN-13: 978-0-444-52780-6.
[4] K. Pavelic, M. Hadzija, *Handbook of Zeolite Science and Technology*, 2003,1141
[5] G. Calzaferri, S. Huber, H. Maas, C. Minkowski, *Angewandte Chemie, International Edition* 2003, 42, 3732.
[6] A. Corma, *Journal of Catalysis* 2003, 216, 298.

OE6

Influence of chemical environment on electron transfer dynamics of organic absorbers bound to nanostructured TiO_2 electrodes

A.F. Bartelt [a]*, R. Schütz [a], A. Neubauer [a], Th. Hannappel [a], and R. Eichberger [a]
a, Dynamics of Interfacial Reactions–SE 4, Helmholtz-Zentrum Berlin für Materialien und Energie, Glienicker Strasse 100, 14109 Berlin, Germany.

In organic-inorganic solar cells, electron transfer across the hybrid interface is essential since the photo-excited electron-hole pair or exciton has to be effectively separated, and charge carrier recombination processes with either the oxidized dye or a hole-transporting medium (HTM) have to be suppressed. The charge separation is mostly governed by the energy difference between injection level and conduction band minimum while for the recombination surface traps play a crucial role. Adsorbates on the semiconductor surface will alter the interface energetics, with effects on the performance of the dye sensitized solar cell (DSSC) when operated either with an electrolyte or a polymer-based HTM. Understanding the influence of the chemical species surrounding the inorganic surface with the attached organic absorber on the electron transfer may guide an interface engineering for improved charge separation and performance.

In this contribution, we will present time-resolved data describing electron injection and early charge recombination of Perylene derivatives bound to colloidal TiO_2 under the presence of various chemical species. Two perylene model chromophores with different anchor/bridge groups, propionic acid and acrylic acid[1], are examined, which exhibit significantly different electronic couplings to the TiO_2 surface. Starting with a dye-sensitized film under vacuum conditions, the electron injection is slowed down as a chemical environment is introduced. Changing from different inert gases to different solvents, the ultrafast sub-50 femtosecond injection process found under vacuum conditions is subsequently retarded up to two orders of magnitude. Thereby, the injection dynamics correlates with the degree of polarity and the density of the chemical species: The more polar and the denser the adsorbing species, the slower the injection process. Furthermore, both molecules are affected similarly with regard to the retardation, independent of the strong differences in their electronic couplings to the semiconductor surface. This suggests an electronic shift of the oxide conduction band relative to the injecting molecular level, due to the electrostatic interaction of the adsorbates with the surface. The charge recombination dynamics will also be compared for the different chemical environments on a time scale of one nanosecond, and the effect of the adsorbate polarity on early and late recombination processes will be discussed.

The experiments were performed with a 20-fs 150 kHz Lasersystem. The injection and recombination process was monitored by recording the transient absorption of the cationic Perylene species with a super-continuum pulse.

References

1. J. Szarko, A. Neubauer, A. Bartelt, L. Socaciu-Siebert, F. Birkner, K. Schwarzburg, and R. Eichberger, *J. Phys. Chem. C* 2008, **112***,* 10542

OE7

Electrodeposition of ZnO in ionic liquids

E. Azaceta, R. Tena-Zaera*, R. Marcilla, D. Mecerreyes, J. Pomposo, H. Grande
New Materials Department, CIDETEC, Centre for Electrochemical Technologies, Parque Tecnológico de San Sebastián, Paseo Miramón 196, Donostia-San Sebastián 20009, Spain

Arrays of single-crystal ZnO nanowires have emerged as promising building blocks for hybrid solar cells.[1] Among the various deposition techniques, electrochemical deposition in aqueous media presents a great potential to obtain arrays of ZnO nanowires with controlled dimensions[2] and tunable electrical properties.[3] Ionic liquids exhibit several attractive properties such as wide electrochemical window, high ionic conductivity and negligible vapor pressure to be used as an alternative electrolyte.[4] Here, we present an innovative electrochemical route to deposit ZnO using room temperature ionic liquids such as *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide ($PYR_{14}TFSI$) as electrolyte. Since the ZnO electrodeposition in aqueous electrolytes is generally based on the reaction between Zn^{2+} and OH^- ions (resulted from the reduction of oxygenated precursors such as O_2, NO_3^- and H_2O_2 in water)[5], the use of aprotic electrolytes may affect significatively the deposition mechanisms. An overview of the differences between the ZnO electrodeposition in ionic liquids and aqueous electrolytes will be given, emphasizing the possibilities of the first route in the domain of the hybrid solar cells.

References

1. M. Law, L.E. Greene, J.C. Johnson, R. Saykally, P. Yang, *Nature Mater.*, 2004, **4**, 455. P. Ravijaran, A. M. Peiro, M.K: Nazeerudin, M. Grätzel, D.D.C. Bradley, J.R. Durrant, J. Nelson, *J. Phys. Chem. B,* 2006, **110**, 7635.
2. J. Elias, R. Tena-Zaera, C. Lévy-Clément, *J. Electroanal. Chem.*, 2008, **621**, 171. R. Tena-Zaera, J. Elias, G. Wang, C. Lévy-Clément, *J. Phys. Chem. C*, 2007, **111**, 16706.
3. R. Tena-Zaera, J. Elias, C. Lévy-Clément, C. Bekeny, T. Voss, C. Bekeny, I. Mora-Seró, J. Bisquert, *J. Phys. Chem. C,* 2008, **112**, 16318.
4. F. Endres, A.P. Abbott; D.R. MacFarlane, *Electrodeposition from Ionic Liquids* (Wiley-VCH, Weinheim, 2008)
5. R. Tena-Zaera, J. Elias, C. Lévy-Clément, I. Mora-Sero, Y. Luo, J. Bisquert, *Physica Status Solidi a,* 2008, **205,** 2345.

OE8

Study of Eosin-Y/ZnO hybrid films electrodeposited in aqueous and organic solvents

M. Moya, M. Mollar and B. Marí*

Departament de Física Aplicada-IDF. Universitat Politècnica de València, Camí de Vera s/n, 46022 València, Spain

Hybrid materials composed by a mix of inorganic and organic compounds have been used for long time as a simple way to take advantage of the specific properties of their components. Hybrid materials can be functionalized to be used as photoinduced electron injectors from organic dyes to inorganic semiconductors for subsequent implementation into dye-sensitized solar cells (DSSCs)[1].

Owing to its high abundance, low price and small toxicity, zinc oxide (ZnO) is a suitable, wide bandgap semiconductor to be used as the inorganic component of hybrid films for photovoltaic devices. In the recent years, cathodic electrodeposition of ZnO in the presence of soluble organic dyes has been proposed as an innovative approach to prepare hybrid materials[2].

The growth conditions, such as the type of supporting electrolyte, solvent and substrate, play an important role in the morphology of the electrodeposited ZnO films. Thin and/or nanostructured ZnO films with different physico-chemical characteristics can be electrochemically obtained[3].

In this paper, we present a study of Eosin-Y/ZnO hybrid films synthesized by electrodeposition using two different solvents, dimethilsulfoxide (DMSO) and H2O. The morphology of electrodeposited ZnO films is highly influenced by the solvent (Figure 1). Consequently, it also influences on the characteristic of the hybrid film. When a non-aqueous solvent like (DMSO) is used, the electrodeposited film is formed by a homogenous, smooth and continuous layer (Fig. 1a). However, using water as solvent, a nanostructured, porous film is obtained (Fig. 1 b). The nanostructured film facilitates the electron passage making the electrodeposition of the hybrid film possible. On the other hand, the presence of Eosin-Y molecules into the continuous structure hinders the electron passage and does not allow the growth of the hybrid film. During the growth, the film becomes progressively non-conductor and electrodeposition is no longer possible.

The characterization of the ZnO hybrid films were performed by EDS (through the ratio Br/Zn) and optical absorption. These measurements allow us to determine the optimal parameters that control the incorporation of the dye into the hybrid film. Several parameters were studied; initial concentration of Eosin-Y, bath temperature and applied potential.

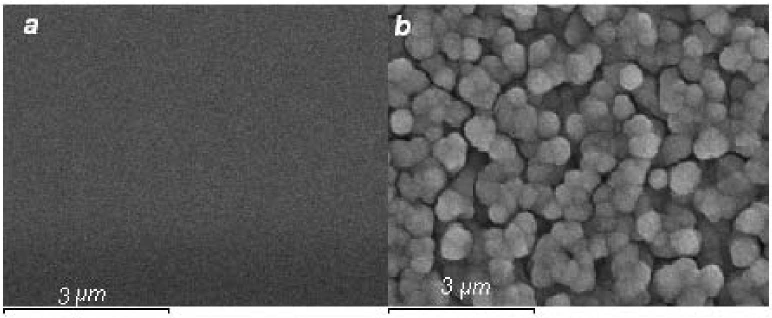


Figure 1. Scanning Electron Micrographs of Eosin-Y/ZnO hybrid films deposited from baths containing: (a) DMSO and 10µM Eosin-Y; (b) H_2O and 100µM Eosin-Y.

References

1 A. Hagfeldt, M. Grätzel, Chem. Rev. 1995, 95, 49.
2 T. Yoshida, H. Minoura, Adv. Mater. 2000, 12, 1219.
3 B. Marí, J. Cembrero, M. Mollar, M. Tortosa, Phys. Stat. Sol. C 2008, 5, 555

OE9

Solvent-free ZnO dye-sensitised solar cells

J. A. Anta[a], C. Fernández-Lorenzo[b], R. Alcántara[b], J. Martín-Calleja[b] E. Guillén[a*]

a, Departamento de Sistemas Físicos, Químicos y Naturales, Universidad Pablo de Olavide, 41013 Sevilla, Spain
b Departamento de Química Física, Universidad de Cádiz, 11510,Cádiz, Spain

Dye-sensitised solar cells based on commercial nanoparticulate zinc oxide in combination with ionic liquid electrolytes are prepared and characterized. The electrolytes are based in a binary mixture of two room temperature ionic liquids, one of them used as source of iodide ions. The composition of the solvent-free, ionic-liquid electrolyte is optimized with respect to the concentration of iodine and iodide and the effect of additives such as lithium and tert-butylpyridine (TBP) on the photovoltaic performance and the recombination rate is analyzed and discussed. It is observed that no significant slow diffusion processes limit the efficiency of the cells, whereas recombination losses become significant in many cases. Lithium ions and TBP are shown to have a similar effect on performance as that found for standard TiO2-based dye solar cell with organic solvents.

References

1 Guillén E., Anta J.A., Vega-Poot A., Rodriguez-Gattorno G., Oskam G., Alcantara R. Fernandez-Lorenzo C., Martin-Calleja J., *Journal of Photochemistry and Photobiology A-Chemistry*, 2008, **200**, 364-370
2. Y.M. Cao, J. Zhang, Y. Bai, R.Z. Li, S.M. Zakeeruddin, M. Grätzel, and P. Wang, *Journal of Physical Chemistry C*, 2008, **112,** 13775-13781
3. D.B. Kuang, C. Klein, Z.P. Zhang, S. Ito, J.E. Moser, S.M. Zakeeruddin, and M. Grätzel, *Small*, 2007, **3,** 2094-2102

OE10

Surface modification of nanoparticulate semiconductor in DSSCs by ALD

Chaiya Prasittichai and Joseph T. Hupp*
Department of Chemistry, Northwestern University, 2145 Sheridan Rd. Evanston, IL, 60208 USA.

Atomic layer deposition (ALD) has been used to create conformal blocking layers on nanoparticulate semiconductor. Results showed that with only one monolayer of this blocking layer could passivate the trap state in particles resulting in slower interfacial charge electron transfer. Subsequent deposition behaves as an electron tunneling barrier layer with different β value depending on the energetic difference of two semiconductors. This slow charge recombination could further provide a new route to successfully employ a rapid redox shuttle.

OF1

CHARACTERIZATION OF ORGANIC SOLAR CELLS MATERIALS AND STRUCTURES BY SPECTROSCOPIC ELLIPSOMETRIC

Christophe Defranoux*, J.P. Piel, A. Bourgeois.
SOPRALAB, 55 avenue de l'Europe, 92400 Courbevoie, France.
christophe.defranoux@sopra-sa.com

Spectroscopic Ellipsometry (S.E) is a well adapted optical technique widely used for the characterisation of all types of thin films for thickness and optical indices on glass or plastic substrates.
S.E. is also being applied to the characterization of materials and multilayer structures of organic materials like organic light-emitting diodes (OLEDs) or Organic Solar Cells.
We present the determination of the refractive indices of organic Solar Cells materials like P3HT, PCBM, Pentacene, Perylene, and their blends. Complex organic materials can be analyzed accurately from their absorption bands in the visible and UV range.
Transmission and absorption can be also measure at the same time and be used to determine the optical properties. Using these refractive indices, measurements of real multi-layer stacks can be done. The refractive indices can be used afterwards to automatically optimise and balance the energy flow dissipation Q inside an organic solar cell composed of a thin film stack. We present example performed on a single cell and tandem bi-layer cell structure.

Since these materials are sensitive to moisture and pollution, it can be necessary to measure the materials optical properties and thickness values through an encapsulated media. We will demonstrate how we can measure single layer properties and multi -layer stacks, through encapsulated samples from the back side of the substrate. This technique can be applied to test structure or real Organic Solar Cell monitoring. Backside measurement combined with a water vapour cell used for ellipsometry porosimetry is used to test the hard and thin film encapsulation.

We also present the characterization of ITO and ZnO transparent electrode by spectroscopic ellipsometry, and how near infra-red ellipsometry is used to determine the ITO resistance, without contact, by using the Drude behaviour on encapsulated samples.

OF2

HYBRID POLYMER: FULLERENE/SILICON PHOTOVOLTAIC CELLS FOR MAXIMIZING THE LIGHT HARVESTING

I. Etxeberria[a], U. Muñecas[a], M. Neophytou[a], J.Ajuria[a,*], C. Waldauf[a] , R. Pacios[a], J.C. Jimeno[b]

a, Microsistemas, Ikerlan, J.M. Arizmendiarrieta 2, 20500, Spain.
b Electrónica, EHU-UPV,Sarriene auzoa z/g, 48940,Spain.

Hybrid organic-inorganic solar cells containing semiconducting nanoparticles have the theoretical potential to integrate both material benefits mainly in the form of tuning the absorption. Nevertheless, this is not always possible due to the very different absorption coefficients of both materials.

However, stacking two different-energies absorbing layers is possible to balance both absorption and current to achieve efficient photovoltaic cells that maximize the light harvesting within the whole visible spectra. We therefore report hybrid polymer: fullerene-on silicon solar cells that show complementary spectra and can be combined to fabricate high efficient hybrid solar cells.

OF3

Photovoltaic solar cells based on Rod-Coil Block Copolymers Containing Poly(3hexylthiophene) and Fullerene

E. Cloutet (1)*, M. Urien (1,2), H. Erothu(1), R.C. Hiorns (1), H. Cramail (1), L. Vignau (2)
(1) Laboratoire de Chimie des Polymères Organiques (LCPO), Université de Bordeaux
UMR CNRS 5629, Ecole Nationale Supérieure de Chimie et Physique de Bordeaux, 16 Av. Pey Berland 33607 Pessac, France
(2) Laboratoire de l'Intégration, du Matériau au Système (IMS), Université de Bordeaux
UMR CNRS 5218, Ecole Nationale Supérieure de Chimie et Physique de Bordeaux, 16 Av. Pey Berland 33607 Pessac, France
cloutet@enscpb.fr ; vignau@enscpb.fr

Semi-conducting □-conjugated polymers have gained increasing interest over the last few years due to their applicability to organic electronics and especially organic photovoltaic cells (OPVs). Among these polymers, highly regioregular poly(3-hexylthiophene) (P3HT) is widely studied and photovoltaic cells with power conversion efficiency close to 5% have been obtained from blends based on the donor-acceptor system P3HT/[6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM).[1]

Nowadays further development of OPVs made from the P3HT/PCBM system is limited due to the difficulty to well control their morphology and nano-structuration in films. Indeed the system has to be optimized in order to enhance both the separation and diffusion of charges through the active layer. In this field, our study consisted in synthesizing C_{60} end-capped rod-coil block copolymers based on P3HT and polystyrene (PS) that are susceptible to self-assemble into different morphologies depending on the weight fraction of each block. In fact the nano-structuration of the active layer through the phase segregation of the block copolymers could give rise to the targeted lamellar structure.[2]

The synthetic route that was followed to synthesize P3HT-*block*-PS consisted in the Huisgen's 1,3-dipolar cycloaddition ('click') of the separately prepared ω-azido-PS and the ω-alkynyl-P3HT, which constitutes the first example of 'click' chemistry in the field of conjugated polymers. ω-azido-PS with different chain lengths were prepared by Atom Transfer Radical Polymerization (ATRP) and ω-alkynyl-P3HTs were prepared by the modified Grignard Metathesis method (GRIM).[3] 'Click' reactions were then carried out between the two homopolymers using Copper Iodide as catalyst.[4] The C_{60} moieties were subsequently attached to the PS end by Atom Transfer Radical Addition (ATRA) onto the terminal bromine atom. C_{60} end-capped rod-coil copolymers with different PS chain lengths have thus been obtained.

All the rod-coil block copolymers obtained in this study were then used as the active layer or as an additive in P3HT/PCBM blends in organic solar cells with Indium Tin Oxide (ITO) and Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT-PSS) as the anode and aluminum as the cathode. Solar cell characteristics will be discussed together with studies of the films morphologies. Interestingly, a substantial improvement in device performance was observed when introducing 5% of the C_{60} end-capped block copolymer as an additive to a P3HT/PCBM blend system (e.g. 30-50% improved efficiencies were obtained compared to the P3HT/PCBM solar cell fabricated without the additive).

(1) Günes, S.; Neugebauer, H.; Sariciftci, N. S. *Chemical Reviews* **2007**, *107*, 1324.
(2) Buxton, G. A.; Clarke, N. *Physical Review B* **2006**, *74*.
(3) Sheina, E. E.; Liu, J.; Iovu, M. C.; Laird, D. W.; McCullough, R. D. *Macromolecules* **2004**, *37*, 3526-3528.
(4) Urien, M.; Erothu, H.; Cloutet, E.; Hiorns, R. C.; Vignau, L.; Cramail, H. *Macromolecules* **2008**, *41*, 7033-7040.

OF4

Life Cycle Assessment of Organic Solar Cells

R. García-Valverde[a,*] N. Espinosa-Martínez[a], J. Padilla[b] J. Abad[c], J. Colchero[c] and A. Urbina[a]
[a], Departamento de Electrónica, Tecnología de Computadores y Proyectos, Universidad Politécnica de Cartagena, Plaza del Hospital, 1, 30203, Cartagena, Spain
[b], Departamento de Física Aplicada, Universidad de Murcia, Universidad Politécnica de Cartagena, Hospital de Marina, s/n, 30203, Cartagena, Spain
[c]. Departamento de Física, Edif. CyON, Universidad de Murcia, Campus de Espinardo,30071 Spain.

Life cycle assessment (LCA) studies aim at comparing and analysing the environmental impacts of products and services. In solar PV systems these studies present the energy use in terms of energy pay back time (EPBT). This is the time required for the solar PV system to generate the equivalent amount of energy consumed in the construction and decommissioning phases, since the operational phase (power generation) is free from fossil use and greenhouse gas (GHG) emissions.

Numerous LCA studies have been carried out on silicon based PV technologies and non-silicon based thin film (CdTe, CIS) [1-4]. These studies fully justify the use of PV systems as primary energy source with Energy pay back times between 1.1 to 2.7 years and 17-48 grams CO_2 eq. per kWh generated as emission factors for roof–top grid-connected PV system under Mediterranean insolation. Moreover these studies include material and energy inventories; these results are very useful to identify inefficient steps or those that could suppose bottlenecks or material limits in a gigawatt PV development.

Our work performs a LCA of a typical organic photovoltaic technology. We have selected, as representative of a broad range of different approaches, a organic solar cell in which the active layer is made of a blend of a fullerene derivative (phenyl-C61-butyric acid methylester, PCBM) and a conjugated polymer (poly-3-hexil-thiophene, P3HT). The proposed substrates and electrodes are also typical of this organic PV technology. The material inventory and the energy embedded in the process will however not differ from other similar approaches which use blends of other functionalized carbon-based nanoparticles and conjugated polymers of other kind, such derivatives of poly-para-phenylene-vinylene (PPV).

For this technology, using references from an extensive literature review, and the knowledge arising from our own device preparation method[5-8], we have calculated a material inventory, and the environmental impact of module fabrication (energy pay-back time, and emissions) using our own laboratory procedures for organic PV cells as a cap for any future large scale industrial process of an organic photovoltaic technology. We show interesting results for the embodied energy of critical input materials (e.g. ITO electrode or PCBM layer) and critical processing procedures (e.g. metal electrode evaporation, nitrogen atmosphere maintenance). The EPBT and the emission factor have been calculated from the material and energy inventories for hypothetical future Organic PV module efficiency of 5% and 10%.

References

1. E.A. Alsema, *Progress on Photovoltaics: Research and Applications,* 2000, **8**(1), 17-25.
2. N. Jungbluth. *Progress on Photovoltaics: Research and Applications,* 2005, **13**(5), 429-446.
3. M. Raugei et al. *Energy*, 32(8),1310-1318.
4. V.M Fthenakis et al. *Envrironmental Science & Technology,* 2008, **42**(6), 2168-2174.
5. J. Abad et al. *European Polymer Journal*, 2008, **44**(8), 2506-2515
6. E. Palacios-Lidon *Advanced Functional Materials*, **16**(15), 1975-1984
7. B. Perez-Garcia et al. *Nanotechnology*, 2008, **19**, 065709
8. A. Urbina et al. *European Physical Journal-Applied Physics*, 2007, **37**(3), 283-286

OF5

Main-chain fullerene polymers for photovoltaic devices

R. C. Hiorns (a)*, E. Cloutet (a)*, E. Ibarboure (a), L. Vignau (b)*, N. Lemaitre (c), S. Guillerez, (c) H. Cramaila
a, LCPO and b, IMS, Université de Bordeaux, ENSCPB, 16 av. P. Berland, 33607, Pessac, France; and c, INES RDI - DTS/LCS, Savoie Technolac, 50 av. du Lac Léman, 73377, Le Bourget du Lac, France.
hiorns@enscpb.fr, cloutet@enscpb.fr, l.vignau@enscpb.fr

Photovoltaic devices based on layers of poly(3-hexylthiophene)-*blend*-[6,6]-phenyl C61 butyric acid methyl ester (P3HT-*blend*-PCBM) are currently around 5 %.1,2 However, new polymers will probably be needed to assure the increase in efficiencies required for market acceptability.

In place of the molecule PCBM, intuitively, a polymeric acceptor should exhibit electron mobilities over longer distances due to covalent bonds and hopping between acceptor groups. It may also form amorphous and crystalline domains to enhance exciton capture and electron transport, respectively. There are some examples of such polymers in the literature, notably modified poly(phenylene vinylene)s.3,4 However, for reasons not completely understood, polymers tend to prefer hole transfer.5 This problem has been circumnavigated by preparing commodity polymers carrying acceptor fullerenes6,7 or perylenes.8 While these examples show extremely deft chemistry, they can involve numerous preparative steps and the polymer properties are complicated by the presence of electronically inert backbones.

Given these indications, we wished to explore facile preparations of polymers that contained fullerene, an exceptionally good electron acceptor, as part of the backbone of the chain, thereby removing the need for commodity polymers and complex preparative steps. There are a number of examples in the literature of polymers based on main-chain fullerene (MCF), however, they generally involve crosslinking, require tedious syntheses or can be 'invasive' with respect to the electronic structure of the C60.9 Here we demonstrate a new class of polymers with a prototype (Figure 1) prepared using atom transfer radical addition of small aromatic groups to C60.10 The MCF was attained in a simple synthetic step that intimated how a variety of inter-C60 groups can be easily incorporated. Additional work showed that for soluble MCFs to be formed, the inter-C60 group should be sterically cumbersome, and it is proposed that the reason for this is the stereo-electronic behaviour of C60. The polymer presents one of the highest known weight ratios of C60 (*ca* 62 %) and retains the aromaticity of the electron acceptor. In spin-cast thin films of MCF and P3HT, the MCF was found to form large aggregates (100 nm by 30 height) that with annealing approached sizes favourable for exciton capture (Figure 2). Photovoltaic characterisations of MCF-*blend*-P3HT showed unoptimised efficiencies at *ca* 1.6%.

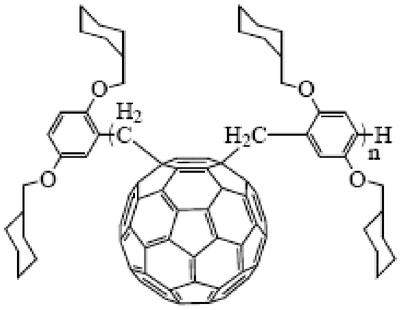


Figure 1. The structure of MCF.

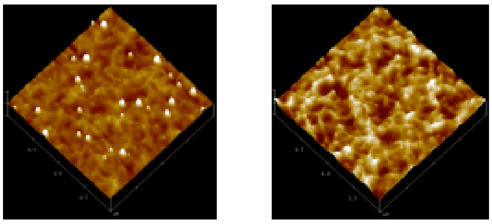


Figure 2. AFM tapping mode height images of P3HT-*blend*-MCF over 1.5 x 1.5 μm showing the effect of annealing; left, 25 °C; right, 110 °C.

References

1. M. Ma, C. Yang, X. Gong, K. Lee, A. J. Heeger, *Adv. Funct. Mater.* 2005, 15(10), 1617.
2. M. Campoy-Quiles, T. Ferenczi, T. Agostinelli, P. G. Etchegoin, Y. Kim, T. D. Anthopoulos, P. N. Stavrinou, D.C. Bradley, J. Nelson, *Nature Materials* 2008, 7, 158.
3. (a) G. Yu, A. J. Heeger *J. Appl. Phys.* 1995, 78, 4510; (b) J. J. M. Halls, C. A. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friend, S. C. Moratti, A. B. Holmes, *Nature* 1995, 376, 498.
4. S.-S. Sun, C. Zhang, A. Ledbetter, S. Choi, K. Seo, C. E. Bonner, Jr., M. Drees, N. S. Sariciftci, *Appl. Phys. Lett.,*2007, 90, 043117.
5. A. Moliton, R. C. Hiorns, *Polym. Int.* 2004, 53, 1397.
6. S. Barrau, T. Heiser, F. Richard, C. Brochon, C. Ngov, K. van de Wetering, G. Hadziioannou, D. V. Anokhin, D. A. Ivanov, *Macromolecules* 2008, 41, 2701.
7. Z. T. Ball, K. Sivula, J. M. J. Fréchet, *Macromolecules* 2006, 39, 70.
8. S. M. Lindner, S. Hüttner, A. Chiche, M. Thelakkat, G. Krausch, *Angew. Chem. Int. Ed.* 2006, 45, 3364.

OF6

Detail balance in morphology for efficient bulk heterojunction solar cell

A. **Ndobe*, C. Kitts, E. Margapotti and M. Muccini**
ISMN-CNR, via P. Gobetti, Bologna, 40129 Italy.

We introduce a new pre-device treatment for bulk heretojunction photovoltaic cells that leads to 7-10% increase in efficiency compared to the already established thermal annealing method. A close look at the film morphology using AFM imaging reveals the formation of a relatively small number of large aggregates and protrusions compared to those present in thermal annealed films; this leads to a rougher films. To identify the nature of these aggregates, localized scanning laser spectro-microscopy (CLSM) was used; this technique enables us to look at the morphology of the film via its emission with a resolution of about 200nm. With this, we were able to establish that the new pre-device process leads to a different packing of P3HT in the film compared to that occurring in thermal annealed films. The hereby introduced process, takes us a step further in trying to achieve the ideal morphology for organic bulk hetero-junction solar cells.

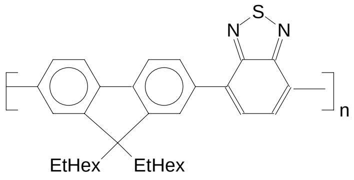
*andobe@bo.ismn.cnr.it

OF7

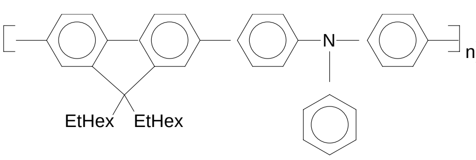
LESR and TRESR characterization of fluorene-based polymer for organic photovoltaic cells

Antonio Toffoletti [a], Lorenzo Franco [a], Lucia Bonoldi [b*], Luciano Montanari [b]
Riccardo Po' [c], Giuliana Schimperna [c], Andrea Pellegrino [c], Maria Caldararo [c]
a Chemical Sciences Department, University of Padova, via Marzolo 1, 35100 Padova, Italy
b ENI, Refining and Marketing Division, Research Centre, via F. Maritano 26, 20097 S.Donato Milanese, Italy
c ENI, Corporate Division, Research Centre for Non Conventional Energies - Eni Donegani Institute,
Via Fauser 4, 28100 Novara, Italy

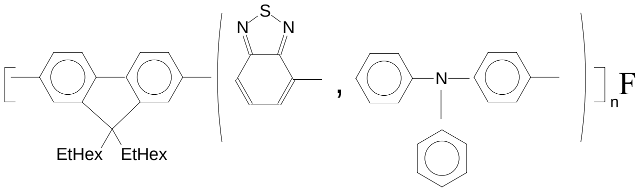
Spectroscopic characterization by conventional continuous wave light induced ESR (LESR) and Transient ESR (TR-ESR) with time resolution in the range of nanoseconds has been performed on three fluorene containing polymeric derivatives **A**, **B**, and **C** (see figure). Continuous and pulsed laser photoexcitation at 532 nm and 355 nm have been used. The polymers have been examined both in frozen solution and in thin film form and either in the absence or in the presence of the acceptor 1-(3-methoxycarbonyl)-propyl-1-phenyl- (6,6)C_{61} (PCBM). The results have been compared with those obtained on two commercial polymers for "standard" photovoltaic applications: poly-3-hexyl-thiophene, (P3HT) and poly[2-methoxy-5-(2'-ethyl-hexyloxy)-p-phenylene vinylene] (MEH-PPV).



F26-BTD (**A**)



F26-TPA (**B**)



F26-BTD/TPA (**C**)

In films of the pure polymers, a very weak LESR signal was observed, assigned to S=1/2 charged species P•+ and P•-, whereas a strong TR-ESR single line with decay time in the range of 1-2 μs was observed. The latter signal was assigned to triplet species with a motionally averaged lineshape. On the contrary in frozen toluene solution of the polymers, well resolved triplet state TR-ESR spectra can be observed, having spectral features similar to that of polythiophene photo excited triplet state.

In PCBM doped polymer C, the signal of the PCBM•- radical anion is observed with ESR even in the dark. It is strongly enhanced under illumination with 355 or 532 nm light, which also induces and increase of the positive polaron signal P•+ in comparison to the pure polymer film, in agreement with a more efficient donor/acceptor charge transfer process1. Also in samples A and B a stronger LESR P•+ signal was observed in presence of PCBM with respect to pure polymer films, but the PCBM•- was not observed.

In all of the polymer/PCBM films, TR-ESR showed the presence of a strong signal of PCBM triplet state, whose spectral shape is significantly varied with respect to the lineshape due to triplet generation by inter system crossing. This difference suggests an alternative route of PCBM triplet production, e. g. by charge carriers recombination.

References

1. V. Dyakonov, G. Zoriniants, M. Scharber , C.J. Brabec, R.A.J. Janssen, J.C. Hummelen and N.S. Saricifitci, Physical Review B, 1999, 59, No 12, 8019.

OF8

CT-State Dissociation and Charge Recombination in Organic Photovoltaic Cells

Roger Häusermanna*, Nils A. Reinkea, Evelyne Hubera,
Thomas Flatzb, Michael Moosb and Beat Ruhstallera,b
a, Institute of Computational Physics, ZHAW, Winterthur, Switzerland.
b, Fluxim AG, Switzerland.

The dissociation of the charge-transfer state (CT) into free charge carriers is a very important process in the modeling of organic photovoltaic cells (OPVs). A theoretical description of this mechanism has been developed by Onsager [1] and Braun [2]. The implications of this theory in real OPVs are not completely clear. Recently there was the proposition to reduce the whole device physics to the mechanisms at the donor-acceptor interface [3]. This has been verified for a wide range of OPV materials, but it also raises questions about the universality of this simplification.

In this study we developed a comprehensive opto-electronic simulator for photovoltaic cells based on organic semiconductors. Our simulations have shown that for polymeric bulk hetero-junction (BHJ) cells a good agreement with measured current-voltage (J-V) curves can be found by omitting dissociation mechanisms and directly let absorbed photons generate charges but at the same time increasing the influence of the Langevin recombination. This shows that distinct features of current-voltage curves are multi-causal and therefore a simplification by leaving out some of the mechanisms leads to an overestimation of the influence of other processes.

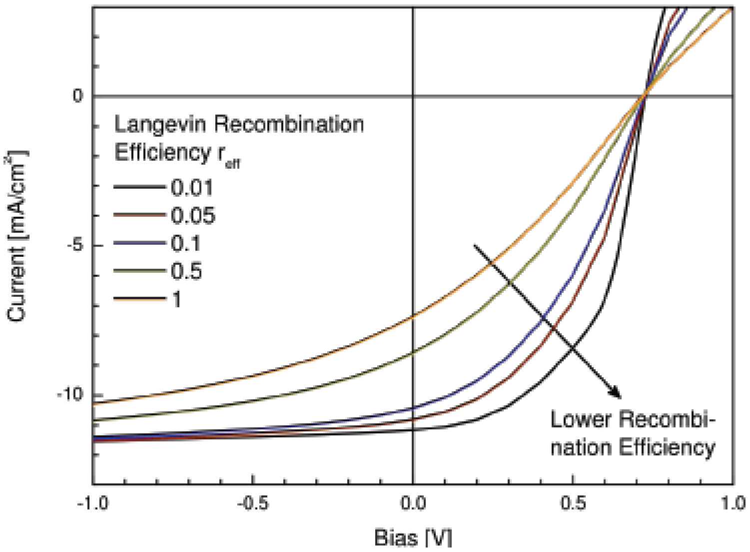


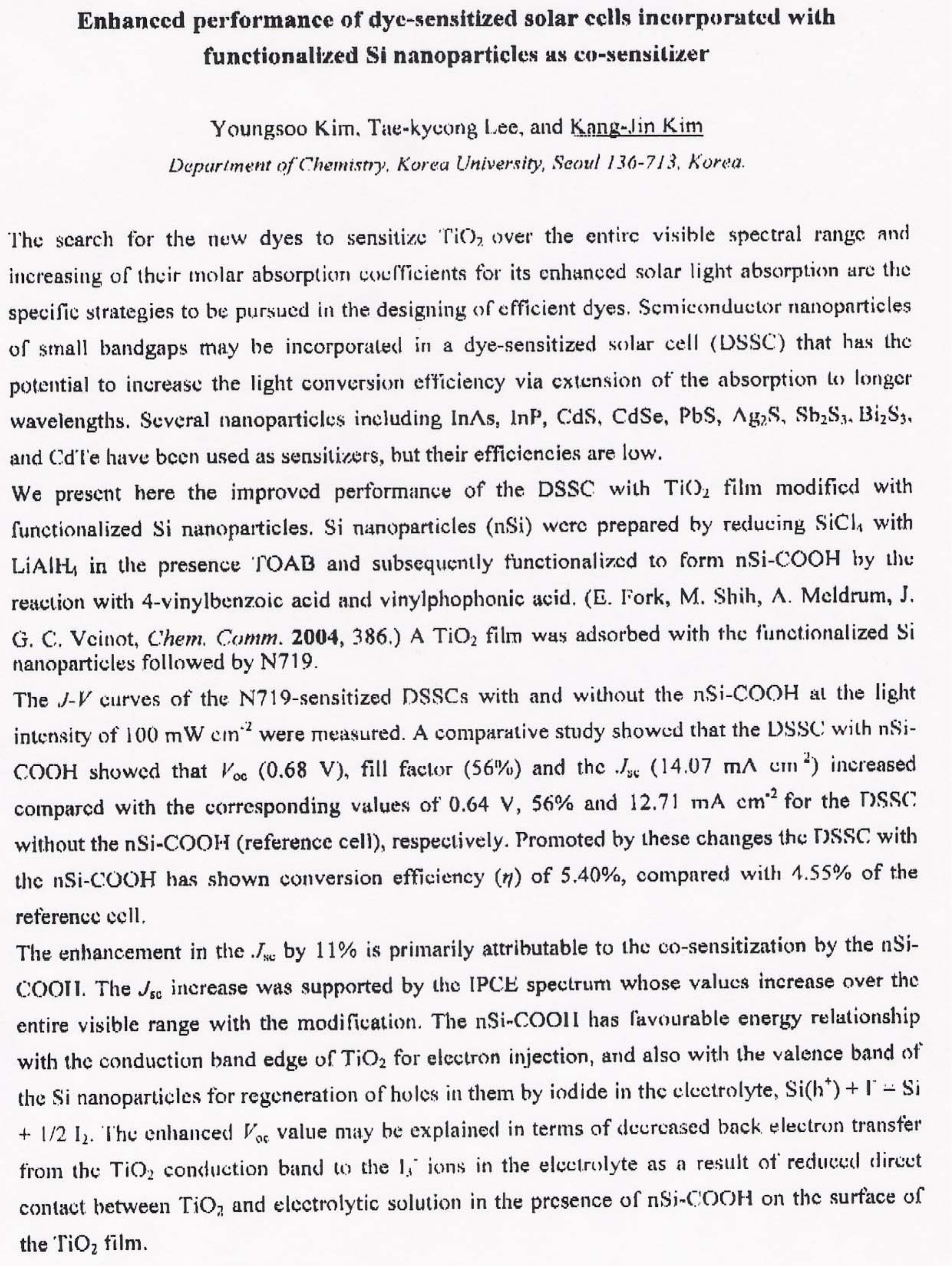
Figure 1. Influence of the Langevin recombination efficiency on the J-V curve of an organic photovoltaic device.

We present the influence of the input parameters for CT-state dissociation, recombination and mobility on the J-V curves and propose ways for extracting the parameters from measurements. The quantitative contributions of the different loss mechanisms, namely decay of excitons and CT-states as well as charge recombination will be addressed as function of material properties.

References

[1] L. Onsager, *Phys .Rev.*, 1938, **54**, 554
[2] C. L. Braun, *J. Chem. Phys.*, 1984, **80**, 4157
[3] Marsh et al., *Nano Lett.*, 2008, **8**, 1393

OF9



Enhanced performance of dye-sensitized solar cells incorporated with functionalized Si nanoparticles as co-sensitizer

Youngsoo Kim, Tae-kyeong Lee, and Kang-Jin Kim
Department of Chemistry, Korea University, Seoul 136-713, Korea.

The search for the new dyes to sensitize TiO_2 over the entire visible spectral range and increasing of their molar absorption coefficients for its enhanced solar light absorption are the specific strategies to be pursued in the designing of efficient dyes. Semiconductor nanoparticles of small bandgaps may be incorporated in a dye-sensitized solar cell (DSSC) that has the potential to increase the light conversion efficiency via extension of the absorption to longer wavelengths. Several nanoparticles including InAs, InP, CdS, CdSe, PbS, Ag_2S, Sb_2S_3, Bi_2S_3, and CdTe have been used as sensitizers, but their efficiencies are low.

We present here the improved performance of the DSSC with TiO_2 film modified with functionalized Si nanoparticles. Si nanoparticles (nSi) were prepared by reducing $SiCl_4$ with $LiAlH_4$ in the presence TOAB and subsequently functionalized to form nSi-COOH by the reaction with 4-vinylbenzoic acid and vinylphophonic acid. (E. Fork, M. Shih, A. Meldrum, J. G. C. Veinot, *Chem. Comm.* **2004**, 386.) A TiO_2 film was adsorbed with the functionalized Si nanoparticles followed by N719.

The J-V curves of the N719-sensitized DSSCs with and without the nSi-COOH at the light intensity of 100 mW cm^{-2} were measured. A comparative study showed that the DSSC with nSi-COOH showed that V_{oc} (0.68 V), fill factor (56%) and the J_{sc} (14.07 mA cm^{-2}) increased compared with the corresponding values of 0.64 V, 56% and 12.71 mA cm^{-2} for the DSSC without the nSi-COOH (reference cell), respectively. Promoted by these changes the DSSC with the nSi-COOH has shown conversion efficiency (η) of 5.40%, compared with 4.55% of the reference cell.

The enhancement in the J_{sc} by 11% is primarily attributable to the co-sensitization by the nSi-COOH. The J_{sc} increase was supported by the IPCE spectrum whose values increase over the entire visible range with the modification. The nSi-COOH has favourable energy relationship with the conduction band edge of TiO_2 for electron injection, and also with the valence band of the Si nanoparticles for regeneration of holes in them by iodide in the electrolyte, $Si(h^+) + I^- \rightarrow Si + 1/2\ I_2$. The enhanced V_{oc} value may be explained in terms of decreased back electron transfer from the TiO_2 conduction band to the I_3^- ions in the electrolyte as a result of reduced direct contact between TiO_2 and electrolytic solution in the presence of nSi-COOH on the surface of the TiO_2 film.

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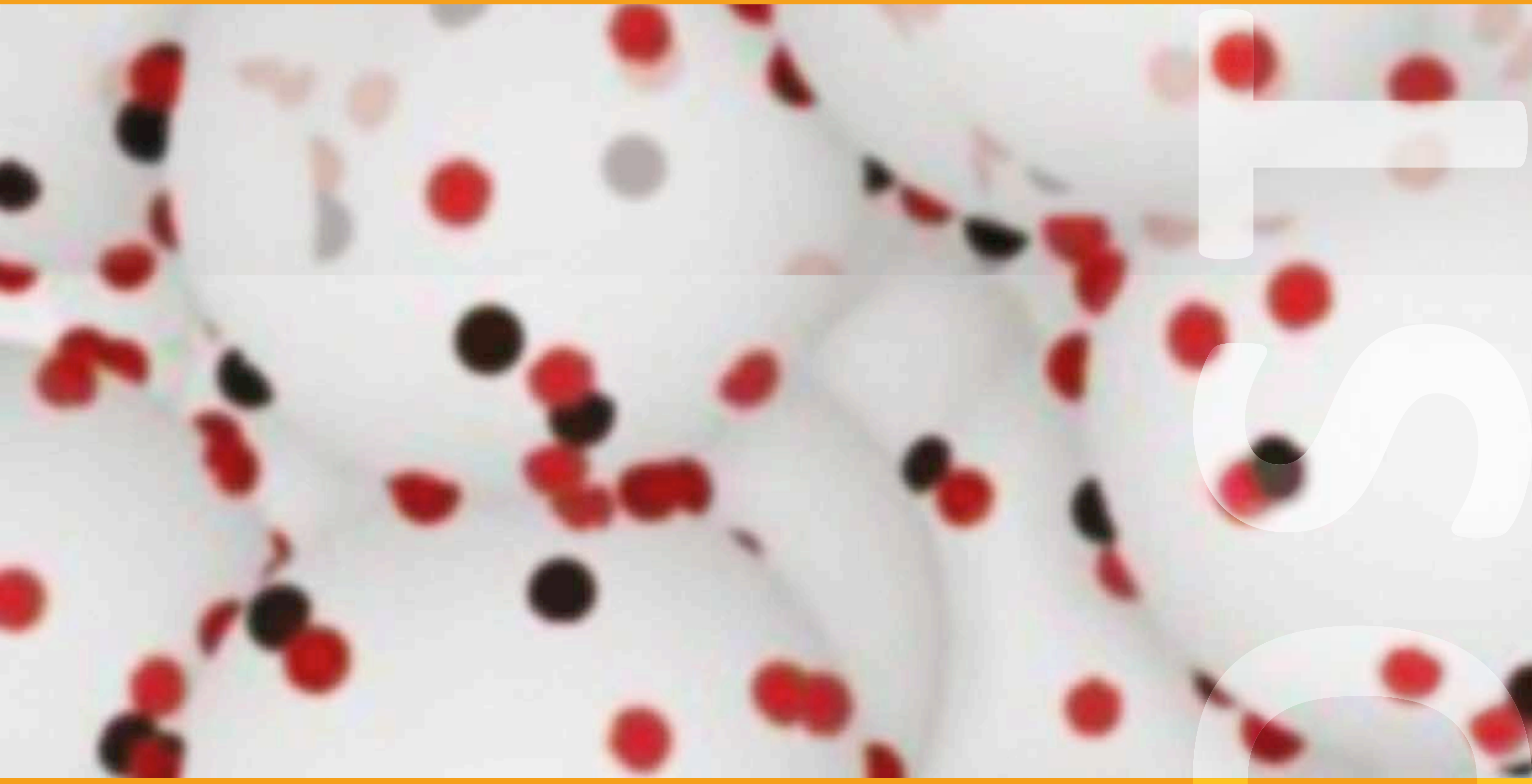

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PA1

ZnO – Porphyrin Dye Sensitized Solar Cells

Fabian Werner[a], Renata Marczak[b], Jan-Frederik Gnichwitz[a], Andreas Hirsch[a], Wolfgang Peukert[b], Emilio Palomares[c] and Dirk M. Guldi[a],*

a, Department of Chemistry and Pharmacy, Friedrich-Alexander-University Erlangen-Nuremberg, Egerlandstr. 3, Germany.
b, Institute of Particle Technology, Friedrich-Alexander-University Erlangen-Nuremberg, Cauerstr. 4, 91058 Erlangen, Germany.
c, Institute of Chemical Research of Catalonia, Avenida Països Catalans 16, Tarragona 4300, Spain.

In recent years, the application of ZnO nanostructures for solar energy conversion has received considerable attention due to the high electron mobility and the nontoxycity of ZnO.[1] On the other side, the role of porphyrins as, for example, in photosynthesis is undisputed.[2] In terms of functionalizing porphyrins and, thus, implementing specific functionalities deprotonated catecholate emerged as versatile groups to bind to TiO_2 through the formation of five-member chelate rings.[3] Yet, their interaction with ZnO has not been investigated. Our current efforts address these aspects, namely the systematic and detailed investigation of photoinduced charge transfer between a catechol functionalized porphyrin and ZnO films. Moreover, we have placed particular emphasis on possible photovoltaic applications. Here, we report on key features such as kinetics of charge injection, charge recombination, charge regeneration, etc.

References

1. M. Law, L. E. Greene, J. C. Johnson, R. Saykally and P. Yang, *Nature Mat.*, 2005, ***4***, 455.
2. M. Hervás, J. A. Navarro and M. A. De la Rosa, *Acc. Chem. Res.*, 2003, **36** (10), 798.
3. R. Marczak, F. Werner, Jan-F. Gnichwitz, A. Hirsch, D. M. Guldi, W. Peukert, *J. Phys. Chem. C*, 2009, **113** (11), 4669.

PA2

Vertically-Aligned Nanostructures of ZnO for Excitonic Solar Cells

I. Gonzalez-Valls[a] and M. Lira-Cantu[a*]

a, Centre d'Investigació en Nanociència i Nanotecnologia, Campus UAB, Edifici ETSE, Bellaterra, 09819, Spain.
* *monica.lira@cin2.es*

Next generation photovoltaics must achieve the following three criteria: large efficiency, lifetime stability and low cost. One way to accomplish the three main goals, could be Exciton Solar Cells (XCS's), including Organic, Hybrid and Dye sensitized Solar Cells.[1] Our research work focuses on the improvement of Hybrid and Dye sensitized Solar Cells by the optimization of the active interfaces between semiconductor oxides and organic semiconductors. One method to increase efficiency is the application of interconnected networks of the materials responsible for light harvesting, allowing the transport of charges in a more efficient way, reducing, for example, internal recombination problems.[2] Networks of vertically aligned materials are a good option to increase the interfacial active area, avoid grain boundary resistances or increase charge carrier mobility, among others.[3]

In this work we present the application of nanostructured electrodes made of ZnO nanorods for Dye sensitized Solar Cells. We have optimized the synthesis of the NRs in order to control their length and diameter with time. We studied the stability of the starting nanoparticles and final nanostructured materials by UV-VIS, SEM, TEM and DRX analyses. We present in this work our initial results on the application of ZnO nanorods synthesised with different dimensions and analysed in Dye sensitized Solar Cells. Different parameters have been modified like type of dye used, electrolyte or thermal treatments. The best photovoltaic response has been observed when using N719 dye, an iodine electrolyte and a platinum electrode (Figure 1). Efficiencies as high as 0.78 %, V_{oc} =0.443 V, J_{sc} =4.9 mA/cm^2 and FF =36 % have been obtained.

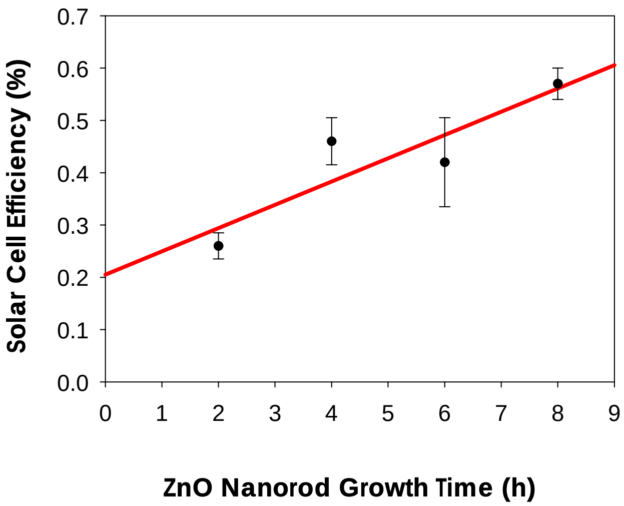


Figure 1. Power conversion efficiency obtained for Dye sensitized Solar Cells applying nanostructured electrodes made of ZnO nanorods of different dimensions. Measurements carried out at ~75 ºC, 1000 W/m^2 A.M.1.5. Analyses performed at the photovoltaics laboratory at CIN2 (CSIC-ICN).

References

1. I. Gonzalez-Valls, and M. Lira-Cantu, *Energy Environ. Sci.*, 2009, **2**, 19.
2. M. Lira-Cantu, F.C. Krebs, P. Gomez-Romero and S. Yanagida, *Mater. Res. Soc. Symp. Proc.,* 2007, 1007-S14-04
3. M. Law, L.E. Greene, J.C. Johnson, R. Saykally and P. Yang, *Nat. Mater.*,2005, **4**, 455.

PA3

ZnO nanorods based spectral splitting for efficient PV systems

Sophia Buhbut, Arie Zaban
Bar-Ilan Institute of Nanotechnology and Advanced Materials
Bar -Ilan University, Ramat Gan,52900, Israel

High efficiency photovoltaics require spectral splitting of the solar radiation into a series of individual cells which are optimized to different parts of the solar spectrum. Most of the known systems are very expensive, which necessitate concentration and sun tracking. We report here on a new approach to spectral splitting that is based on selective scattering by nanorods. The system that acts as a flat concentrator has low dependence on the illumination direction.

Oriented nanorods can expose different dimension to the radiation with lengths that are much larger but a diameter that is much smaller than the wavelength. This structure can enhance scattering perpendicular to the long axes of the rods. In other words, nanorods that are grown perpendicular to the substrate can enhance scattering parallel to the substrate. The wavelength to be scattered depend on the diameter of the rods which opens the way for spectral selectivity.

In this work we utilize ZnO nanorods grown on a glass substrate. ZnO is a low cost material with high refractive index, 2.1, that can be grown in large scale via chemical bath deposition. Preparation of the oriented ZnO nanorods is based on sputtering of a thin ZnO slayer followed by dipping in a stirred solution comprising sodium hydroxide and zinc ion, at low temperature (70^0c). It is possible to control the dimensions of the resulting nanorods by changing the time intervals of different preparation- step.

First results show that growth of 20-120 min in chemical bath deposition yields rods of 200-1500 nm in length with a diameter of 25-100 nm. The scattering measured from these films is affected by the layer morphology, the diameter and length of ZnO nanorods and the distance between them. Our aim to orient the scattering parallel to the substrate is not yet achieved but strong deviation from spheres based scattering is clear.

PA4

Slowing Charge Recombination in Solid-State Devices with ALD Deposited Barrier Layers

Tina C. Li,a Márcio S. Góes,b,c Francisco Fabregat-Santiago,*b Juan Bisquert,b Paulo R. Bueno,c Chaiya Prasittichai,a Joseph T. Hupp,*a and Tobin J. Marksa

a, Department of Chemistry, the Argonne-Northwestern Solar Energy Research Center, and the Materials Research Center, Northwestern University, Evanston, IL 60208-3113, USA.

b, Photovoltaic and Optoelectronic Devices Group, Departament de Física, Universitat Jaume I, 12071 Castelló, Spain.

c Departamento de Físico-Química, Instituto de Química de Araraquara, Universidade Estadual Paulista, R. Prof. Francisco Degni s/n, 14800-900 Araraquara SP, Brazil.

Replacement of the volatile I-/I3- redox couple in dye-sensitized solar cells with a solid-state analog has been of particular interest in order to avoid leakage of the electroltye and thus prolong the stabililty of the cells.1,2 However, advancements using spiro-OMeTAD, or 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene, have been limited due to the fast recombination kinetics of this hole transport layer with electrons in the titania nanoparticulate framework.3,4 Here we study the effects of inserting interfacial layers on the semiconductor with angstrom precision via atomic layer deposition to suppress electron interception by spiro-OMeTAD. Changes in cell capacitance is monitored by electrochemical impedance spectroscopy, giving insight to the slope variations observed in the charge lifetime plots, as determined by open-circuit voltage decay.

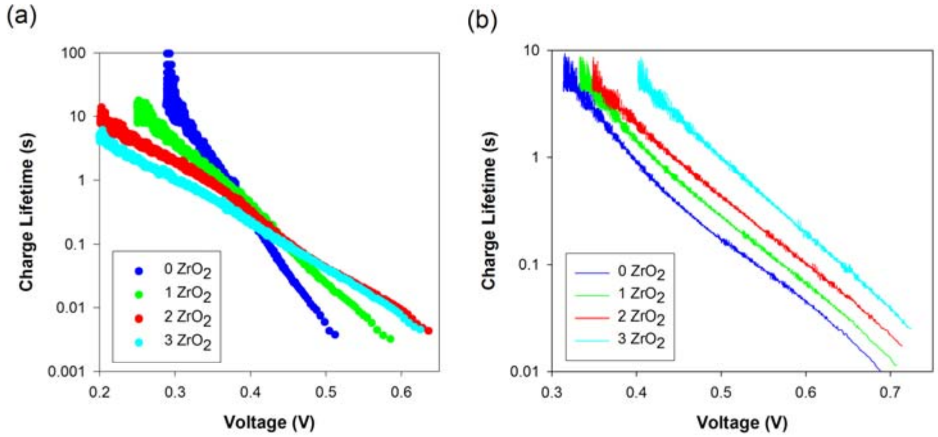


Figure 1. Charge lifetime plots of dye-sensitized solar cells with (a) spiro-OMeTAD and (b) liquid-based I-/I3- with varying atomic layer deposition cycles of zirconia conformally grown on the nanoparticulate framework.

References

1. U. Bach, D. Lupo, P. Comte, J. E. Moser, F. Weissörtel, J. Salbeck, H. Spreitzer, and M. Grätzel, Nature, 1998, 395, 583.
2. H. J. Snaith and L. Schmidt-Mende, Adv. Mater. 2007, 19, 3187.
3. F. Fabregat-Santiago, J. Bisquert, L. Cevey, P. Chen, M. Wang, S. M. Zakeeruddin, and M. Grätzel, J. Amer. Chem. Soc., 2009, 131, 558.
4. J. E. Kroeze, N. Hirata, L. Schmidt-Mende, C. Orizu, S. D. Ogier, K. Carr, M. Grätzel, and J. R. Durrant, Adv. Funct. Mater. 2006, 16, 1832.

PA5

Continuing Study of the Performance of Hybrid Solar Cells Incorporating different Dense TiO2 Layers

Sylvia Paul, Dieter Neher
University of Potsdam, Institute of Physics, Karl-Liebknecht- Street 25, 14476 Potsdam, Germany
E-Mail: *sypaul@uni-potsdam.de*

Hybrid solar cells combine an organic with a suitable inorganic semiconductor. In most cases, transparent metal oxides (TMOs) serve as inorganic semiconductors therein, among which TiO2 is the mostly promising electron acceptor. Besides studies on the well-known Grätzelcell, the combination of a dense or nanostructured TMO layer with a soluble conjugated polymer has been subject to recent investigations. Hereby, the morphology and surface characteristics of the TiO2-films are of great importance, as they affect the exciton difusión length and carrier transport properties of the TMO in the inorganic/polymeric hybrid-cell. It is expected that the way of layer preparation has a large impact on these properties.

We have systematically investigated the effect of different preparation processes on the performance of hybrid photovoltaic cells using a soluble derivative of PPV or a derivative of P3HT as hole acceptor. The following techniques for preparing the TiO2 layer were applied: TiO2 layers compounded via sputtering, dip-coating of preformed crystalline nanoparticles, dip-coating of preformed TiO2 by sol-gel process and combination of all methods. Structural characteristics were investigated by atomic force microscopy (AFM), transmissions electrón microscope (TEM), scanning electron microscope (SEM), infrared and Raman spectroscopy while the optical properties were studied with ellipsometry. The influence of TiO2 layer preparation and surface morphology on cell performance was examined. In particular we show that dense and defect-free layers could be prepared from preformed TiO2 nanoparticles and that these layers in combination with the sol-gel layer gave the best performance in Irbid photovoltaic devices. With a PPV derivative as electron donator, an open circuit voltage Voc of approximately 0.9 V and a fill factor of more than 40% was achieved.

We furthermore systematically investigated the effect of UV irradiation and time-dependent measurements on the performance of hybrid photovoltaic cells. Devices were prepared as bilayer systems, employing a derivative of poly (p-phenylene-vinylene) (PPV) as donor and a thin layer of TiO2 nanoparticles as electron acceptor. Our studies show an interrelationship between the measuring conditions respectively the sample preparation procedures and the current-voltage solar cell characteristics. We found out, that the open-circuit voltage increases by around 50 % within 220h of device fabrication. The short-circuit current first reaches an improvement of 20 % at around 45h after fabrication, after which it is found to slowly fall back to values comparable to those of fresh devices.

PA6

Low-Dimensional Nanostructures based hybrid Photovoltaic

Mi Yeong Park[a], Yeong-Tae Kim[a], Kyu Hwan Lee[a], Young Soo Jeong[a], Dong Chan Lim[a]*
a, Korea Institute of Materials Science, Department of surface Technology, 531 Changwondaero, Changwon, Gyeongnam, 641-831, Korea

Low dimensional nanostructures consisting of vertically aligned metal doped ZnO nanowires (1-D) decorated with quantum dots (0-D) like CdSe and/or CdTe were adopted onto organic-inorganic hybrid solar cell as a cathode side for facile charge transport to collector electrode and enhanced photo response characteristics by a simple electrochemical deposition method. Single crystalline ZnO NWs arrays with ~ 60 nm in width, ~ 400 nm in length and ~ 50 nm space between NWs were grown vertically on ITO coated glass or PET substrates as well as metallic substrates in aqueous solution of zinc chloride at 80℃. CdSe and/or CdTe quantum dots were synthesized separately. The photovoltaic nanocomposites were then formed with a poly (3-hexylthiophene) (P3HT) by spin coating or electro-polymerization method. Poly (3.4-ethylenedioxythiophene) polystyrenesulfonate (PEDOT:PSS) has been used to increase effectively generated hole collection. Deposited hybrid nanostructures were characterized by X-ray diffraction (XRD), Field emission scanning electron microscope (FE-SEM), Transmission electron microscope (TEM), UV/Vis. spectroscopy and photoluminescence (PL). Based on the optical and electrical characteristics, one can suggest that low dimensional nanostructures can be considered to be the most promising candidate for hybrid solar cell. As compared to a conventional device without ZnO nanowires and/or quantum dots, incorporation of low dimensional nanostructures resulted in an improvement of both the short circuit current density (Jsc) and the fill factor (FF) significantly.

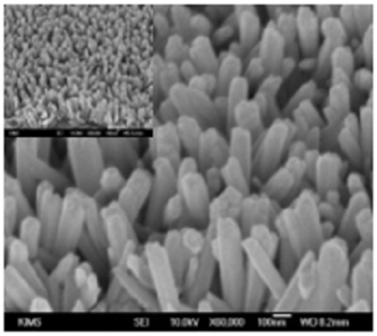


Figure1. ZnO nanowires deposited on ITO coated glass substrate

PA7

Templated Synthesis and Characterization of Modified TiO_2 Nanotubes

I. Tacchini, A. Ansón-Casaos*, E.M. Terrado, J.D. Núñez, A.M. Benito, W.K. Maser, and M.T. Martínez*
Department of Carbon Nanostructures and Nanotechnology, Institute of Carbochemistry (CSIC), Miguel Luesma Castan 4, 50018, Zaragoza, Spain.

TiO_2 nanotubes were synthesized by a template procedure including a vacuum impregnation of the template [1] with liquid titanium precursors. The duration of the vacuum stage was observed to be critical for the correct impregnation of the template. The precursors tested for the TiO_2 nanotube synthesis were titanium isopropoxide, titanium propoxide, titanium butoxide, and titanium chloride. An annealing stage at 500°C in air or inert atmospheres was applied after the impregnation to convert all the titanium into crystalline anatase TiO_2. Alumina membranes were utilized as the template for the synthesis of nanotubes with diameters around 200 nm (Figure 1). The alumina templates were removed with a mixture of phosphoric and chromic acid after the impregnation and annealing stages. Multi wall carbon nanotubes (MWCNT) produced by catalytic vapor deposition (CVD) were utilized for the templated synthesis of TiO_2 nanotubes with diameters around 50-60 nm (Figure 2). External surfaces of the MWCNT were completely coated by TiO_2. The morphology of TiO_2 nanostructures was observed by scanning electron microscopy (SEM) and atomic forces microscopy (AFM); their crystalline structure was controlled by X-ray diffraction and Raman spectroscopy; their optical activity was studied by ultraviolet-visible spectroscopy.

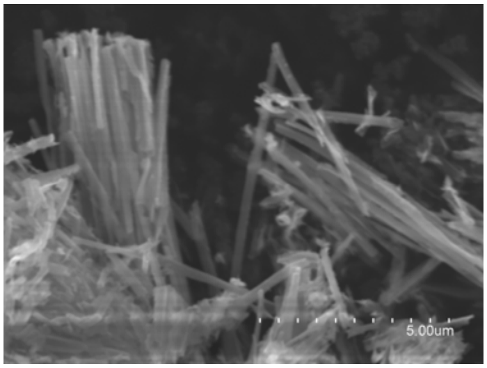


Figure 1. SEM image of TiO_2 nanotubes synthesized by the alumina template technique.

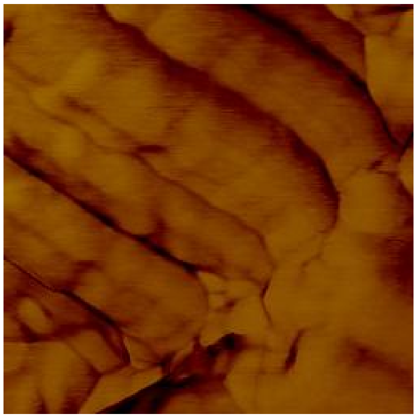


Figure 2. AFM image (300x300 nm) of MWCNT coated with TiO_2.

References

1. A. Michailowski, D. AlMawlawi, G. Cheng, and M. Moskovits, *Chem. Phys. Lett.*, 2001, **349**, 1.

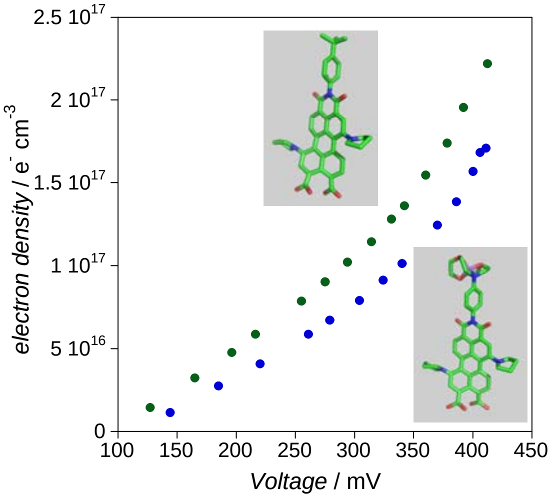
PA8

Supramolecular interactions in Dye Sensitized Solar Cells

Miquel Planells,[a] F. Javier Céspedes-Guirao,[b] Angela Sastre-Santos,[b] Fernando Fernández-Lázaro[b] and Emilio Palomares[a*]

a, Institut Català d'Investigació Química (ICIQ), Avda. Països Catalans 16. 43007 Tarragona, Spain..
b, División de Química Orgánica, Universidad Miguel Hernández, Avda. Universidad s/n, 03202 Elche, Spain.

A new Li^+ coordinating perylene monoimide dye has been synthesized. The dye has been used as sensitizer in Dye-sensitized Solar Cells (DSCs) and the effect of Li^+ coordination on the device performance has been analyzed using different spectroscopical techniques.



PA9

Characterization of surface passivation for dye sensitized solar cells, using the ferrocene redox couple

Sandra M. Feldt, Gerrit Boschloo and Anders Hagfeldt
Department of Physical and Analytical Chemistry, Uppsala University, Lägerhyddsv. 1, 751 05 Uppsala, Sweden.

It is of interest to find an alternative redox mediator to the iodide/triiodide redox couple for dye sensitized solar cells (DSSCs) in order to enhance open circuit voltages and conversion efficiencies. So far the best cell performances in DSSCs are obtained for the iodide/triiodide redox shuttle because of its ability to efficiently regenerate the dye combined with its slow kinetics for electron transfer from TiO_2 to I_3^-. The main drawback, however, with the I^-/I_3^- system is the large driving force of at least 0.5 V needed for dye regeneration. The energy mismatch between its redox potential and the HOMO level of the sensitizers lowers the open circuit voltage and thereby the conversion efficiency of the DSSC. One electron outer-sphere redox couples such as ferrocene/ferrocenium are a promising alternative to the iodide/triiodide redox couple since they should reduce the driving force needed to regenerate the dye.

Unfortunately, one electron redox couples also show enhanced recombination with electrons in the TiO_2 conduction band and methods to inhibit this recombination are needed for functioning DSSCs. In this study, a surface passivation technique using trichloromethylsilane as a silanization agent proposed by Gregg et al.[1] was examined in order to decrease the fast recombination rates. The surface passivation technique was characterized with electrochemical, photo-electrochemical and spectroscopic techniques. The silanization procedure increased the lifetime of the electrons in the TiO_2 and thereby the efficiency of the DSSC. However, Photoinduced Absorption Spectroscopy (PIA) revealed that the silane coatings might also block the regeneration of the dye, to some extent.

References

1. B.A. Gregg, F. Pichot, S. Ferrere, C.L. Fields, *J. Phys. Chem. B*, 2001, **105**, 1422.

PA10

Exciton enhanced dye sensitized solar cells

Eva Unger[a], Anders Hagfeldt[a] and Gerrit Boschloo[a]*
a, Physical and Analytical Chemistry,Uppsala University, Lägerhyddsvägen 1,75237 Uppsala, Sweden

The optical thickness of the adsorber layer is a limiting factor for the performance of solar cells. There are different solutions to increase the optical thickness of organic and hybrid photovoltaic devices, e.g. by sensitizing nanostructured metal oxides in dye-sensitized solar cells (DSC) or the organic bulk heterojunction.

In solid state dye sensitized solar cells, a good interpenetration of the mesoporous metal oxide and the hole conductor is crucial. This limits the thickness of the mesoporous metal oxide film reaching a maximum around 2 μm for these devices. A monolayer of dye on such a thin film however results in a quite low optical thickness and thus incomplete light absorption.

The scope of this work is to enhance solid state dye sensitized solar cells by adding a second dye layer (D2) onto the monolayer-sensitized (D1) metal oxide electrode. This additional "bulk" dye layer could provide additional excitation energy to the junction. A premise for this is that the additional dye layer can transfer the excitation energy to the "injection" dye (D1) and at the same time regenerate the oxidised injection dye after electron injection.

We will present results on the photovoltaic performance of hybrid devices that employ dense TiO_2 in combinations with triphenylamine based dyes. The efficiency of the energy transfer between the dyes depends on their energetic and optical properties, which will be investigated by electrochemical methods and flash photolysis.

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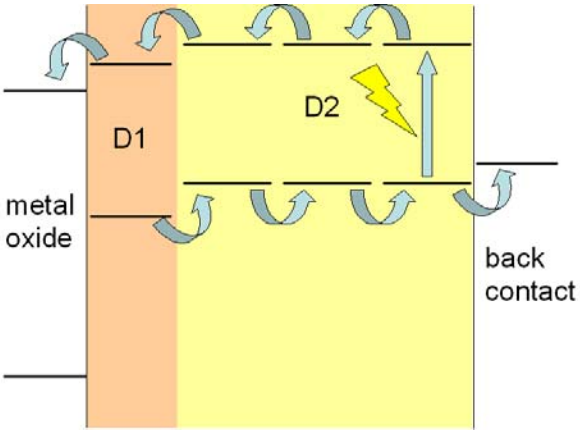


Figure 1: Schematic representation of the exciton enhanced dye-sensitized solar cell

PA11

Volume versus surface-mediated recombination in titania nanoparticles

Lucia Cavigli,[a,b] Anna Vinattieri[b], Valentina Faso[c], Giovanni Baldi[c] and Franco Bogani [a]
a, Dipartimento di Energetica, Università di Firenze, Via S. Marta, 3 - 50139 Firenze, Italy.
b, Dipartimento di Fisica, Università di Firenze, Via G. Sansone, 1 - 50019 Sesto Fiorentino (Fi), Italy.
c, Ce.Ri.Col. Colorobbia Italia, Via Pietramarina 53 - 50053 Sovigliana-Vinci (Fi), Italy.

Anatase (TiO_2-titania) nanoparticles (NPs) have recently been addressed in view of promising applications in different fields, such as photocathalysis,[1] optical coating,[2] dye-sensitized solar cells (DSC)[3] and more generally in view of future nanoengineering. Nevertheless the degree of success for such applications is strongly dependent on the knowledge and deep understanding of the fundamental physical processes ruling the carrier dynamics in such nanosystems. Despite that significant results have been reached in DSC and in water/air decontaminants based on TiO_2 NPs, much fundamental research is needed to improve parameters such as efficiency, lifetime, etc. strictly related to the carrier behaviour in the NPs. In particular the studies addressing the dependence of the optical properties of titania on the size and the environment where the NPs are dispersed focus onto specific aspects and a complete understanding is still lacking.

Here we report a detailed experimental study of the carrier recombination dynamics in anatase TiO_2 NPs by means of time-integrated (TI) and time-resolved (TR) photoluminescence (PL) spectra. We investigated a set of samples consisting of size-controlled TiO_2 nanocrystals in water solution and diluted in methanol to modify the surface states.

We show that by a cross analysis of data obtained with TI and TR PL measurements as a function of several parameters such as NPs size, temperature and excitation intensity is possible to distinguish between surface and bulk recombination, since spectral shift and different time dynamics allow to clearly quantify the different contribution.

We found that in TiO_2 NPs the main contribution to PL emission comes from surface recombination and bulk recombination is detected only in a fast transient of duration about 100 ps. The bulk emission emerges only when the surface recombination is inhibited by some carrier scavenger, like methanol. The surface and bulk spectra turn out to be very similar, with only an energy shift of about 50 meV between them, and originate from a self-trapped exciton[4,5] and a phonon assisted bound exciton recombination.[6,7]

Our results prove that optical measurements allow to discriminate between surface and volume contributions, which turns out to be of relevance in the NPs characterization and in the test of their catalytic activity and transport properties.

References

1. X. Chen and S. Mao, *Chem. Rev.*, 2007, **107**, 2891.
2. Y. Leprince-Wang, K. Yu-Zhang, V. N. Van, D. Souche, and J. Rivory, *Thin Solid Films*, 1997, **307**, 38.
3. M. Grätzel, *J. Photochem. Photobiol. C-Photochem. Rev.*, 2003, **4**, 145.
4. W. Zhang, M. Zhang, Z. Yin, and Q. Chen, *Appl. Phys. B*, 2000, **70**, 261.
5. S. Mochizuki, T. Shimizu, and F. Fujishiro, *Physica B*, 2003, **340-342**, 956.
6. G. Mattioli, F. Filippone, P. Alippi, and A. A. Bonapasta, *Phys. Rev. B*, 2008, **78**, 241201.
7. B. Liu, X. Zhao, Q. Zhao, X. He, and J. Feng, *J. Electr. Spectr. Rel. Phen*, 2005, **148**, 158.

PA12

p-Type Dye Sensitized Solar Cells

Libby Gibson[a*] A. L. Smeigh[b], P. Qin[c], L. Li[c] J. Fortage[d], F. Odobel[d], L. Sun[c], L. Hammarström[b], G. Boschloo[a], A. Hagfeldt[a]
[a]*Department of Physical and Analytical Chemistry, Uppsala University, Box 518 SE-751 20 Uppsala, Sweden*
[b]*Chemical Physics, Department of Photochemistry and Molecular Science, Uppsala*
University, Box 523 SE-751 20 Uppsala, Sweden
[c]*Department of Organic Chemistry, Royal Institute of Technology (KTH), Teknikringen 30,*
100 44 Stockholm, Sweden
[d]*Laboritoire de Synthèse Organique, UMR 6531 CNRS&FR 2465, Université de Nantes,*
Faculté des Sciences et des Techniques de Nantes, BP 92208; 2 rue de la Houssinière, 4322
Nantes Cedex 03, France

Despite the enormous attention focused on n-type DSC's over the last two decades, comparatively little work has been reported on the p-type system. Dye sensitization of p-type semiconductors give rise to a photoactive electrode whereby cathodic photocurrents are generated on visible light excitation. Functional, mesoporous, NiO-based p-type devices have been reported in which the iodide-triiodide redox couple[1] and dyes including coumarin 343, perylene derivatives[2] and diphenylaniline derived 'p-dyes'[3] have been incorporated. IPCE values of up to 21% have so far been reported for such devices. Incorporation of a photocathode in tandem with a TiO_2-based n-type photoanode produces a device whereby the V_{OC} is the difference between the fermi level in the conduction band in the n-type semiconductor and the valence band in the p-type semiconductor, thereby giving a substantial increase over the V_{OC} of the individual n- and p-DSCs[4]. By choosing sensitizers which absorb the high energy photons on one electrode and low energy photons on the other, the full solar spectrum can be utilized. Whilst gains in conversion efficiency brought about by this alternative configuration are likely to be substantial, the field of p-type DSCs is still in its infancy. A number of improvements to the devices are needed before competitive efficiencies are reached.

We have made substantial improvements to NiO-based p-DSCs by designing dyes which promote charge separation and limit recombination between the sensitizer and the semiconductor. Improvements to the semiconductor material have also been made, including incorporation of a compact blocking layer between the conducting glass charge collector and the electrolyte and alternative preparations of the mesoporous NiO to increase porosity and reproducibility. Alternative redox couples have also been used which, when used in conjunction with a suitable sensitizer, give a four fold increase in efficiency over the previous record for a p-type DSC. Research into new p-type semiconductors, which we hope will further increase the V_{OC}, is ongoing.

References

[1]Zhu, H.; Hagfeldt, A.; Boschloo, G.; J. Phys. Chem. C.; 2007; 111(47); 17455-17458.
[2]Morandeira, A.; Fortage, J.; Edvinsson, T.; Le Pleux, L.; Blart, E.; Boschloo, G.; Hagfeldt, A.; Hammarström, L.; Odobel, F.; J. Phys. Chem. C.; 2008; 112(5); 1721-1728.
[3]Qin, P.; Zhu, H.; Edvinsson, T.; Boschloo, G.; Hagfeldt, A.; Sun, L.; J. Am. Chem. Soc.; 2008; 130; (27); 8570-8571.
[4]He, J.; Lindström, H.; Hagfeldt, A.; Lindquist, S.-E; Sol. Energy Mat. Sol. Cells; 2000; 62; 265-273.

PA13

Porphyrin Dyes and Unconventional Photoelectrodes in Dye-Sensitized Solar Cells

Rebecca A. Jensen*,[a] Hal Van Ryswyk[b] and Joseph T. Hupp[a]
a, Department of Chemistry, Northwestern University, Evanston, IL, 60208, United States.
b, Department of Chemistry, Harvey Mudd College, Claremont, CA, 91711, United States.

We are designing porphyrin-based "super chromophores" with high extinction spanning the visible and infrared.[1] Small changes to dye structure have been found to profoundly effect energy transfer within assemblies and charge injection. For example, rapid energy transfer (3.8 ps^{-1}; 8 times faster than a similar porphyrin ensemble[2]) was observed between adjacent porphyrin subunits of a cyclic self-assembled tetramer (Figure 1), as established by femtosecond transient absorption and anisotropy spectroscopies.[3]

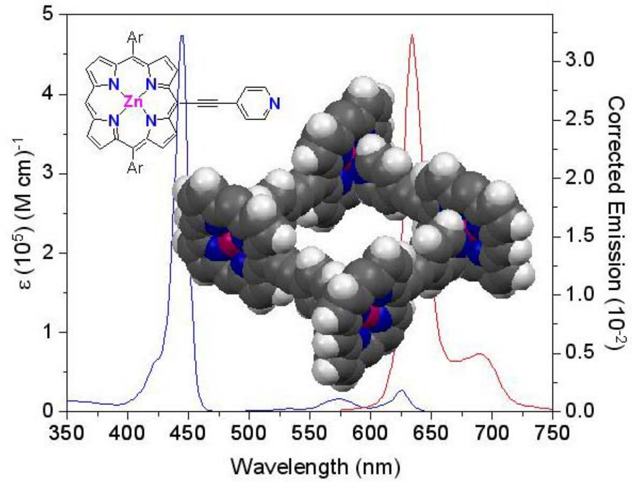
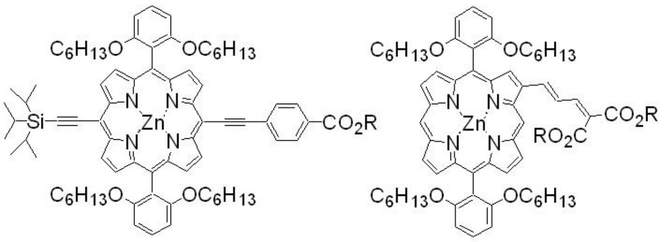


Figure 1. Porphyrin monomer structure and corresponding absorption (left trace) and emission spectra (right trace; 553 nm excitation) and cyclic tetramer space-filling model (solubilizing groups are removed for clarity). The tetrameric structure was established by solution-phase X-ray scattering and diffraction.

Similarly, two porphyrin dyes with carboxylic acid tethers of differing acidity (Figure 2) load and inject in both protonated and deprotonated form on TiO_2 nanoparticle photoanodes. Whereas on ZnO nanotube photoanodes,[4] the dyes have similar surface coverages but only the more acidic dye in the acid form injects well. This is the only one of the four dyes examined that corrodes the ZnO. These results are consistent with a requirement that ZnO films must be corroded by the dye in order for efficient injection to occur.[5]



1 a) R = H
b) R = K

2 a) R = H
b) R = Li

Figure 2. Porphyrin dyes

References

1. T. W. Hamann, R. A. Jensen, A. B. F. Martinson, H. Van Ryswyk, and J. T. Hupp, *Energy and Environmental Science*, 2008, **1**, 66-78.
2. M. M. Yatskou, R. B. M. Koehorst, H. Donker, and T. J. Schaafsma, *Journal of Physical Chemistry A*, 2001, **105**, 11425-11431.
3. R. A. Jensen, R. F. Kelley, S. J. Lee, M. R. Wasielewski, J. T. Hupp, and D. M. Tiede, *Chemical Communications*, 2008, 1886-1888.
4. A. B. F. Martinson, J. W. Elam, J. T. Hupp, and M. J. Pellin, *Nano Letters*, 2007, **7**, 2183-2187.
5. R. A. Jensen, H. Van Ryswyk, and J. T. Hupp, *Langmuir*, 2009, [almost] submitted.

PA14

The effect of organic dyes on the redox electrolyte recombination in Dye-Sensitized Solar Cells

Tannia Marinado,[a] Kazuteru Nonomura,[a] Daniel P. Hagberg,[a] Licheng Sun[a] and Anders Hagfeldt[a,b]*

a, Department of Chemistry, Center of Molecular Devices, KTH Chemical Science and Engineering, 10044 Stockholm, Sweden.

b, Department of Physical and Analytical Chemistry, Uppsala University, Box 259, 75105, Uppsala, Sweden.

Dye-sensitized solar cells, DSCs, based on triphenylamine organic dyes with varying linker conjugation (polyene) were studied in terms of how they affect the recombination with the electrolyte. Based on previous studies there seem to be a relation between degree of conjugation and open-circuit voltage.[1-2] This have been assigned to redox electrolyte recombination resulting in different electron lifetimes.[2] Different dyes might have different surface coverage abilities. Therefore, electron lifetimes were measured as a function of dye load. Higher dye loads resulted in longer lifetimes and could simply be due to surface shielding effects. On the other hand, changing the sensitization conditions higher dye load also resulted in constant or even a decrease in lifetime. This observation is in agreement with recent studies on carbazole and coumarin dyes.[3] The recombination is thought to be dependent on how well the dyes are ordered on the surface, referred to as their self assembly properties. The degree on conjugation seems to influence the nature of sensitization and hence the surface coverage. This effect seems to be of major importance in particular for organic dyes when dye aggregates are frequently discusses. Further details will be presented at the conference.

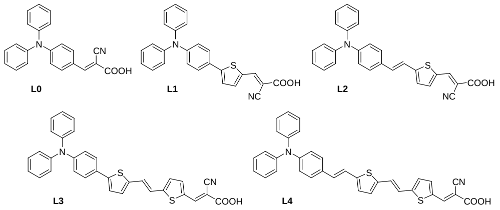


Figure 1. Structure of the dyes.

References

1. D. P. Hagberg, T. Marinado, K. M. Karlsson, K. Nonomura, P. Qin, G. Boschloo, T. Brinck, A. Hagfeldt, L. Sun, L, *J. Org. Chem.* 2007, **72**, 9550-9556.
2. T. Marinado, D. P. Hagberg, M. Hedlund, T. Edvinsson, E. M. Johansson, G. Boschloo, H. Rensmo, T. Brinck, L. Sun, A. Hagfeldt, *Phys. Chem. Chem. Phys*, 2009, **11**, 133-141.
3. M. Miyashita, K. Sunahara, T. Nishikawa, Y. Uemura, N. Koumura, K. Hara, A. Mori, T Abe, E. Suzuki, S. Mori, J. Am. Chem. Soc. 2008, **130**, 17874-17881.

PA15

Lanthanide luminescent organic complexes: effect of N-based co-ligands on photophysical properties

A. Alessi, P. Biagini, S. Fanutti, N. Perin, M. Salvalaggio*, S. Spera and A. Tacca
Eni Corporate, Centro Ricerche per le Energie non Convenzionali, Istituto Eni Donegani, via G. Fauser, 4, Novara, I-28100, Italy
*mario.salvalaggio@eni.it

The unique photophysical properties of lanthanide ions (long lifetimes and very sharp and narrow emission bands) have encouraged vigorous research activities in view of photonic applications such as tunable lasers, components of the emitting materials in multilayer organic light emitting diodes (OLED) and light convertion molecular devices[1]. It is well-known that the coordination of suitable ligands as highly absorbing "*antennae*" is required to overcome the very low absorption coefficients of the lanthanide ions. β-diketones are commonly used sensitizing antennae as they can efficiently transfer energy to Ln$^{(III)}$ ions and are able to form stable and strong adducts with all the metals of the lanthanide series[2]. Moreover, ancillary co-ligands such as bipyridines and phenanthrolines can impressively influence the emission intensity of these complexes[3].

The above considerations prompted us to synthesize and characterize various octa-coordinated lanthanide β-diketonate complexes of general formula: Ln(acac)$_3$(L) [where Ln= Eu, Sm, Tb, Dy; acac = 4,4,4-trifluoro-1-(2-naphtyl)-1,3-butanedionate or 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedionate; L = 2,2'-bipyridine, 1,10-phenanthroline, 5-nitro-1,10-phenanthroline, 3,4,5,7-tetramethyl-1,10-phenanthroline]. These Ln$^{(III)}$ complexes were characterized by NMR and FT-IR spectroscopy and their photophysical properties were studied by UV-Vis absorption and by steady state and time resolved photoluminescence spectroscopies, with the aid of cyclic voltammetry measurement.

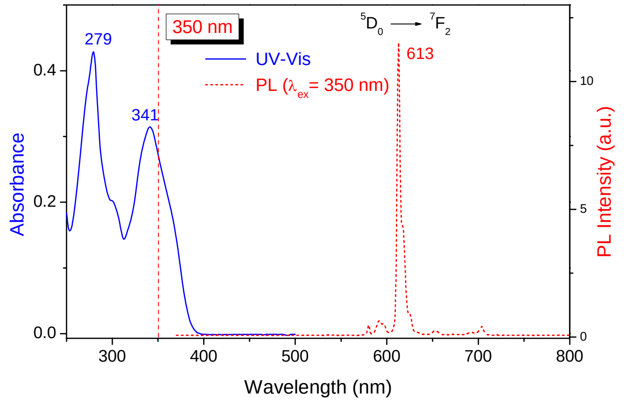


Figure 1.

Ligand-sensitized luminescence characteristic of the different Ln$^{(III)}$ centres are mainly based on β-diketonate ligand excitation around 350 nm. Otherwise, N-based bidentate ligand influence overall quantum yields evidencing different sensitization efficiencies[3] depending on β-diketonate ligand and rare earth centre. These co-ligands effects are discussed in terms of electron donor/acceptor character of the ligands.

References

1. J-C. G. Bünzli and C. Piguet, *Chem. Soc. Rev.*, 2005, **34**, 1048; A. de Bettencourt-Dias, *Dalton Trans.*, 2007, 2229; R. Hao, M. Li, Y. Wang, J. Zhang, Y. Ma, L. Fu, X. Wen, Y. Wu, X. Ai, S. Zhang and Y. Wei, *Adv. Funct. Mater.*, 2007, **17**, 3663.
2. J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1304; G.F. De Sa, O.L. Malta, C. de Mello Denega, A.M. Simas, R.L. Longo, P.A. Santa-Cruz and E.F. da Silva, Jr, *Coord. Chem. Rev.*, 2000, **196**, 165.
3. A.M. Klonkowski, S. Lis, M. Pietraszkiewicz, Z. Hnatejko, K. Czarnobaj and M. Elbanowski, *Chem. Mater.*, 2003, **15**, 656; C.R. De Silva, J.R. Maeyer, R. Wang, G.S. Nichol and Z. Zheng, *Inorg. Chim. Acta*, 2007, **360**, 3543.

PA16

Utility of Cyclometalated Ru Chromophores in the Dye-Sensitized Solar Cell

K. C. D. Robson,*(a)* P. G. Bomben,*(a)* B. D. Koivisto,*(a)* C. P. Berlinguette,*(a)**

(a)Department of Chemistry, University of Calgary, 2500 University Drive NW, Calgary, Alberta, Canada T2N-1N4, Canada.

Because optimal power output in the dye-sensitized solar cell (DSSC) is achieved by utilizing lightharvesting units based on derivatives of [Ru(bpy)3]2+ (e.g., [Ru(bpy-COOH)2(NCS)2]), the vast majority of dyes reported in the literature have been based on related Ru-polypyridyl complexes. Departing from this line of inquiry, our program1 is exploring the viability of a structurally related family of cyclometalated metal complexes2 to accomplish the necessary light absorption and charge-injection events. This approach not only helps to improve the thermal and photostability of the dye complex, it also serves to extend the absorption profile into the NIR region of the solar spectrum (Figure 1). This presentation will provide an assessment of the performance of these organometallic Ru complexes in the DSSC.

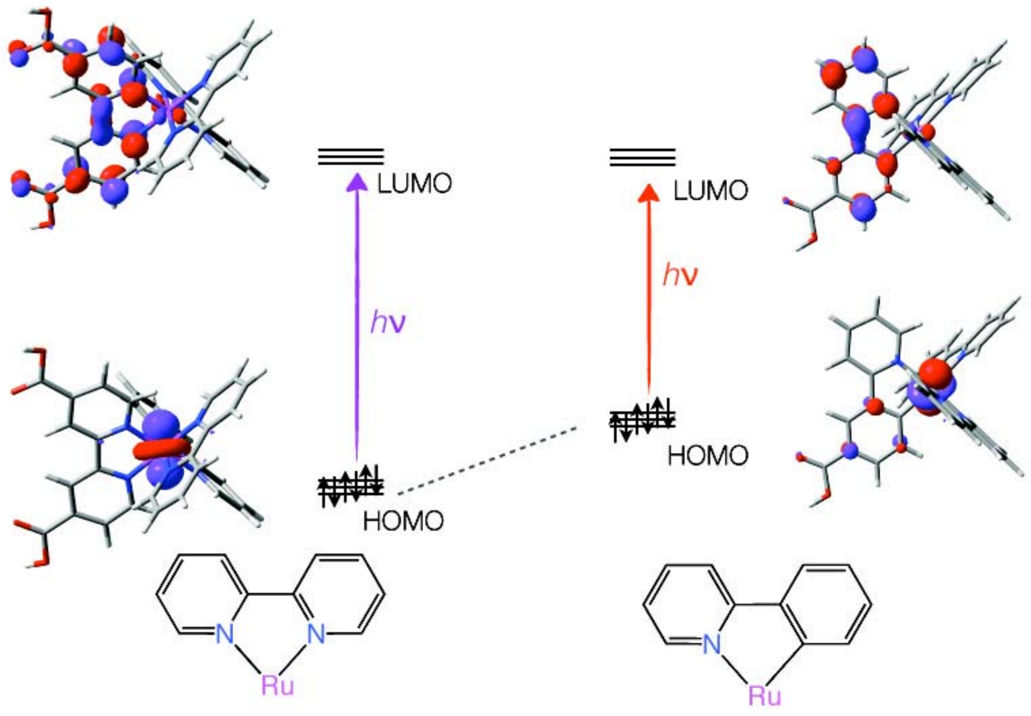


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Figure 1.

References

1. (a) P. G. Bomben, K. C. D. Robson, C. P. Berlinguette 2009, *Submitted*; (b) B. D. Koivisto, K. C. D. Robson, C. P. Berlinguette 2009, *Submitted.*
2. (a) E. C. Constable, J. M. Holmes *J. Organomet. Chem.* 1986, **301**, 203. (b) S. H. Wadman, M. Lutz, D. M. Tooke, A. L. Spek, F. Hartl, R. W. A. Havenith, G. P. M. van Klink, G. van Koten, *Inorg. Chem.* 2009, **48**, 1887.

PA17

Microwave Assisted Synthesis of $CuInSe_2$ Nanopowder

A. Gertsin,[a] G. Muradova,[a] A. Shoka,[a] D. Kim,[b] S. Bereznev,[c]* A. Tverjanovich,[a] J. Kois,[c] A. Öpik[c] and Yu. Tveryanovich[a]

a, Department of Chemistry, Saint-Petersburg State University, Staryi Petergof, Universitetskiy pr. 26 Saint-Petersburg, 198504, Russia.
b, Korea Institute of Machinery and Materials, Sangnam-Dong 66, Kyungnam, 641-010, South Korea.
c, Department of Materials Sciences, Tallinn University of Technology, Ehitajate tee 5, Tallinn, 19086, Estonia

$CuInSe_2$ (CISe) is a promising material for solar cell application, because this photoabsorber is stable, has a high absorption coefficient and band gap value close to optimal for effective sun light absorption. The preparation of composite structures based on the distribution of photoabsorber nanoparticles in organic or polymer matrixes deserves a serious attention. From this point of view, the synthesis of CISe nanopowder is perspective direction of investigations[1]. For preparation of CISe nanopowder the method of microwave assisted synthesis was chosen[2]. The main factors which influent on the process of CISe nanoparticles formation are the following: source reagents, microwave power, solvent and temperature of solvent, conductivity of intermediate phases.

The influence of source reagents on properties of CISe photoabsorber powders prepared by microwave assisted synthesis in triethylene glycol (TEG) and polyethylene glycol (PEG) was studied. Prepared CISe powders were investigated by using the X-ray diffraction (XRD) technique, scanning electron microscopy (SEM) equipped with EDS analyzer and MicroRaman spectroscopy to control composition, structure and morphology of the synthesized powders. It was found, that microwave assisted polyol method is useful technique for synthesis of CISe nanopowders.

Synthesis with metallic In and Cu precursors resulted in residue of unreacted indium in the products of reaction and deviation of composition of the resulted CISe powder from the stoichiometry. On the other hand, using of soluble salts of In(III) and Cu(I) as the source reagents leads to preparation of practically stoichiometrical CISe powder. Chalcopyrite structure of prepared CISe powder and polynanocrystalline morphology was confirmed by XRD, SEM and Raman techniques. The purest CISe powder was synthesized from CuCl, $In(OOCCH_3)_3$ and Se source reagents dissolved in PEG. It was found that the average size of prepared CISe powder grains depends on the average molecular weight of the solvent (polyol). Using of PEG-600 as the reaction solvent gives practically uniform polynanocrystalline CISe powder with average size of crystals around 80 nm (Figure 1).

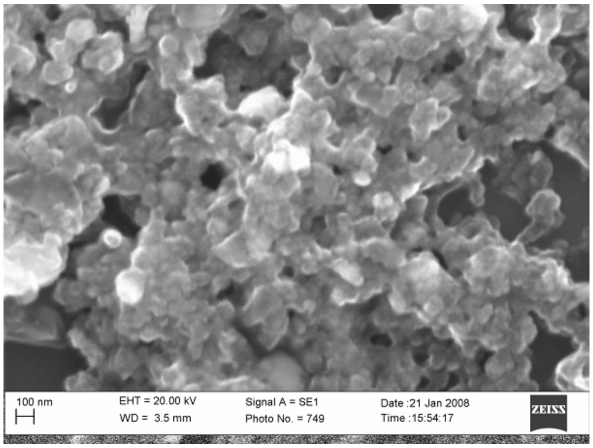

Figure 1. SEM micrograph of CISe powder synthesized from CuCl, $InCl_3$ and Se solution in PEG-600.

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References

1. E. Arici, H. Hoppe, F. Schäffler, D. Meissner, M. Malik, and N.S. Sariciftci, *Thin Solid Films*, 2004, **451-452**, 612.
2. H. Grisaru, O. Palchik, A. Gedanken, V. Palchik, A.M. Weiss, and M.A. Slifkin, *Inorganic Chemistry*, 2003, **42 (22)**, 7148.

PA18

Preparation and characterization of TiO_2 thin films by screen printing: Evaluation of material property and parameter effects

Kee Eun Lee[a], Cecile Charboneau[a], Guobin Shan[a], Raynald Gauvin[a], George P. Demopoulos[a,*] and Oumarou Savadogo[b]
a. Materials Engineering, McGill University, Montreal, QC, H3A 2B2, Canada and
b. Genie Chimique, Ecole Polytechnique, Montreal, QC, H3A 3A7, Canada

TiO_2 nanocrystalline films were prepared from commercial and laboratory synthesized precursors by screen printing[1] with the purpose of correlating physical properties and processing protocols (annealing and $TiCl_4$ treatment) to DSSC performance[2,3]. Their morphological features were characterized in terms of particle size, shape, BET surface areas, Raman spectrum and AFM analysis[4-7]. The light harvesting efficiency and electron transfer yield were studied for DSSC performance using UV/Vis spectrometer. The particle size, distribution and film thickness are discussed as key parameters of determining the light harvesting efficiency[8,9]. Impedance spectroscopy was applied to study the electrical potential distribution in DSSC and the energy distribution of the surface states[10, 11].

References

1. Seigo Ito, Peter Chen, Pascal Comte, Mohammad Khaja Nazeeruddin, Paul Liska, Peter Pechy and Michael Gratzel, *Prog. Photovolt: Res. Appl.* 2007, **15**, pp 603-612

2. Larry N. Lewis, James L. Spivack, Shellie Gasaway,Eric D. Williams, John Y. Gui, Venkatesan Manivannan,Oltea P. Siclovan. *Solar Energy Materials & Solar Cells,* 2006, **90**, pp 1041–1051
3. P. M. Sommeling, B. C. O'Regan, R. R. Haswell, H. J. P. Smit, N. J. Bakker, J. J. T. Smits, J. M. Kroon, and J. A. M. van Roosmalen, *J. Phys. Chem. B.* 2006, **110***,* 19191-19197
4. Tammy P. Chou, Qifeng Zhang, Bryan Russo, Glen E. Fryxell, and Guozhong Cao, *J. Phys. Chem. C* 2007, **111***,* 6296-6302
5. Masakazu Anpo, Takahito Shima, Sukeya Kodama, and Yutaka Kubokawa, *J. Phys. Chem.* 1987, **91**, 4305-4310
6. Morten E. Simonsena, Henrik Jensenc, Zheshen Li b, Erik G. Søgaarda, *Journal of Photochemistry and Photobiology A: Chemistry* 2008, **200**, 192–200
7. Toshiaki Ohsaka, Fujio Izumi and Yoshinori Fujiki, *JOURNAL OF RAMAN SPECTROSCOPY*, 1978, **7**, 321-324
8. Yasuhiro Tachibana, Kohjiro Hara, Kazuhiro Sayama, and Hironori Arakawa, *Chem. Mater.* 2002, **14***,* 2527-2535
9. Daibin Kuang, Seigo Ito, Bernard Wenger, Cedric Klein, Jacques-E Moser, Robin Humphry-Baker, Shaik M. Zakeeruddin, and Michael Gratzel, *J. AM. CHEM. SOC.* 2006, **128**, 4146-4154
10. Toyohisa Hoshikawa, Ryuji Kikuchi, Koichi Eguchi, Journal of Electroanalytical Chemistry 2006, **588**, 59–67
11. Qing Wang, Jacques-E. Moser, and Michael Gratzel, *J. Phys. Chem. B* 2005, **109***,* 14945-14953

PA19

Dye Sensitized Solar Cell fabrication at CIN2:
Paste formulation for commercial (P25) and hydrothermal synthesized TiO_2

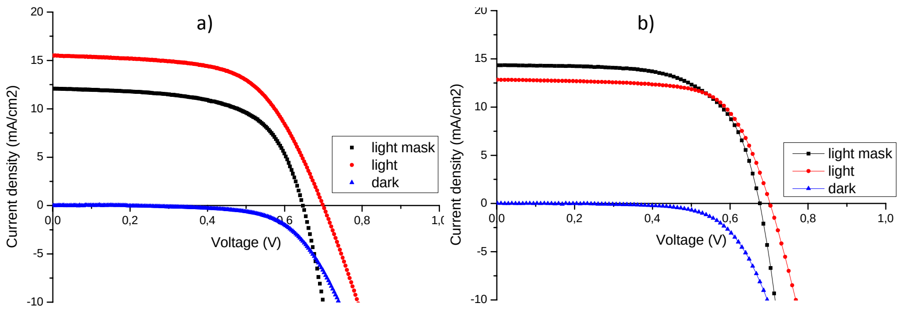
Natalia González-Pech[a,b] and Monica Lira-Cantu[b*]

a. *Chemistry department, Instituto Tecnologico y de Estudios Superiores de Monterrey (ITESM), Av. Eugenio Garza Sada. Monterrey, (Nuevo León), 64640, México.*

b. *Centre de Investigaciò en Nanociencia i Nanotecnologia, Campus UAB, Edifici ETSE 2nd Floor. Bellaterra (Barcelona), E-08193, Spain.*

* monica.lira@cin2.es

As part of the set up of our laboratory we present here our initial results on the preparation technique to obtain TiO_2 pastes and the fabrication of nanostructured electrodes for Dye sensitized Solar Cells (DSCs). To fabricate this pastes, we use a commercially-available TiO_2 (P25, Degussa) and hydrothermal synthesized TiO_2 in basic media. The TiO_2 pastes were made by the method already published applying terpineol and ethyl cellulose[1-3]. A buffer layer of TiO_2 made by the sol-gel solution was applied on a FTO glass before the pastes were applied. A sandwich-type cell was fabricated by assembling a sensitized TiO_2 electrode with a Pt counter electrode. For the hydrothermal synthesized nanoparticles of TiO_2 we characterized the materials by TEM and XRD. The thickness of the TiO_2 layer used in the DSCs was characterized by SEM. I-V curves were determined under standard atmospheric conditions (AM1.5). Efficiencies as high as 6.49% have been obtained as observed in Figure 1.



	Mask	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	Efficiency %
(a)P25	with	0,65	12,26	0,62	4,98
	without	0,69	12,87	0,66	5,84
(b)Synthesis hydrothermal	with	0,65	12,99	0,55	4,64
	without	0,69	17,29	0,50	6,00

Figure 1. Dye Sensitized Solar Cell made with TiO_2 P25 from Degussa (a) and synthesized by the hydrothermal method (b).
Measurements carried out at ~77 ºC, 1000 W/m^2, A.M1.5.
Analyses performed at the photovoltaics laboratory at CIN2 (CSIC-ICN).

References

1. S. Ito, P. Chen, P. Comte, M. K. Nazeeruddin, P. Liska, P. Péchy and M. Grätzel. *Prog. Photovolt: Res. Appl.* 2007, **15,** 603**.**
2. P. Wang, S. M. Zakeeruddin, P. Comte, R. Charvet, R. Humphry-Baker and M. Grätzel. *J. Phys. Chem. B.*2003, **51**, 14336.
3. W. J. Lee, E. Ramasamy, D. Y. Lee and J. S. Song. *Journal of Photochemistry and Photobiology A: Chemistry*, 2006, **183,** 133.

PA20

Low-temperature preparation route for nanocrystalline TiO_2 in multigram scale using R_2TiF_6 ($R=BetH^+$, Cho^+) ionic liquid like precursor solutions: Application in Dye-Sensitized Solar Cells.

David Gutiérrez-Tauste[a,*], José A. Ayllón[b], Laurent Aubouy[a], Gabrielle Nelles[c], Yvonne Joseph[c]
[a]*LEITAT Technological Center, Passeig 22 de Juliol, 218, 08221 Terrassa (Barcelona), Spain.*
[b]*Chemistry Department, Autonomous University of Barcelona, Campus UAB, 08193 Bellaterra, Spain.*
[c]*Sony Deutschland GmbH, Material Science Laboratory, Hedelfingerstrasse 61, 70327 Stuttgart, Germany.*

Ionic Liquids (ILs) have provided a new tool to design alternative strategies in the chemical synthesis and separation processes, although their use in the preparation of materials is only in the initial stage[1]. Titanium dioxide (TiO_2) is a key material, with numerous applications in fields as diverse as photocatalysis or Dye Sensitised Solar Cells[2].

Here, nanocrystalline TiO_2 prepared in multigram scale at low temperature by our previously reported method[3] is applied for fabricating DSSCs photoelectrodes. Briefly, R_2TiF_6 ($R=BetH^+$, Cho^+) IL-like precursor solutions are simply prepared by mixing commercial H_2TiF_6 (60 wt. % in H_2O) with Betaine (Bet, $Me_3N^+\text{-}CH_2\text{-}COO^-$) or Choline Chloride (ChoCl, $[Me_3N\text{-}CH_2\text{-}CH_2OH]Cl$). The high concentration of ions in these solutions leads to a situation similar to the ILs, considering the low amount of water present in the media[3]. Under this conditions, R_2TiF_6 concentrated solutions act as "all-in-one": solvent, precursor and crystal growth directing media for titania. The titanium precursor is destabilised by using a fluoride scavenger (*i.e.* H_3BO_3) at temperatures as low as 65ºC in a process analogue to high-concentration Liquid Phase Deposition, finally yielding nanocrystalline TiO_2. Although precautions should be taken into account due to the corrosive character of the precursor, the method presents numerous advantages: simplicity, low-cost chemicals, no organic solvent must be added, by-products separation with water, titania yield almost 100%, TiO_2 mass obtained/volume of reaction mixture nearly 1 g/10 ml.

Sandwich type DSSCs are built as follows: (i) 30 nm TiO_2 blocking layer formed on FTO-glass by spray pyrolysis; (ii) 8 cycles of spraying/drying processes of 2% ethanol based suspensions of home-made titania particles; (iii) Conventional sintering at 450ºC for 30 min; (iv) Red dye Ru 535 TBA sensitisation; (v) Acetonitrile-based liquid electrolyte interpenetration; (vi) Cell assembly with a Pt mirror counter electrode, 30 μm spacer. Current-voltage characteristics are registered under illumination with white light from a sulphur lamp at an intensity of 100 mW/cm^2.

Porous titania photoelectrodes are successfully prepared via the low-cost and additive-free approach simply based on spraying a suspension of the corresponding home-made nanoparticles in ethanol. DSSCs fabricated with choline-derived nanoparticles presented remarkable performances in terms of J_{SC}, V_{OC}, FF and η. The highest value of solar-to-electrical conversion efficiency (8.5 % approx.) is obtained for titania nanoparticles prepared from $[Cho]_2TiF_6$ IL-like precursor solutions forming porous photoelectrodes only 5 μm thick.

1. M. Antonietti, D. Kuang, B. Smarsly, Y. Zhou, *Angew. Chem. Int. Ed.*, 2004, **43**, 4988-4992.
2. M. Grätzel, *Nature*, 2001, **414**, 338-344.
3. D. Gutiérrez-Tauste, X. Domènech, C. Domingo, J.A. Ayllón, *Chem. Commun.*, 2007, 4659-4661.

PA21

Electrochemical Fluorescence Spectroscopy applied to the study of Energy Transfer in Conjugated Polymer Blends

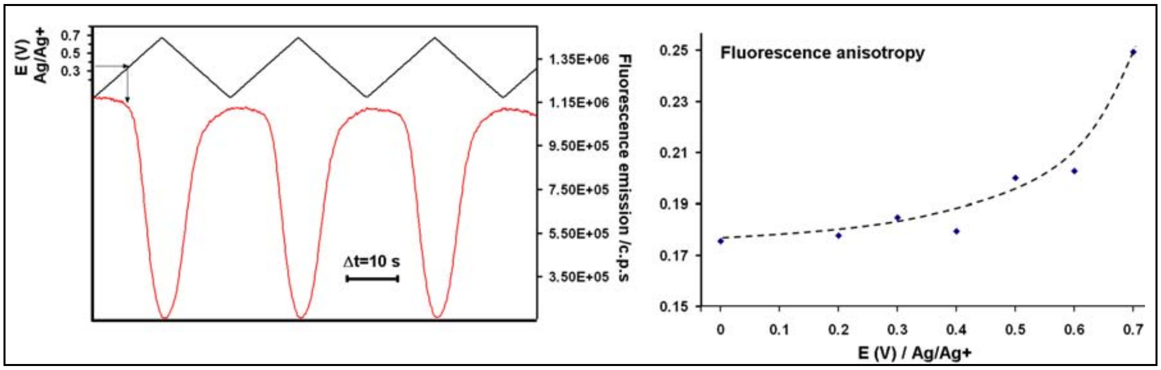
Francisco Montilla y María Angeles Cotarelo
Departamento de Química Física e Instituto Universitario de Materiales de Alicante.
Universidad de Alicante. Apdo. de Correos 99. E03080. Alicante Spain
francisco.montilla@ua.es.

Fluorescence Spectroscopy coupled to an electrochemical system is a powerful tool for the characterization of conjugated polymers, such as polyfluorene or PPV polymers, which find applications in organic LEDs or photovoltaic devices [1,2]. Several properties of these polymers can be determined by the simple following of the emission intensity as a function of the applied potential [3,4]. Furthermore the technique provides a prediction tool for the working performance of the conjugated polymers in organic electronic devices.

Advanced fluorescence techniques coupled to an electrochemical system, like Fluorescence Anisotropy have been employed to study the exciton dynamics in these polymers. Exciton dynamics are of great importance for the application of conjugated polymers to light-emitting or photovoltaic devices. On the one hand, the efficiency of light-emitting diodes decreases by exciton migration to the cathode or to interchain quenching sites. On the other hand, high diffusion lengths are required for photovoltaic application, where the exciton must move to an interphase site for an effective charge separation. The combination of the electrochemical control of a solid│liquid interface with the measurement of the emission anisotropy of conjugated light-emitting polymers upon electrochemical doping provides information on the excited-state dynamics [5].

The present work presents the exciton dynamics studied in several conjugated polymers (MEH-PPV and fluorene-based conjugated polymers) and in PPV-polyfluorene blends.

In the experiments performed with polarized excitation we observed a partial depolarization of the emission coming from the MEH-PPV. Considering the polymer layer as an isotropic material of randomly oriented chromophores unable to rotate, the Förster resonance energy transfer between chromophores serves to randomize the orientational distribution of the excited molecules.



The lowering of the emission intensity due to doping at potentials higher than 0.35V (as observed in figure 1, left) is related to electrochemical quenching processes by hole injection that decreases the exciton lifetime. The path length of the exciton also decreases, increasing the probability of the emission from a molecule with similar direction of the dipole transition moment. In that situation, the anisotropy of the emitted light from the polymer increases, as observed in figure 1 (right). The diffusion coefficient of the exciton may be determined for several polymers, making use of a Förster model for resonance energy homotransfer. Similar experiments have been performed for the study of heterotransfer between polymeric blend. The polyfluorene blue emitter is partially quenched by the resonance energy transfer to MEH-PPV. The evolution of the emission from PPV and Polyfluorene components of the blend upon electrochemical treatments provides information of exciton dynamics in the polymer's interfacial region.

References

1.Montilla, F. et al. *J. Phys. Chem. C* 2008, 112 (42), 16668.
2. Montilla, F. and Mallavia, R. *Adv. Funct. Mater*. 2007, 17 (1), 71.
3. Montilla, F. and Mallavia, R. *J. Phys. Chem. B* 2006, 110 (51), 25791.
4. Montilla, F. et al. *J. Phys. Chem. B* 2006, 110 (12), 5914.
5. Montilla, F. et al. *J. Phys. Chem. C* 2007, 111 (49), 18405.

PA22

Er- and Yb-complexes with fluorinated ligands for photonic applications in Telecommunications

M. Ramos-Silva, A. Matos-Beja,
CEMDRX, Universidade de Coimbra, Portugal
P. Martín-Ramos, P. Chamorro-Posada, L.M. Navas-Gracia, J. Martín-Gil*
ETSIT and ETSIA, Universidad de Valladolid, Spain

Lanthanides doped materials are of decisive importance to Photonics and are becoming to be widely deployed in solid-state lasers. Er^{3+} is for this reason the most popular lanthanide ion for the characteristic emission around 1550 nm (coming from the $^4I_{13/2}\rightarrow{}^4I_{15/2}$ transition), which is the currently most used wavelength in fiber-optic communications. Yb^{3+} ions also are useful because they absorb in the NIR around 980 nm ($^2F_{5/2}\rightarrow{}^2F_{7/2}$ transition), where laser diodes work efficiently.

To make lasers it is needed to avoid unwanted pair interactions of the lanthanide ions within the whole body of the substrate by restricting their presence only to the shallow surface layer. We are studying new approaches of introducing Er^{3+} (Yb^{3+}) ions onto thin surface layers of glass substrates. A good approach, from Z. Sofer *et al.* 2007, is based on soaking of solutions of Er/Yb-complexes into porous silicate glass followed by annealing to decompose the complexes and to sinter the porous glass material. To achieve homogeneous distribution of ions in the glass matrix large molecules of Er/Yb-complexes should be spread in regularly located micro or nano pores of the glass. The Er/Yb-complexes should fulfill the following criteria: they should have large ligands (so as to avoid ion clustering) with the number of donor oxygen atoms kept as low as possible (in order to avoid OH groups, which would shorten some of the Er^{3+} excited states lifetimes) and they should allow for synthesizing in non-aqueous solutions (to avoid OH groups). Moreover, the complexes should be decomposable by heating without leaving any unwonted residues. All these requirements are accomplished by our Er- and Yb-complexes with heterocyclic ligands.

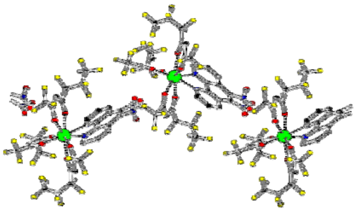


Figure 1. Structure of tris (1,1,1,5,5,6,6,7,7,7-decafluoro-2,4-heptadionato)-5-nitro-1,10-phenantroline erbium(III)/ytterbium(III), recently synthesized

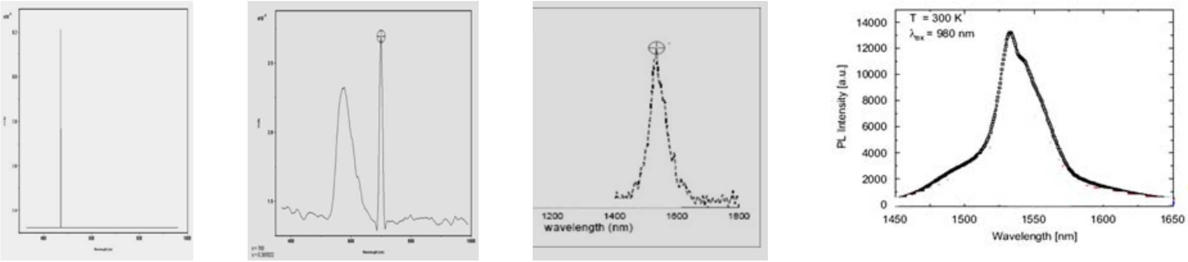


Figure 2. Excitation and emission spectra of the new Er-complex *(left)*; Photoluminescence of erbium doped glass substrates *(right)*

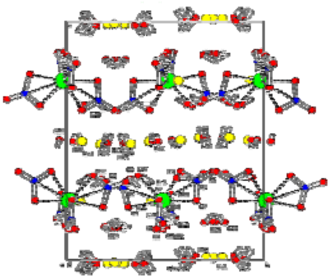


Figure 3. Structure of $[Er/Yb(NO_3)_4]^-$ $[Na_5(OH)_4]^+.14H_2O$

Whereas the OH groups shorten some of the Er^{3+} excited states lifetimes (as we have evidenced from $[Er/Yb(NO_3)_4]^-[Na_5(OH)_4]^+ \cdot 14H_2O$, recently synthesized and whose structure is reported on the right side), the F atoms increase the solubility in typical organic solvents and reduce the non-radiative deactivation of terminal oscillators (C-F instead C-H).

Conclusion: both the use of fluorine-substituted ligands and fluorosilicated glass are favourable contributions to enhance the photoluminescence. Nevertheless, the reliability of fluorinated glass fibers depends on pretreatment of the preform to reduce surface crystallization.

PA23

Surface-initiated polycondensation: a new tool for the preparation of complex architectures of conjugated polymers for solar cells

Volodymyr Senkovskyy[a], Manfred Stamm[a], Suren A. Gevorgyan[b], Frederik C. Krebs[b], and Anton Kiriy[a]*
a Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Straße 6, 01069 Dresden, Germany
b Risø National Laboratory for Sustainable Energy, Technical University of Denmark, Frederiksborgvej 399, DK-4000 Roskilde, Denmark

Improper morphology of active layers in polymer bulk heterojunction solar cells is one of the bottle-neck problems limiting the performance of solar cells. To solve the problem, a new generation of polymeric materials able to self-assemble into desired morphologies are needed. A propensity of complex architectures of polymers, such as block copolymers, graft copolymers, stars, polymer brushes, etc., to form variety of well-defined morphologies via self-assembly was nicely exemplified in the case of non-conjugated and non-conductive polymers, however, their pi-conjugated counterparts are much less available. This is because the synthesis of CPs usually involves polycondensation reactions that proceed through a step growth mechanism. McCullough[1] and Yokozawa[2] groups have made an important discovery that Ni-catalyzed Kumada-polycondensation of 2-bromo-5-chloromagnesio-3-alkylthiophene (**1**) into regioregular poly(3-hexylthiophene) (P3HT) involves not the step growth mechanism, as it was believed for decades, but instead, follows the chain growth scheme. We made a step further developing surface initiated polycondensation process allowing one to grow P3HT from photo-cross-linked poly(-4-bromostyrene) (PS-Br) [3], or from block copolymer films.[4] The process involves catalyst-transfer polycondensation (CTP) of **1** selectively from the sites on the surface where $Ni(PPh_3)_4$ catalyst was covalently immobilized. In principle, the chain growth nature of the CTP might provide the access to other architectures of CPs, including block copolymers and stars. However, the great potential of this reaction was not yet explored. We will highlight our recent achievements in the development of CTPs utilizing different catalytic systems. In the present contribution we wish to report our recent results along these lines and discuss photovoltaic properties of new architectures of polythiophenes prepared by the surface-initiated polycondensation route.

References

1. McCullough, R. et al. *Macromolecules* **2005**, *38*, 8649
2. Yokozawa, T. et al. *J. Am. Chem. Soc.* **2005**, *127*, 17542
3. Senkovskyy, V.; Khanduyeva, N.; Komber, H.; Oertel, U.; Stamm, M.; Kuckling, D.; Kiriy, A. *J. Am. Chem. Soc.* **2007**, *129*, 6626.
4. Khanduyeva N, Senkovskyy V, Beryozkina T, Horecha M, Stamm M, Uhrich C, Riede M, Leo K, Kiriy A. *J. Am. Chem. Soc.* **2009**; *131*; 153-61.

PA24

Computational Determination of the Molecular Structure and Properties of Nanostructured Materials for Organic Photovoltaics

Teresita Ruiz-Anchondo, Hazel Morales-Rodríguez, Alberto Flores-Hidalgo and Daniel Glossman-Mitnik*
Grupo NANOCOSMOS, CIMAV, SC, Miguel de Cervantes 120, Complejo Industrial Chihuahua, Chihuahua, Chih. 31109, México.

Our society is based on coal, oil and natural gas, but these fossil fuels will be depleted someday in the future because they are limited. Carbon dioxide is produced in the combustion of fossil fuels and the rapid increase of carbon dioxide concentration has affected the consequence of climate, resulting in the global warming effect. Under these circumstances, interest in photovoltaic (PV) solar cell is increasing rapidly as an alternative and clean energy source [1].

Photovoltaic solar cells provide clean electrical energy because the solar energy is directly converted into electrical energy without emitting carbon dioxide. The solar energy is not limited, free of charge and distributed uniformly to all human beings. Crystalline silicon solar cell has been extensively studied and used for practical terrestrial applications. However, the expensive material cost and lots of energy necessary for manufacturing have caused high cost and long energy payback time, which have prevented
the large spread of PV power generation [1].

Dye-sensitized nanostructured solar cells (DNSCs) based on nanostructured metal oxide films have attracted much attention in recent years. They offer the prospect of low-cost photovoltaic energy conversion. Promising solar-to-electrical energy conversion efficiencies of more than 10% has been achieved and good progress has been made on long-term stability [1].

The objective of this work is to report the results of the calculation of the molecular structure and properties of beta-carotene and carotenoid compounds that could act as photosensitizers in dye-sensitized nanostructured solar cells, as well as ZnO nanowires and ZnO ring nanoclusters. The results are compared with the experimental available data.

References

1. Nanostructured Materials for Solar Energy Conversion, Tetsuo Soga (Ed.), Elsevier B.V., Amsterdam, The Netherlands, 2006.

PA25

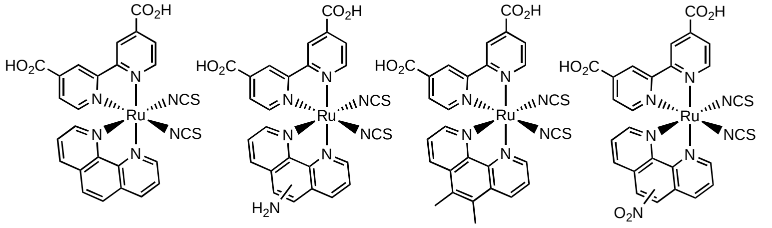
Understanding the relationship between dye structure and device efficiency

Amparo Forneli [a], Eugenia Martínez-Ferrero [a], Antonio Sánchez-Díaz [a], Anton Vidal Ferran,[a, b] , Brian C. O'Regan[c], Anna Reynal Verdú [a*] and Emilio Palomares [a, b]
a, Institut Català d'Investigació Química (ICIQ), Avda. Països Catalans, 16, 43007, Tarragona, Spain.
b, Institució Catalana de Recerca i Estudis Avançats (ICREA), Passeig Lluís Companys, 23, 08010 Barcelona, Spain.
c, Imperial College of London, South Kensington Campus, SW7 2AZ, London, United Kingdom.

The study of charge transfer reactions that take place at the different interfaces of dye sensitized solar cells (DSSC) shows that electron transfer reactions are very much optimised. However, there are recombination reactions between the oxidised dye and the photoinjected electrons, and between these electrons and the oxidised electrolyte, which result critical for the overall efficiency of the devices.

Recently, it has been demonstrated that several dyes, which show poor light-to-energy conversion performance, increase the rate of electron recombination between the photoinjected electrons and the oxidised electrolyte when used as sensitizers. These dyes have in common the presence of extended π-conjugated systems that lie close to the semiconductor surface.

Taking into account this observations, we have designed a series of heteroleptic ruthenium (II) complexes where one of the 4,4'-dicarboxy-2,2'-bipyridine ligands has been substituted by a phenanthroline moiety. Furthermore, the phenanthroline ligand has been modified with the introduction of electron donating or electron withdrawing groups to achieve the desired control over the molecular orbitals. Whilst electron-donationg groups will increase the energy gap (HOMO-LUMO gap), the introduction of electron withdrawing groups will have the opposite effect.



AR20 AR24 α & β (2 diastereoisomers) AR25 AR27 α & β (2 diastereoisomers)

Figure 1.

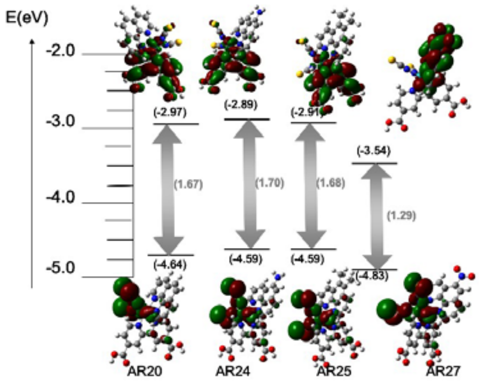


Figure 2.

Our aim is to study and rationalise the possible effects over the interfacial charge transfer reactions, under working device conditions that the introduction in the dye of a more conjugated ligand, such as a phenanthroline, and its functionalisation will have on the overall device efficiency.

References

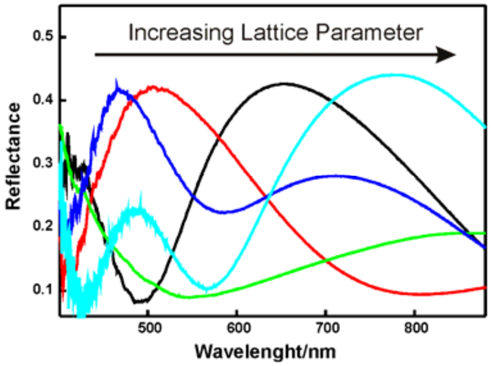
1. A. Reynal, A. Forneli, E. Martinez-Ferrero, A. Sánchez-Díaz, a. Vidal-Ferran, B. C. O'Regan, E. Palomares, *J. Am. Chem. Soc.*, 2008, **130**, 13558.

PA26

Photoconducting Bragg Mirrors Based on TiO_2 Nanoparticle Multilayers

Mauricio E. Calvo,[a] Silvia Colodrero, Manuel Ocaña and Hernán Míguez*
Institute of Materials Science of Sevilla, Américo Vespucio 49, 41092 ,Sevilla, España

Herein we present a synthetic route to build photoconducting films of TiO_2 nanoparticles that display bright structural color, which arises as a result of the periodic modulation of the refractive index.[1] This is achieved by controlling the degree of porosity of each alternate layer through the particle size distribution of the precursor suspensions, which were cast in the shape of a film by spin coating. This method allows tailoring the lattice parameter of the periodic multilayer, thus tuning the Bragg peak spectral position (i.e., its color) over the entire visible region, as it can be seen in the Figure 1. Photoelectrochemical measurements show that those Bragg mirrors are conductive and distort the photocurrent response as a result of the interplay between photon and electron transport through them (Figure 2).



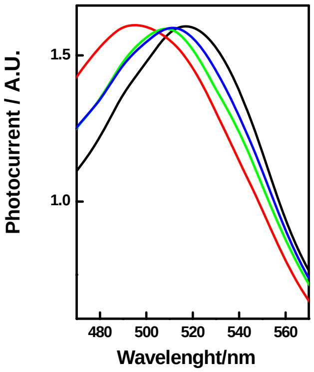


Figure 1 Figure 2

References

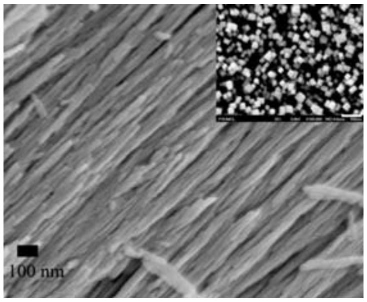
1. M.E. Calvo, S. Colodrero, T.C. Rojas, M. Ocaña, J.A. Anta, H. Míguez, *Adv. Func. Mater.* 2008, **18**, 2708.

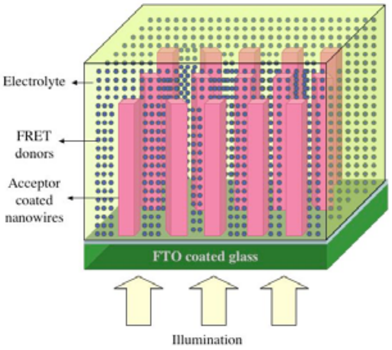
PA27

Enhanced Harvesting of Red Photons in Nanowire Array Solar Cells Using Resonance Energy Transfer

Karthik Shankar, Xinjiang Feng and Craig A. Grimes*
1The Department of Electrical Engineering,
The Pennsylvania State University, University Park, Pennsylvania 16802. E-mail: cgrimes@engr.psu.edu

The use of long range Förster-type resonance energy transfer (FRET) has been contemplated as an alternative mechanism for charge separation and a way to improve exciton harvesting by placing the exciton close to the heterojunction interface.1,2 We report here on the use of FRET to boost the quantum yield for red photons at 675 nm to 680 nm by a factor of four for N-719 and a factor of 1.5 for black dye. The close packed single crystal rutile nanowire array architecture3 developed by us, see Fig. 1, is an essential ingredient of our strategy because it allows placement of donor and acceptor molecules at distances comparable to a Förster radius.4 Fig. 2 illustrates our device configuration, with microscopy, spectral characteristics and basic modeling indicating the nanowire array based device to be nearly ideal for FRET-based enhancement in photoconversion efficiency. In our device configuration ZnPc-TTB molecules were introduced directly into the tri-iodide redox electrolyte at a (high) concentration of 5 mg/ml. As seen in Fig. 3, a dramatic increase in the quantum yield for red photons in the spectral region 670-690 nm was immediately observed, over and above the quantum yields exhibited by N-719 and Black dye sensitized nanowire solar cells. Resonance energy transfer of excitons generated in ZnPc-TTB molecules from red photons to surface bound N-719 dye results in a four-fold enhancement of quantum yield at 675 nm to 680 nm. Since the extinction coefficient of ZnPc-TTB molecules in the spectral region 670-690 nm is far greater than that of N-719, we believe the entire quantum yield of ~28% at the donor absorption maximum is attributable to FRET and is close to the measured fluorescence quantum yield of ZnPc-TTB in solution.5 At the high concentrations used, Zinc pthalocyanine forms multimolecular aggregates with a reduced quantum yield. A self-sieving effect of the nanowires admitting only monomeric and dimeric forms into the inter-wire spaces may account for the nearly quantitative efficiency of energy transfer from ZnPC-TTB in solution to surface anchored N-719 and black dye molecules.





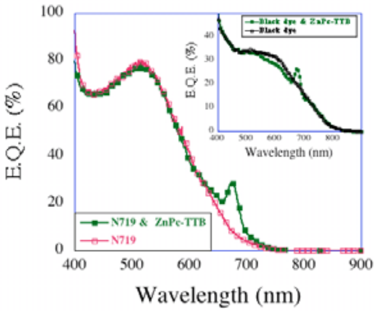


Fig. 4 (L): FESEM cross-section and (inset) top-view of the rutile nanowire arrays.

Fig. 2 (C): Depiction of the FRET enhanced nanowire dye sensitized solar cell.

Fig. 3 (R): Action spectrum of nanowire solar cell comprised of N-719 coated rutile as acceptors, with and withoutZnPC-TTB molecules in electrolyte as the donors. Inset shows action spectrum for black dye coated rutile acceptors with and without ZnPc-TTB donors. Ten percent of data points are shown.

1. Liu, Y.X., Summers, M.A., Scully, S.R. & McGehee, M.D. Resonance energy transfer from organic chromophores to fullerene molecules. Journal of Applied Physics 99 (2006).
2. Lu, S. & Madhukar, A. Nonradiative resonant excitation transfer from nanocrystal quantum dots to adjacent quantum channels. Nano Letters 7, 3443-3451 (2007).
3. Feng, X.J. et al. Vertically Aligned Single Crystal TiO2 Nanowire Arrays Grown Directly on Transparent Conducting Oxide Coated Glass: Synthesis Details and Applications. Nano Letters 8, 3781-3786 (2008)
4. K. Shankar, X. Feng, C. A. Grimes. Enhanced Harvesting of Red Photons in Nanowire Solar Cells Using Resonance Energy Transfer, In review, Nature Photonics.
5. Fernandez, D.A., Awruch, J. & Dicelio, L.E. Photophysical and Aggregation Studies of t-butyl–substituted Zn phthalocyanines. Photochemistry and Photobiology 63, 784-792 (1996).

PA28

Bandgap Modulation in Efficient n-Thiophene Absorbers for Dye Solar Cell Sensitization

Eva Mª. Barea*[a], Rubén Caballero,[b] Francisco Fabregat-Santiago[a], Pilar de la Cruz[b] , Lourdes Márquez,[a] Fernando Langa, [b] and Juan Bisquert[a]
[a]*Photovoltaics and Optoelectronic Devices Group, Departament de Física. Universitat Jaume I, 12071, Castelló, Spain.*
[b]*Instituto de Nanociencia, Nanotecnología y Materiales Moleculares (INAMOL). Universidad de Castilla – La Mancha. Campus de la Antigua Fábrica de Armas, Avda. Carlos III, s/n 45071, Toledo, Spain***An**

A main criterion to optimize new photon harvesting sensitizers for DSC s to achieve a wide absorption band.[1,2] But it must also be understood to what extent the molecular modification towards narrow bandgap correlates with an improved photovoltaic performance. Based on the previously reported organic dye,[3] we describe here a progressive expansion of the absorption band towards longer wavelengths from 0.55 to 0.75 µm in a series of 5 sensitizers by increasing the conjugation length. A clear correlation of increasing photocurrent with the extension of the conjugation is observed up to an optimal length. Further extension of the conjugation increases the absorption but additional effects like self-quenching or recombination process reduce the photocurrent and consequently the overall efficiency of the DSC.

The absorbers are based on π-conjugation of n oligothienylvinylene units, and are denoted FL*n* (*n* = 2, 3, 4, 5 and 6) being FL4 the RC4-17[3] (Figure 1). The donor unit is an oligomer of thienylvinylene with different lengths and the acceptor is a cyanoacetic acid moiety. The risk of decreased electron injection by π-stacked dye aggregation is prevented with attached alkyl groups[4]

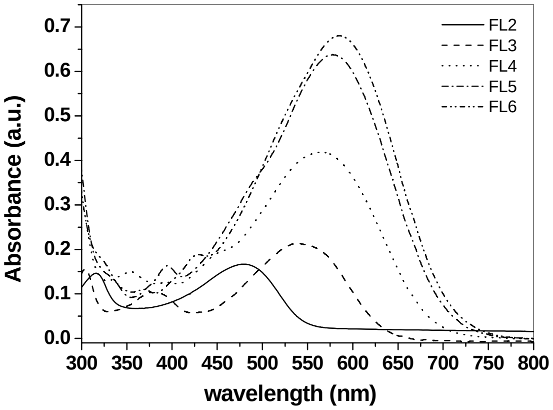


Figure 1.

References

1. K. Hara; T. Sato; R. Katoh; A. Furube; Y. Ohga; A. Shinpo; S. Suga; K. Sayama; Sugihara, H.; and H. Arakawa *J. Phys. Chem. B,* **2003**, *107*, 597.
2. K. Hara; Z. S. Wang; T. Sato; A. Furube; R. Katoh; H. Sugihara; Y. Dan-oh; C. Kasada; A. Shinpo; and S. Suga *J. Phys. Chem. B,* **2005**, *109*, 15476.
3. R. Caballero, E. Barea, F. Fabregat-Santiago, P. de la Cruz, L. Márquez, F. Langa, J. Bisquert *J. Phys. Chem. C,* **2008**, *112*, 18623-18627.
4. Koumura, N.; Wang, Z. S.; Mori, S.; Miyashita, M.; Suzuki, E.; Hara, K. *J. Am. Chem. Soc.* **2006**, *128*, 14256-14257.

PA29

NANOSCALE ULTRAVIOLET AND OZONE DEGRADATION OF P3OT FILMS STUDIED BY SCANNING PROBE MICROSCOPY

J. Abad[a], A. Urbina[b] and J. Colchero[a]
[a], *Centro de Investigación en Óptica y Nanofísica (CIOyN), Universidad de Murcia,*
Campus Espinardo, E-30100 Murcia, Spain
[b], *Dep. de Electrónica, Universidad Politécnica de Cartagena, E-30202 Cartagena, Spain*

In the field of organic solar cells the power conversion efficiency and the durability are issues that have to be addressed before this technology is competitive with traditional silicon solar cells. One of the research lines of our group is devoted to a better understanding of how the nanoscale properties determine the macroscopic behaviour of such devices[1,2,3,4].

To study the durability of plastic solar cells, in the present work we investigate the modification of thin P3OT films by ultraviolet (UV) radiation and ozone degradation. Films of 50-200 nm thickness have been prepared by spin-coating on conducting as well as insulating substrates. The samples were analysed using force microscopy techniques (SFM) and optical transmission measurements for every cycle of UV radiation and O3 exposure. Our experimental technique allowed us to perform a nanoscale study of the same area of the sample and therefore we can attribute the observed changes to the real effect of radiation as compared to possible statistical variations of surface properties. This allows powerful correlation studies between nanoscale structure and macroscopic measurements.

Different non-contact Scanning Force Microscopy techniques have been applied in this study, in particular Kelvin Probe Microscopy and local conductivity imaging. Our results can contribute to explain the degradation mechanism of the devices when exposed to solar light. The observed nanoscale structural changes are correlated on the one hand with changes of the macroscopic transport properties and on the other hand with the optical absorption of the samples, and thus finally with the overall performance of the fabricated devices.

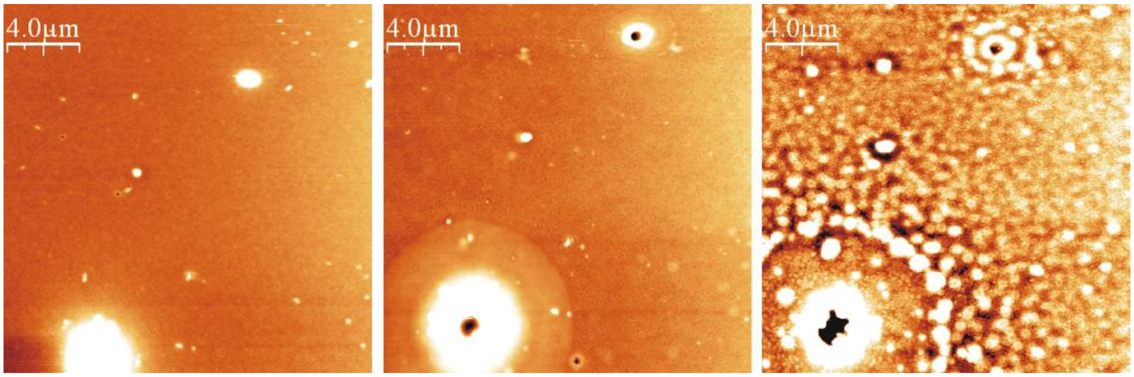


Figure 1.
Topographic images of P3OT thin films UV irradiated. Left figure: Pristine sample. Middle figure: 10 minutes of UV irradiation. Right figure: 30 minutes of UV irradiation.

References

1. C. J. Brabec et al. Adv. Funct. Mater. 11 (2001) 15.
2. E. Palacios-Lidón et al. Adv. Funct. Mat. 16 (2006) 1975.
3. B. Pérez-García et al. Nanotechnology 19 (2008) 065709.
4. J. Abad et al. European Polymer Journal 44 (2008) 2506.

PA30

Comparison of different processing techniques for organic photoactive layers, with respect to efficiency and life time.

M.Neophytou[a,b,*] , I.Etxebarria[a] , U.Munecas[a] , J.Ajuria , C.Waldauf[a] , R.Pacios[a]
a .Microsystems Department , Ikerlan,P°. J. Mª. Arizmendiarrieta 2, 20500 Spain.
b, Department of Mechanical Engineering and Materials Science and Technology, Cyprus University of Technology, 16 Saripolou Street Limassol, 3036, Cyprus
*, mneophytou@ikerlan.es

The environment suffers from misuse and abuse. Therefore alternative energy resources are obligatory to be found since all the available fossil resources are presumably running out.Organic photovoltaics(OPVs) is a competitive cost-effective renewable energy compatible with the environment and sustainability.

In this work, we have studied the optimization of polymer:fullerene bulk heteronjuction solar cells concerning ratio,semiconductor film deposition methods and post-treatment techniques. In addition, the life time of bulk-heterojunction devices was thouroughly studied concerning their stability in air and under constant illumination. The results obtained through this detailed study provide strong evidences to, ensure that efficiencies and stability of bulk-heterojunction solar cells are sufficient to fulfill the requirements of some market applications where low cost is demanded. Furthermore, we will prove that competitive conversion efficiencies are measured on organic solar cells independently on the deposition technique employed to coat the semiconductor film. It is consequently possible to further optimize the cost-efficiency relationship depending on whether selective deposition (ink-jet printing) or large area coating (Dr. Blade) are needed.

PA31

Hybrid Inorganic-Organic Light Emitting Diodes (HYLEDS): Relationship between charge carrier transport and efficiency

J. Albero,a A. Forneli,a E. Palomares,a,b E. Martinez-Ferreroa*
a, Institut Català d'Investigació Química (ICIQ), Avda. Països Catalans 16, 43007 Tarragona, Spain.
b, ICREA.

Hyleds represent a new alternative in the light generating optoelectronic devices due to their enhanced stability to air and oxygen moisture.1, 2 The use of an inert metal oxide like MoO3 as hole injection layer at the counter electrode avoids the application of Ca or Ba that are very reactive to air, and thus, avoids the extra encapsulation steps. On the other hand, the electron injection layer is a metal oxide like TiO2, ZnO or ZrO2 that can be used to match the LUMO position of the light emitting material. Needless to say that the different metal oxide band gap give rise to different results.3,4,5 Finally, the light emitting layer consists in a conjugated polymer which molecular structure determines the emission wavelength, opening the possibility to tune the emitting colour from red to blue. The most important aspects of these devices are the correspondence between energetic levels of the components, the mobility of the charge carriers and the organic-inorganic interface since it will control the charge carrier eventual accumulation and their recombination.

For these reasons, the chemical preparation of the different solutions and the processing will determine the final efficiency. In this sense, we have studied the influence of several parameters on the semiconducting metal oxide layer in the final efficiency of the device, presenting the results in this communication.

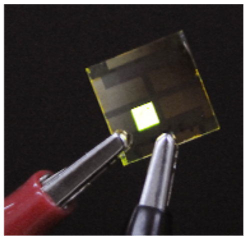


Figure 1

References:

1. K. Morii, M. Ishida, T. Takashima, T. Shimoda, Q. Wang, M. K. Nazeeruddin and M. Gratzel, Applied Physics Letters, 2006, 89, 183510/1.
2. H. J. Bolink, E. Coronado, D. Repetto, M. Sessolo, E. M. Barea, J. Bisquert, G. Garcia-Belmonte, J. Prochazka and L. Kavan, Advanced Functional Materials, 2008, 18, 145.
3. H. J. Bolink, E. Coronado, D. Repetto and M. Sessolo, Applied Physics Letters, 2007, 91, 223501/1.
4. S. A. Haque, S. Koops, N. Tokmoldin, J. R. Durrant, J. Huang, D. D. C. Bradley and E. Palomares, Advanced Materials (Weinheim, Germany), 2007, 19, 683.
5. N. Tokmoldin, N. Griffiths, D.D.C. Bradley, S.A. Haque, Adv. Mater. In press

PA32

Nanomorphology of conjugated polymer blends probed in real and reciprocal space with soft X-ray spectromicroscopy and resonant scattering

Chris McNeill,[a]* Sufal Swaraj,[b] Cheng Wang,[b] Ben Watts[c] and Harald Ade[d]
a, Cavendish Laboratory, University of Cambridge, J J Thomson Ave, Cambridge, CB3 0HE, United Kingdom.
b, Department of Physics, North Carolina State University, Raleigh, NC 27695, USA
c, Swiss Light Source, Paul Scherrer Institut, Villigen-PSI, CH-5232, Switzerland,

Optimising the morphology of polymer blends on the length scale of 10s of nanometres is a key challenge for the realisation of efficient organic photovoltaic devices. This challenge requires not only the ability to produce nanoscale architectures with controllable domain size, but also the ability to characterise these structures with nanoscale precision. In this contribution I will present two synchrotron-based soft X-ray techniques that have been used to characterise the structure of nanoscale polymer blends with sub-100 nm resolution. Scanning transmission X-ray microscopy utilises differences in the Near-Edge X-ray Absorption Fine Structure spectra of different organic materials as a means of contrast. These differences in X-ray absorption stem from differences in π* electronic structure providing unambiguous chemical contrast in the absence of differences in electron or mass density. Through the use of a zone plate with theoretical Raleigh resolution of 30 nm, sub-100 nm bulk structure is imaged in real space with this technique.[1] Used in conjunction with this approach is Resonant soft X-ray scattering (RSoXS). A reciprocal space technique, RSoXS returns information regarding average feature sizes in polymer blends with an equivalent real space best resolution of 2 nm. Both techniques have been utilised in the study of nanostructured photovoltaic polyfluorene blends, with excellent agreement between measured feature sizes. The influence of film nanostructure on device performance will be discussed, with optimised devices found to balance charge generation efficiency (exciton dissociation) with charge separation efficiency.[2]

References

1. C.R. McNeill, B. Watts, S. Swaraj, H. Ade, L. Thomsen, W.J. Belcher, P.C. Dastoor, *Nanotechnology* 2008, **19**, 424015.
2. C.R. McNeill, S. Westenhoff, C. Groves, R.H. Friend, N.C. Greenham, *J. Phys. Chem. C* 2007, **111**, 19153

PA33

Microwave Assisted Synthesis of CuInSe2 Nanopowder

A. Gertsin,a G. Muradova,a A. Shoka,a D. Kim,b S. Bereznev,c* A. Tverjanovicḥ,a J. Kois,c A. Öpikc and Yu. Tveryanovicha
a, Department of Chemistry, Saint-Petersburg State University, Staryi Petergof, Universitetskiy pr. 26 Saint-Petersburg, 198504, Russia.
b, Korea Institute of Machinery and Materials, Sangnam-Dong 66, Kyungnam, 641-010, South Korea.
c, Department of Materials Sciences, Tallinn University of Technology, Ehitajate tee 5, Tallinn, 19086, Estonia

CuInSe2 (CISe) is a promising material for solar cell application, because this photoabsorber is stable, has a high absorption coefficient and band gap value close to optimal for effective sun light absorption. The preparation of composite structures based on the distribution of photoabsorber nanoparticles in organic or polymer matrixes deserves a serious attention. From this point of view, the synthesis of CISe nanopowder is perspective direction of investigations1. For preparation of CISe nanopowder the method of microwave assisted synthesis was chosen2. The main factors which influent on the process of CISe nanoparticles formation are the following: source reagents, microwave power, solvent and temperature of solvent, conductivity of intermediate phases.

The influence of source reagents on properties of CISe photoabsorber powders prepared by microwave assisted synthesis in triethylene glycol (TEG) and polyethylene glycol (PEG) was studied. Prepared CISe powders were investigated by using the X-ray diffraction (XRD) technique, scanning electron microscopy (SEM) equipped with EDS analyzer and MicroRaman spectroscopy to control composition, structure and morphology of the synthesized powders. It was found, that microwave assisted polyol method is useful technique for synthesis of CISe nanopowders.

Synthesis with metallic In and Cu precursors resulted in residue of unreacted indium in the products of reaction and deviation of composition of the resulted CISe powder from the stoichiometry. On the other hand, using of soluble salts of In(III) and Cu(I) as the source reagents leads to preparation of practically stoichiometrical CISe powder. Chalcopyrite structure of prepared CISe powder and polynanocrystalline morphology was confirmed by XRD, SEM and Raman techniques. The purest CISe powder was synthesized from CuCl, In(OOCCH3)3 and Se source reagents dissolved in PEG. It was found that the average size of prepared CISe powder grains depends on the average molecular weight of the solvent (polyol). Using of PEG-600 as the reaction solvent gives practically uniform polynanocrystalline CISe powder with average size of crystals around 80 nm (Figure 1).

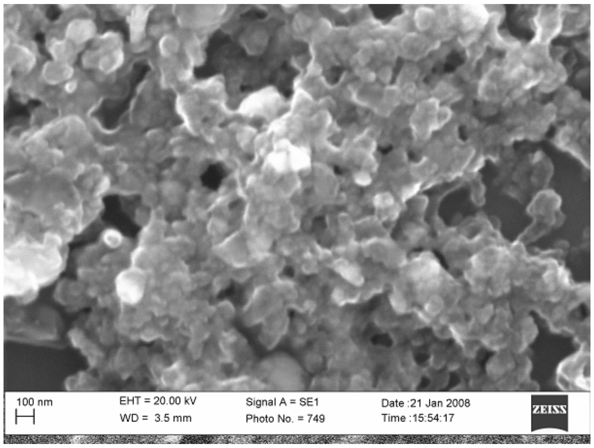


Figure 1. SEM micrograph of CISe powder synthesized from CuCl, InCl3 and Se solution in PEG-600.

Financial support from the Estonian Science Foundation (G7595 and G7669) is acknowledged.

References

1. E. Arici, H. Hoppe, F. Schäffler, D. Meissner, M. Malik, and N.S. Sariciftci, Thin Solid Films, 2004, 451-452, 612.
2. H. Grisaru, O. Palchik, A. Gedanken, V. Palchik, A.M. Weiss, and M.A. Slifkin, Inorganic Chemistry, 2003, 42 (22), 7148.

PB1

The Improvement of Stability and Efficiency of CdS-QDs Solar Cell Using an Amorphous TiO_2 Coating

Menny Shalom, Snir Dor, Larissa Grinis, Arie Zaban*

Bar-Ilan Institute of Nanotechnology and Advanced Materials

Bar -Ilan University, Ramat Gan,52900, Israel

Dye sensitize solar cell (DSSC) has been extensively studied recently due to its ability to become a low cost alternative to silicon based systems. DSSC consists of inexpensive, abundance materials and is based on simple manufacturing equipment. DSSCs are based on the photoinjection of electrons from dye molecules into an inorganic semiconductor and holes transport by a redox mediator. The high light to energy conversion efficiencies achieved with DSSCs may be attributed to the nanoporous semiconductor electrodes. These electrodes have a very large surface area that compensates for the low absorption coefficient of the dye. Theoretically replacement of the dye with inorganic sensitizers can decrease the required surface area and increase the cell stability. However thus far, this approach did not result in efficient cells.

We report here on an alternative sensitizer to the ruthenium complex utilizing CdS quantum dots. The CdS quantum dots were assembled onto the mesoporous TiO_2 by chemical bath deposition resulting in very low performance and instability. Analysis show that the low performance and instability are associated with the CdS surface states that trap the photogenerated holes thus slowing the regeneration process and accelerating self oxidation of the quantum dots. Passivation of the surface states with a thin layer of amorphous TiO_2 solved both problems. This layer was formed by electrophoretic deposition of stabilized $Ti(O_iC_3H_7)_4$ precursor over the CdS sensitized TiO_2. Consequently, these cells show improvement in all parameters, a total efficiency of 1.4% and good stability under illumination. We believe that this passivation method is relevant to many quantum dot based sensitizers thus opening the path for spectral matching and multi-bandgap approaches.

PB2

Ellipsometric Porosimetry : Fast and Non Destructive Method of Porosity Characterization Of Porous Thin Films like DSSC.

A.Bourgeois*, C.Defranoux, J.P. Piel.
SOPRALAB, 55 avenue de L'Europe, 92400 Courbevoie, France

Spectroscopic Ellipsometry is the technique of choice to characterise thickness and refractive indices of thin layers. Ellipsometry Porosimetry (EP)1 measures the change of the optical properties and thickness of the materials during adsorption and desorption of an adsorbate inside a thin porous film. This non contact and non destructive technique becomes an effective method to characterize porosity, pore size distribution (PSD) and Young modulus of thin porous films. It does not require any preparation or scratch of the film, and does not need low temperature.

Detailed description of the technique will be exposed. Both types of measurement tools commercialized by SOPRALAB will be described. The first one uses water as adsorptive2 and allows measurements at atmospheric pressure and ambient temperature. It is well suited to measure mesoporous films. The second one allows the use of different adsorptives such as toluene, methanol, Isopropyl Alcohol (and also many others) and requires low pressure experiment. A wide range of pore size going from micro to large mesopores can be thus studied. Comparison of adsorption cycles obtained with these different adsorptives (water and other organic adsorptives) will be presented.

Several examples of thin porous Titanium oxides films will be presented. Single layer as multilayer samples like TiO_2 on TCO have been studied. Example of Graded porosity will also shown.

References :
(1)Determination of pore size distribution in thin films by Spectroscopic Ellipsometry. M.R Baklanov and al. IMEC. 2000. American Void Society.
(2)Porosity and mechanical properties of mesoporous thin films assessed by Environmental Ellipsometry porosimetry. C. Boissière and al. LCMC Paris University. 2005. American Chemical Society

PB3

Organic Dyes Containing Fluorene Entity in the Spacer for Solar Cells Application

Dr. Ming-Si Wu , Dr. Der-Gun Chou *
Everlight Chemical Industrial Corporation,
No.12, Industrial Third Road, Kuanyin Industrial Park, Taoyuan Hsien, Taiwan,R.O.C..
E-mail: mingsi@ecic.com.tw; Tel: 886-3-4838088 Ext.331; Fax: 886-3-4832795

Series of dyes containing a fluorene entity in the spacer have been designed, synthesized, and characterized. These dipolar compounds contain an arylamine or dialkylamine as the electron donor, a 2-acrylic acid as the electron acceptor, and a conjugated spacer between the donor and the acceptor. Typical dye-sensitized solar cells (DSSCs), with an appropriate illumination area, were fabricated with a liquid electrolyte composed of iodide reagent in polar solvent. The device performance data were obtained under AM 1.5 illumination. DSSCs using these materials as the sensitizers exhibited good performance (η), ranging from 4.58 %-5.82 %, which reached 67 %-85 % with respect to that of the standard cell from N719-based device fabricated under similar condition.

Keywords: dye-sensitized solar cells; fluorine; arylamine

Reference

(1) K. R. Justin Thomas, J. T. Lin, Y.-C. Hsu, K.-C. Ho, *Chem. Commun.* **2005**, 4098 –4100.

(2) Sanghoon Kim, Kee-hyung Song, Sang Ook Kang, Jaejung Ko, *Chem. Commun.* **2004**, 68 –69.

(3) J. S. Yaday, B. S. S. Reddy, A. K. Basak, B. Visali, A. V. Narsaiah, K. Nagaiah, *Eur. J. Org. Chem.*, **2004**, 546-551.

PB4

CdSe Quantum dot-sensitized TiO_2 electrodes: Effect of Quantum Dot Coverage and Mode of Attachment

Néstor Guijarro Carratalá, Teresa Lana-Villarreal*, Roberto Gómez
Institut Universitari d´Electroquímica i Departament de Química Física, Universitat d´Alacant, Apartat 99. E-03080 Alacant (Spain).Teresa.Lana@ua.es

Semiconductor QDs, such as CdSe, have emerged as new light absorbers for solar cells, instead of dyes. In fact, Kamat et al [1,2] have recently shown the viability of quantum dot solar cells and the significance of CdSe-TiO_2 architecture. However, up to now, one of the more important hurdles is the difficulty of assembling QDs into the nanoporous TiO_2 obtaining a full monolayer and an effective electron injection.

A colloidal suspension of CdSe QDs capped with TOP has been prepared by a solvothermal route, which allows size control. Subsequently, two different approximations have been employed to sensitized nanoporous TiO_2 (Degussa P25) electrodes: direct adsorption of capped CdSe QDs and adsorption through a linker. In the latter, a bifunctional molecule (such as mercaptopropionic acid –MPA-), previously adsorbed on the oxide surface, acts as a molecular cable. It is noteworthy that solvent of colloidal suspension was changed depending on the mode of attachment employed. In both cases, the CdSe QDs coverage has been controlled by changing the adsorption time.

Interestingly, for equivalent QD loading, direct adsorption leads systematically to higher IPCE values than mediated-MPA adsorption. That points out that reducing spatial separation between QDs and TiO_2 enhances electron injection. In addition, IPCE-QD loading dependence (**figure 1**), shows a maximum for direct adsorption and a monotonous increase up to a constant saturation value for adsorption through MPA. AFM images of nanostructured and monocrystalline sensitized TiO_2 electrodes reveal that, in contrast with MPA-mediated adsorption, direct adsorption leads to a high degree of aggregation, particularly for long adsorption times. This aggregation hinders the electron injection from QD to TiO_2 and also, it blocks the surface of the electrode, making the charge transport more difficult. A remarkable observation is that the maximum coverage obtained is only 14% of the real surface area, probably because of a large extent of the surface remains inaccessible for QDs (bottle necks, channels full of twist and turns).

Therefore, new strategies devoted to increase IPCE have to be focused to enlarge QD coverage and diminish spatial separation between QD and TiO_2.

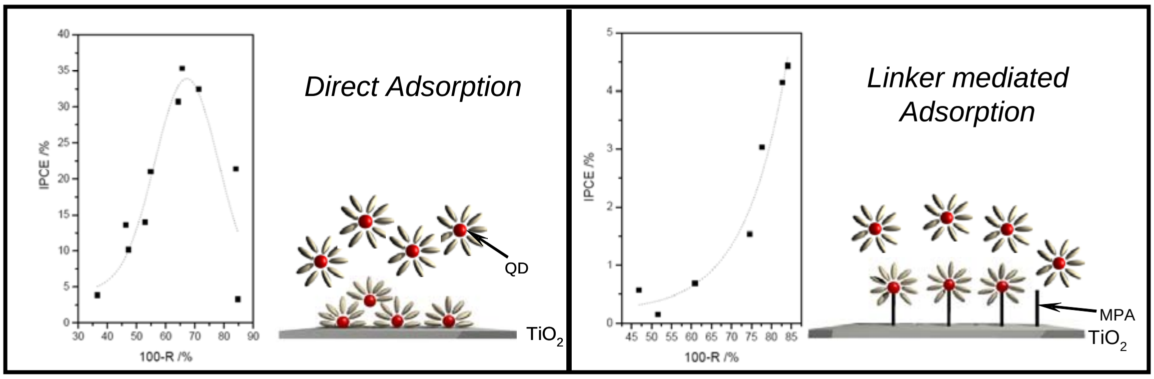


Figure 1

References

[1] Robel, I; Subramanian, V; Kuno, M; Kamat, P. *J. Am. Chem. Soc. 2006,* ***128****, 2385-2393*
[2] Kongkanand, A; Tvrdy, K; Takechi, K; Kuno, M; Kamat, P. *J. Am. Chem. Soc. 2008,* ***130****, 4007-4015*

PB5

Using SILAR to sensitize TiO_2 electrodes with CdSe quantum dots: optimization, characterization and comparison with other types of attachment

Néstor Guijarro*, Teresa Lana-Villarreal, Roberto Gómez
Institut Universitari d´Electroquímica i Departament de Química Física, Universitat d´Alacant, Apartat 99. E-03080 Alacant (Spain). E-mail: Nestor.Guijarro@ua.es

Semiconductor quantum dots (QDs) have been recently employed to harvest light in photovoltaic devices. Interestingly, the type of attachment of the QDs to the oxide matrix plays an important role in the performance of the solar cell.[1] We have explored the possibility of directly growing CdSe QDs on TiO_2 nanoparticulate electrodes by the so-called successive ionic layer adsorption and reaction (SILAR) method, which allows direct contact between the QDs and TiO_2 particles. From a preparative viewpoint, its main drawback is that there is no separate control of QD size and coverage.

The sensitization of TiO_2 electrodes by the SILAR method has been optimized by adjusting the pH of both ionic precursor solutions (cadmium acetate and sodium selenosulfate). As shown in the reflectance spectra for the sensitized electrodes (figure 1), QD loading and size have been controlled by changing the number of cycles in the SILAR method. Subsequently, the $CdSe/TiO_2$ films have been characterized by TEM, EDX, Raman and AFM. TEM images (figure 2) reveal that the CdSe SILAR method gives rise to small nanoparticles uniformly distributed over the TiO_2 particles. EDX and, particularly, Raman spectra clearly confirm that these are crystalline CdSe nanoparticles.

Information about the possible use of the $CdSe/TiO_2$ electrodes prepared by SILAR in photoelectrochemical solar cells has been obtained through emission spectra, photopotential, photocurrent and IPCE measurements. All these results have been compared with those corresponding to TiO_2 electrodes sensitized with presynthesized colloidal CdSe QDs capped with TOP. In this case, CdSe QDs have been attached through a molecular linker (such as cysteine, cysteamine, 4-mercaptobenzoic acid, mercaptopropionic acid) or by direct adsorption.

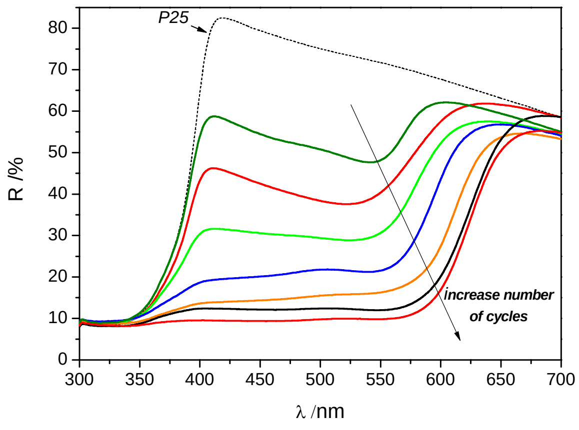


Figure 1

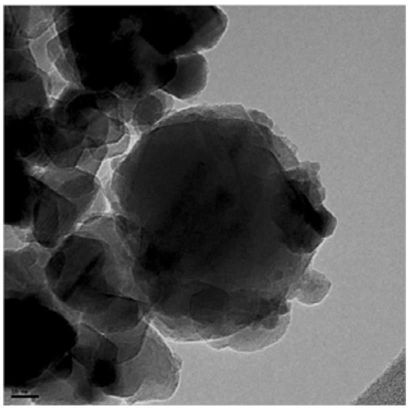


Figure 2

References

[1] Guijarro, N; Lana-Villarreal, T; Mora-Seró, I; Bisquert, J; Gómez, R. *J. Phys. Chem. C, 2009.* ***113*** *(10), 4208-4214*

Improving the performance of Quantum Dot Solar Cells. The role of ZnS treatment

Néstor Guijarro, Teresa Lana-Villarreal, Roberto Gómez
Institut Universitari d´Electroquímica i Departament de Química Física, Universitat d´Alacant, Apartat 99. E-03080 Alacant (Spain). E-mail: Nestor.Guijarro@ua.es

The so-called Quantum Dot Solar Cells (QDSCs) are being developed following the Dye-sensitized solar cell scheme, but employing semiconductor quantum dots instead of dyes as light absorbers. The use of semiconductor QDs in solar cells could be advantageous because of their favorable properties: tunable band gap, large extinction coefficient, rapid charge separation and the theoretical capability of achieving quantum yields larger than unity. Nevertheless, up to date, photovoltaic conversion efficiencies of QDSCs are still low. Recently, Toyoda et al.[1] have reported an important enhancement of the QDSC efficiency by aplying a ZnS layer over the nanostructured CdSe-sensitized TiO_2 electrode. However, the role of the ZnS is still an open question.

A colloidal suspension of CdSe QDs capped with TOP has been prepared by a solvothermal route which allows size control. Nanoporous TiO_2 (Degussa P25) electrodes have been prepared on titanium foil (with a TiO_2 blocking layer) and subsequently, direct adsorption from a QD colloidal dispersion has been carried out. The ZnS layer was applied onto bare and CdSe-sensitized TiO_2 electrodes by two cycles of SILAR. Concretely the following electrodes were prepared and tested: TiO_2, TiO_2/ZnS, TiO_2/CdSe, TiO_2/ZnS/CdSe, TiO_2/CdSe/ZnS and TiO_2/ZnS/CdSe/ZnS. Cyclic voltammetry in the dark and photocurrent experiments in contact with a polysulfide electrolyte have been employed to assess the effect of the ZnS treatment on the recombination of photogenerated electrons with the electrolyte via the TiO_2 and/or the CdSe surface.

As shown in **figure 1**, the deposition of ZnS onto the mesoporous TiO_2 (TiO_2/ZnS) results in a significant reduction of the recombination, as deduced from the drastic diminution in the cathodic current corresponding to polysulfide reduction. However, it is noteworthy that the ZnS treatment generates a discontinuous layer (with uncovered areas) as confirmed by AFM measurements on TiO_2 monocrystalline samples. A similar effect (to a lesser extent) is observed for TiO_2/CdSe. Experiments done with TiO_2/ZnS/CdSe, TiO_2/CdSe/ZnS and TiO_2/ZnS/CdSe/ZnS electrodes reveal that in addition to the passivation of the TiO_2 surface, the ZnS treatment has a beneficial effect in the reduction of recombination of the photogenerated electrons from QDs to the electrolyte.

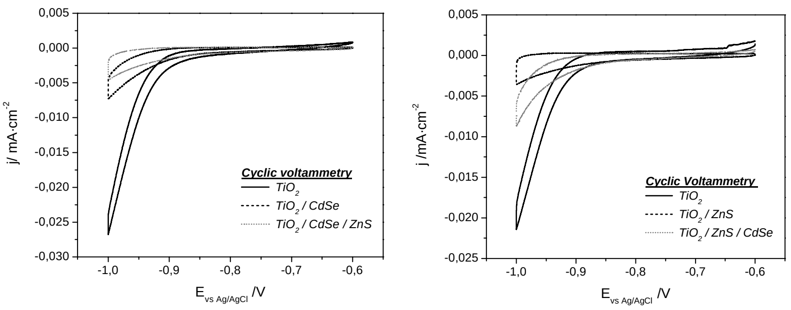


Figure 1

References

[1] Shen, Q; Kobayashi, J; Diguna, L; Toyoda, T. *J. Appl. Phys. 2008, 103,* 084304

PB7

The electrochemistry of quantum dot sensitized TiO_2 nanoparticulate and nanotube thin films

Irene Barceló, Néstor Guijarro, Teresa Lana-Villarreal, Roberto Gómez

Institut Universitari d´Electroquímica i Departament de Química Física, Universitat d´Alacant, Apartat 99. E-03080 Alacant (Spain). E-mail: Irene.Barcelo@ua.es

Semiconductor quantum dots (QDs) can be used as light absorbers in solar cells. In fact, Kamat et al.[1,2] have recently shown the viability of quantum dot solar cells and the significance of the CdSe-TiO_2 architecture. Using a similar approach, we have prepared QD sensitized TiO_2 samples with different morphologies. QDs of CdSe have been synthesized by a solvothermal route[3] that allows size control, using trioctylphosphine as capping agent. Well-defined TiO_2 substrates composed of nanotubes have been prepared by anodic oxidation of titanium metal in the presence of HF[4]. TiO_2 nanoparticulate electrodes have been prepared by doctor-blade from commercial powders (Degussa P25). CdSe QDs were assembled onto the TiO_2 nanostructures by direct adsorption[5]. The amount of deposited CdSe QDs has been controlled by changing the adsorption time in order to obtain different surface coverage degrees.

A different (photo)electrochemical behavior in 0.5 M Na_2SO_3 is found for both TiO_2 nanostructures. For nanoporous samples, the incident-photon-to-current efficiency initially increases with the loading, but a maximum is defined for intermediate coverages[5]. For high QD loadings, the diminution in the IPCE values was ascribed to QD aggregation, probably at the outermost electrode surface. In the case of TiO_2 nanotubes, higher QD coverages can be obtained. The more open structure not only facilitates the entrance of the CdSe QDs, but, in addition, it considerably diminishes the blockage of the nanopores due to QD aggregation. Consequently, the photocurrent increases with the adsorption time even if some aggregation takes place. On the other hand, the larger amount of attached QDs in the case of TiO_2 tubes is also revealed from cyclic voltammetry in the dark. In such experiments, a new, quasi-reversible pair of well-defined peaks is observed for high QD loadings. We could tentatively ascribe them to the filling/emptying of QD states[6] because their peak current is proportional to the QD loading. Interestingly, such a voltammetric signal was barely discernible in the case of the nanoparticulate electrodes, probably due to aforementioned nanopore blockage. In general vein, these results point to the key role of the TiO_2 structure on the properties of QD sensitized solar cells.

References

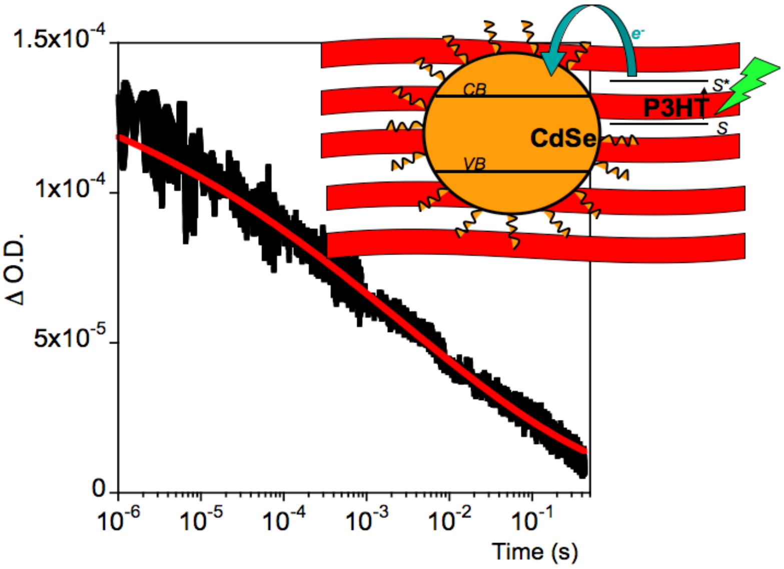
[1] A. Kongkanand, K. Tvrdy, K. Takechi, M. Kuno and P.V. Kamat, J. Am. Chem. Soc. 2008, **130**, 4007.
[2] P.V. Kamat, J. Phys. Chem. C 2008, **112**, 18737.
[3] Q. Wang, D. Pan, S. Jiang, X. Ji, L. An and B.J. Jiang, J. Cryst. Growth 2006, **286**, 83.
[4] Y. Yin, Z. Jin and F. Hou, Nanotechnology 2007, **18**, 495608.
[5] N. Guijarro, T. Lana-Villarreal, I. Mora-Seró, J. Bisquert and R. Gómez, J. Phys. Chem. C 2009, **113**, 4208.
[6] A.J. Houtepen and D. Vanmaekelbergh, J. Phys. Chem. B 2005, **109**, 19634.

PB8

Electron Recombination Dynamics in CdSe/P3HT Hybrid Heterojunctions.

J. Alberoa , E. Martinez and E. Palomares*
a, Institute of Chemical Research of Catalonia (ICIQ). Avda. Països Catalans, 16. Tarragona. E-43007. Spain.

The combination in hybrid heterojuction of nanocrystals and semiconductor polymers has great potential for light-to-energy conversion devices. For this reason, a great number of different quantum dots/polymer molecular solar cells have been investigated. However, less attention has been paid to the photo-induced charge transfer processes in the interface of these systems. Here we report a detailed time resolved spectroscopic study of the most important electron transfer steps of CdSe/P3HT bulk heterojunction films. From the data obtained using Time Correlated Single Photon Counting we have inferred that electron injection from the P3HT excited state to the CdSe conduction band occurs faster than 250 ps and the electron injection yield is higher than 90%. On the other hand, the use of Laser Transient Absorption Spectroscopy allowed us to observe that all the studied interfacial charge transfer process can be fitted to dispersive stretched exponentials kinetics, independently of the QD's concentration, thereby offering evidence of multiple decay process in CdSe/P3HT solar cells.



PB9

Direct synthesis of PbS nanocrystals in MDMO-PPV semiconducting polymer.

J.C. Ferrer,[a,]* A. Salinas-Castillo[b] J.L. Alonso,[a] S. Fernández de Ávila,[a] and R. Mallavia.[b]
a, Área de Electrónica, Universidad Miguel Hernández, Av. Universidad, s/n, Ed. Torrepinet,03202, Elche (Alicante), Spain.
b, IBMC, Universidad Miguel Hernández, Av. Universidad, s/n, Ed.Torregaitan, 03202, Elche (Alicante), Spain.
* jc.ferrer@umh.es

We report on the synthesis of PbS nanocrystals, or quantum dots, directly in poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) semiconducting polymer. The interest is due to the potential of quantum dots to increase the efficiency of photon conversion in organic photovoltaic solar cells and to extend the absorption range of the polymer to the whole visible spectrum.

For the nanocrystal synthesis, a starting 0.2% solution of $Pb(SC_6H_4F)_2$: MDMO-PPV (95% : 5%) in toluene and di-methylsulfoxide (80%:20%). Four aliquots were extracted to synthesize different concentrations of PbS nanocrystals. The rest of the solution was kept for reference purposes. Different volumes of a 0.1% solution of elemental sulfur in toluene were added to the aliquots: 25, 50, 100 and 200 µl. After addition, reaction took place resulting in orange to dark brown, optically clear solutions, which indicates that PbS nanocrystals were synthesized.

The absorption spectra of the pure MDMO-PPV reference solution and the series of solutions containing PbS nanocrystals are presented in fig. 1. All samples were diluted in order to avoid an excesive absorbance. The spectra present a peak located at 2.51 eV (494 nm) which corresponds to the maximum absorption of MDMO-PPV. As the sulfur amount is raised in the solutions, the optical density of the samples increases, which indicate a higher concentration of PbS. Although a precise measurement of the absorption edge is not possible due to the overlaping of the MDMO-PPV peak, the spectra suggest that strong quantum confinement has been achieved since the band gap energy of bulk PbS is 0.41 eV.

The concentration of PbS nanocrystals also influences the photoluminescence of the polymer. The reference sample has an emission peak located around 2.13 eV (580 nm) which losses intensity as the PbS amount in the solution increases. No influence of quantum dot concentration on the maximum emission wavelength has been detected.

Transmission electron microscopy allowed to verify the formation of nanometer sized PbS crystals in the hosting polymer solution. Fig. 2 shows a representative picture of a nanocrystal ensemble corresponding to sample with a volume of sulphur solution of 50 µl. The mean particle diameter has been roughly estimated to be 4 nm. The fact that the size is similar for the samples with different sulphur concentrations suggests that the addition of further sulfur is followed by the formation of a higher number of quantum dots instead of increasing their size.

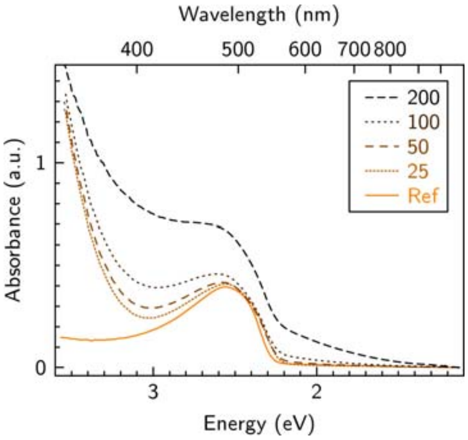


Figure 1. Absorption spectra of reference sample and solutions with 25, 50, 100 and 200 µl of sulfur solution.

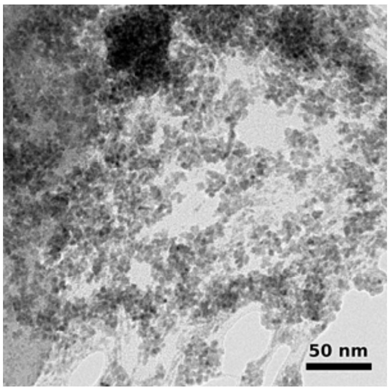


Figure 1. Transmission electron microscopy image of solution containing 50 µl of sulfur solution.

PB10

Nanostructured bulk heterojunction devices using conjugated block copolymers

M. Sommer, S. Huettner, R. Lohwasser, M. Thelakkat **
Applied Functional Polymers, Department of Macromolecular Chemistry I, University of Bayreuth, 95440 Bayreuth, Germany

One of the challenging aspects in designing and developing novel functional materials is to incorporate the desired optical and /or electrical properties maintaining their film-forming and thermal characteristics which make them suitable for thin film device applications. An important criterion for most of the applications in the field of energy research such as photovoltaics, batteries, fuel cells etc. is that these materials should have well-defined nanostructured morphology in thin films in order to be capable of fulfilling the complex functions of charge carrier/ ion transport in confined channels/geometries without adversely affecting the other complementary functions. This morphological control on a nanoscopic level controls the interface between the functional domains as well as the long term stability of such devices. We have demonstrated the chain of control on all length scales -from molecular to mesoscopic to macroscopic- using the self-assembly principle of a fully functionalised block polymer for photovoltaic applications as represented in fig 1.

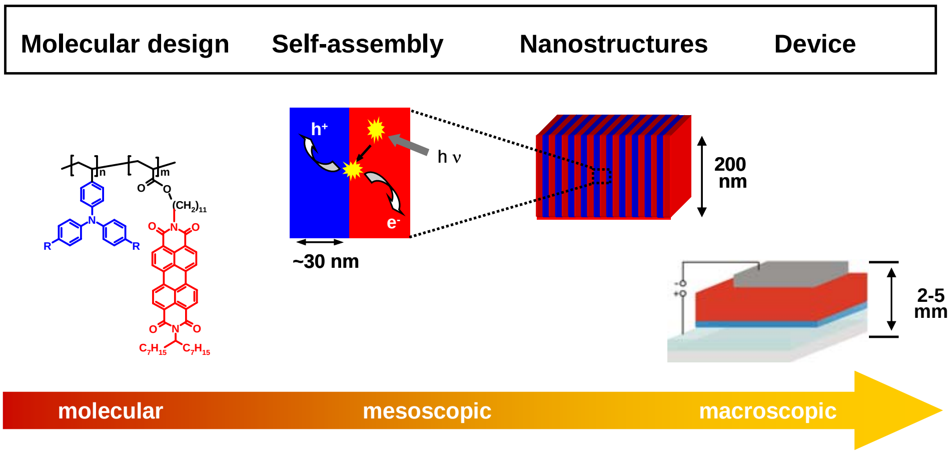


Figure 1.*Schematic representation of the interconnection of molecular structure, morphology and device functions and an example to realize this using tailor-made synthesis and self-assembly of a block copolymer.*

This contribution covers the design, synthesis and properties of some novel low molecular weight semiconductors as well as block copolymers carrying poly(3-hexylthiophene) segments and perylenebisimide units. Block copolymers those allow the incorporation of semiconductor quantum dots or nanocrystals to get hybrid systems with morphology control suitable for solar cell applications will also be discussed. The characterization of these materials in thin films and their application in devices will be presented.

References

1. S. M. Lindner, M. Thelakkat, Macromolecules 37, 8832 (2004)
2. S. M. Lindner et al. Angew. Chem. Int. Ed 45, 3364 (2006)
3. S. M. Lindner et al. Organic Electronics 8, 69-75 (2007)
4. M. Sommer et al. European Physical Journal; Applied Physics 36, 245-249 (2007)
5. M. Sommer, S.M. Lindner, M. Thelakkat, Adv. Fun. Mat. 17, 1493-1500 (2007)
6. M. Sommer, A. S. Lang, M. Thelakkat, Angew. Chem. Int. Ed. 47, 1-5 (2008)

PB11

Charge Transport and recombination in TiO_2:P3HT:PCBM devices

S. Sandén[a*], G. Sliaužys[b], Q. Xu[c], G. Juška[b], M. Lindén[c] and R. Österbacka[a]
a, Center For Functional Materials, Department of Physics, Åbo Akademi University, Porthaninkatu 3, FI-20500 Turku
b, Department of Solid State Electronics, Vilnius University, Sauletekio 9, LT-01513, Vilnius, Lithuania
c, Center For Functional Materials, Department of Physical Chemistry, Åbo Akademi University, Porthaninkatu 3,FI- 20500 Turku

We have used the inorganic semiconductor TiO_2 and the organic semiconductors P3HT and PCBM to manufacture a hybrid organic/inorganic solar cell. The charge transport has been studied using several different transient techniques. Charge extraction by linearly increasing voltage (CELIV) uses a triangular voltage pulse applied in reverse bias to extract charges, the initial current step is caused by the geometric capacitance of the sample, the following rising current is caused by free carriers in the sample and from the maximum position of this curve one can calculate the mobility of the charge carriers. In time of flight (ToF) a square voltage pulse is applied in reverse bias and after a delay time a laser pulse is used to generate charge carriers in the sample, these carriers will drift through the sample and be extracted at the contact. By determining the transit time of the carriers the mobility can be determined. Double injection (DoI) uses a square voltage pulse applied in forward bias which leads to injection of carriers through both contacts, which drift through the sample and recombine in the bulk. By analysing the current transients one can determine the mobility of the slowest carrier and the sum of the carriers.

Devices fabricated with P3HT:PCBM uses the ITO-electrode is the hole extracting contact and aluminium as electron extracting contact. When using TiO_2 the ITO is used as electron extracting contact and gold as hole extracting contact, this could have a positive effect as the TiO_2 blocks holes from reaching the ITO contact.

Recombination in TiO_2:P3HT films have previously been shown to be trimolecular with trapping occurring in the TiO_2:P3HT interface[1]. It is the purpose of this work to extend this study to clarify recombination and trapping in TiO_2:P3HT:PCBM films using transient techniques such as CELIV, ToF and DoI.

References

1. G. Sliaužys, G. Juška, K. Genevičius, J. H. Smått, M. Lindén and R. Österbacka , *SPIE Proceedings* 2008, **7142**, 71420K

PB12

Weight Ratio Dependent Transport Studies on P3HT:PCBM Solar Cells

Mathias Nyman*, Simon Sandén and Ronald Österbacka
Department of Physics, Åbo Akademi University, Porthansgatan 3, 20500 Turku, Finland.

We present mobility studies on bulk heterojunction solar cells based on the conjugated polymer poly(3-hexylthiophene-2,5-diyl) (P3HT) and the fullerene derivative [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM).

Using the photo-CELIV (Charge Extraction by a Linearly Increasing Voltage) we have measured the charge transport in P3HT:PCBM solar cells. We have varied the P3HT:PCBM weight ratios and studied its impact on the mobility. Similar studies have been performed earlier on MDMO-PPV:PCBM solar cells by other groups[1]. P3HT:PCBM solar cells have a strongly reduced recombination of charges due to the lamellar structure of P3HT, therefore it is of interest to study how the mobility is affected when the P3HT content is lowered.

Knowing the weight ratio impact on the mobility might provide helpful information to fully understand the recombination dynamics.

References

1. G. Dennler, A. J. Mozer, G. Juška, A. Pivrikas, R. Österbacka, A. Fuchsbauer and N. S. Sariciftci, *Org. El.* **7** (2006) 229-234

PB13

High Voltage Photovoltaics

Shay Yahav, Sven Rühle, Arie Zaban
Department of Chemistry, Bar Ilan University, Ramat Gan 52900, Israel

Dye Sensitized Solar Cell (DSSC) is an efficient, low cost photovoltaic alternative to *p-n* junction silicon cells. So far the photovoltage of the illuminated cell is still limited by the energy difference between the TiO_2 conduction band edge and the redox potential of the electrolyte. To increase the photovoltage, either a semiconductor with a conduction band edge closer to the vacuum level has to be used or a redox couple with a more positive redox potential.

The porous nature of the semiconductor in DSSCs, the dye coverage of the mesoporous network and the permeability of the electrolyte into the pores can affect the photovoltage of the cell. To investigate novel oxide materials for DSSC application we have chosen a flat model system using a thin compact wide bandgap oxide layer deposited onto a conducting Fluorine doped Tin oxide (FTO) covered glass substrate. The oxide was sensitized with a monolayer of dye, which is recharged by the iodide/iodine redox electrolyte upon solar cell operation. Though a monolayer of dye generates only very low currents it provides a sufficient photovoltage response to analyze its potential to increase the photovoltage in DSSCs. Spray pyrolysis was used for thin film preparation and the electronic properties such as the doping level of the films were controlled by the deposition temperature, the type of carrier gas, precursor composition and deposition rate. Finally thin wide bandgap oxide layers can also serve as window layers for p-n heterojunction solar cells in conjunction with a medium bandgap semiconductor absorber (~2 eV), demonstrating the importance of thin oxide layers.

PB14

Metal oxide sensitized solar cells

Idan hod*, Arie Zaban

Bar-Ilan Institute of Nanotechnology and Advanced Materials

Bar -Ilan University, Ramat Gan,52900, Israel

Dye-sensitized solar cells (DSSCs) arouse intense interest owing to their low cost and low-tech preparation procedures. They provide a technically and economically credible alternative concept to standard p-n junction photovoltaic devices. In contrast to the conventional systems, where the semiconductor assumes both the task of light absorption and charge carrier transport, the two functions are separated here. Light is absorbed by a sensitizer which is anchored to the surface of a wide band gap semiconductor. Charge separation takes place at the interface via photo-induced electron injection from the dye into the conduction band of the solid. Carriers are transported in the conduction band of the semiconductor to the charge collector while the holes travel in an electrochemical mediator to the back contact.

Our work focuses on the development of metal oxide thin film absorber layers in order to replace the molecular dye. That kind of absorbers holds a huge potential for improving cell stability, reducing material costs and possibly increasing cell efficiency. Specifically we aim at higher photovoltage. The use of metal oxides requires the development and application of new nano-materials or extremely thin layers.

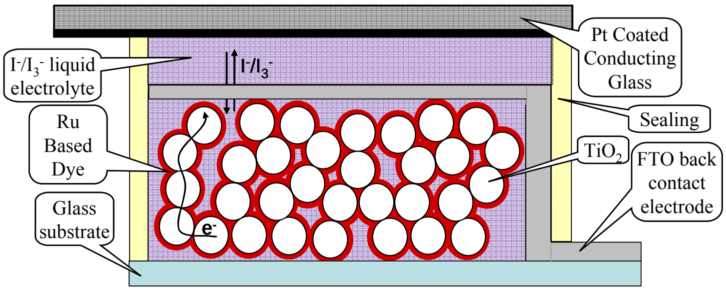
First results were obtained using three well studied metal oxides: WO_3, Cu_2O and CeO_2. This far the efficiencies obtained are low but the fundamental processes occur. We refer the low efficiency to recombination processes that are treated by application of barrier layers within the system.

PB15

FTO Back Contact Electrode for Dye Sensitized Solar Cells

Zion Tachan , Snir Dor , Arie Zaban
Bar-Ilan Institute of Nanotechnology and Advanced Materials
Bar-Ilan University, Ramat-Gan 52900, Israel

Much effort is made to achieve high energy conversion efficiency in Dye Sensitized Solar Cells (DSSC). In this work we present a new DSSC structure intending to reduce the incident light loss due to reflection and absorption at the transparent conducting oxide (TCO) electrode. In the new DSSC design, the front TCO based electrode is replaced by a simple glass and a thin collector layer is deposited on top of the photoactive area. Consequently, the photogenerated electrons are collected behind the photoactive area allowing maximum utilization of the incident photons. The new configuration is thus, denoted a back contact electrode (BCE)
To achieve this goal we developed the synthesis of Fluorine doped Tin oxide (FTO). The FTO is fabricated onto a mesoporous TiO2 film, deposited on a glass substrate using spray pyrolysis. The FTO is produced using HF and Tin chloride salt dissolved in ethanol solution. The properties of the FTO such as conductivity, thickness and morphology can be controlled by adjustment of the substrate temperature, precursor concentration and flow rates.
The new BCE was sensitized with a Ru-dye before it was immersed into a redox electrolyte while the electrical circuit was closed by a Pt counter electrode. The results using the new back electrode configuration indicate the need for higher FTO porosity and conductivity. Other cell designs like intermediate current collector for thick film were developed and will be examined to find a cell that can exceed the current performance limit.



PB16

Improved photocurrents in hybrid solar cells: suppression of recombination reaction in the presence of SWNT

Wonjoo Lee, R. S. Mane, Sun-Ki Min, Sung-Hwan Han
Department of Chemistry, Hanyang University, Haengdang-dong 17, Sungdong-ku, Seoul, (Korea) 133-791
shhan@hanyang.ac.kr; Tel: +822-2292-5212; Fax: +822-2299-0762

The polyacetylene photosensitizer with quaternary pyridinium salts were layered on CdS nanocrystalline film by in situ polymerization of 2-ethynylpyridine and 4-bromobutyric acid. The in situ polymerization enhances an interfacial contact between inorganic semiconductors and conjugated polymers. The hydrophilicity of polymer photosensitizers was controlled by the anion exchange to deposit good quality P3HT layers by spin coating. The hybrid cell shows a power conversion efficiency of 2.19% under air mass (AM) 1.5 condition (I = 30 mW/cm2). The presence of single-walled carbon nanotubes (SWCNTs) on indium-doped tin oxide (ITO) substrate enhanced the charge collection and reduced recombination reaction in the cell. Nanocomposite system of In2S3/In2O3/SWCNTs, which was assembled using spray coating and wet chemical processes, shows 52.9% increment of power conversion efficiency in the presence of SWNT.

Wonjoo Lee, Seunghoon Shin, Sung-Hwan Han, Byung Won Cho, Appl. Phys. Lett. 2008, 92, 193307.
Wonjoo Lee, Jungwoo Lee, Sangjin Lee, Whikun Yi, Sung-Hwan Han, Byung Won Cho, App. Phys. Lett. 2008, 92, 153510.
Wonjoo Lee, Sun-Ki Min, Seunghoon Shin, Sung-Hwan Han, Soo-Hyoung Lee, Appl. Phys. Letters 2008, 92, 023507.

1. Wonjoo Lee, Jungwoo Lee, Haiwon Lee, Whikun Yi, Sung-Hwan Han, *Appl. Phys. Lett.* **2007**, *91*, 043515.
2. Wonjoo Lee, R. S. Mane, Sun-Ki Min, Tae Hyun Yoon, Sung-Hwan Han, Soo-Hyung Lee, *Appl. Phys. Lett.* **2007**, *90*, 263503.

PB17

Analysis of the dark current-voltage-temperature characteristics of ITO/P3HT:PCBM/Ca solar cells

Jairo C. Nolasco[a], R. Cabré[a], Roberto Pacios[b], Christoph Waldauf[b], Marios Neophytou[b], Emilio Palomares[c], L. F. Marsal[a] , and J. Pallares[a,*].

[a]*Department d'Enginyeria Electronica, Electrica, i Automatica, Universitat Rovira i Virgili, Av. Paisos Catalans 26, 43007 Tarragona Spain (*email: josep.pallares@urv.cat)*

[b]*Department of Microsystems, IKERLAN-IK4 S. Coop., P°J.M. Arizmendiarrieta, 2, 20500 Arrasate-Mondragon, Gipuzkoa, Spain.*

[c]*Ins. Chem Res. Catalonia ICIQ Tarragona 43007 Spain.*

In order to get a deeper understanding of the conduction mechanisms limiting the electrical characteristics of ITO/PEDOT:PSS/P3HT:PCBM/Ca solar cells, dark current-voltage measurements at different temperatures were analyzed using a compact electrical equivalent circuit previously used in non-ideal p/n junctions[1]. At medium voltages, the current-voltage characteristic is modeled by two exponentials terms (I_{D1} and I_{D2}). For larger voltages, the model takes into account a combination of space-charge limited process and series resistance (SCLC and R_S respectively). For lower voltages a shunt resistance is considered (R_{SH}). From the temperature analysis, I_{D1} can be described by a tunnelling process.

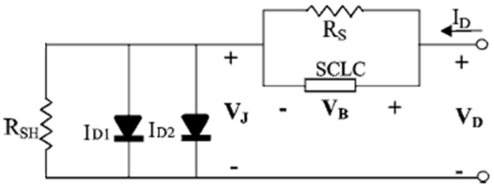


Fig. 1 Electrical equivalent circuit used to fit the experimental dark current-voltage-temperature characteristics.

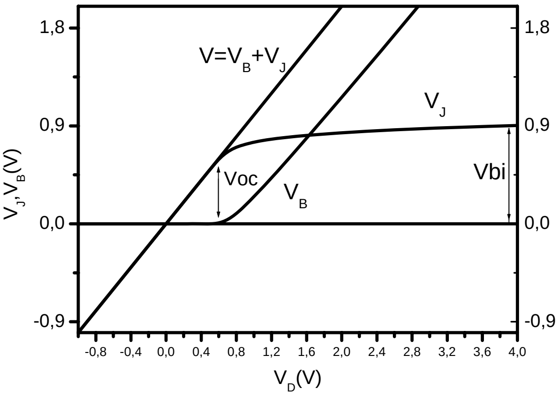


Fig. 2 Junction (V_J) and bulk (V_B) voltage variations with applied voltage V_D at 300K.

Additionally the equivalent circuit used enables to separate the applied voltage in two regions, namely the voltage drop in the junction (V_J) and the voltage drop in the bulk (V_B). The voltage drop in the junction saturates for high applied voltages. This saturation voltage value is in the range of values reported in the literature for the difference between HOMO and LUMO levels of the P3HT and PCBM, respectively[2]. In addition, the open-circuit voltage value measured from the solar cell characteristics is similar with the applied voltage value where the bulk effect starts to be non-negligible.

References

1 J. Pallarès. R. Cabré, L. F. Marsal, and R.E.I. Schropp, *J. Appl. Phys*., 2006, 100, 084513.

2 C. Waldauf, M. C. Scharber, P. Schilinsky, J. A. Hauch, and C. J. Brabec, *J. Appl. Phys*., 2006, 99, 104503.

PB18

Injection efficiency from single photon counting analysis in dye sensitized solar cells

Tracy Dos Santos, Ana Morandeira, Sara Koops, Andrea Listorti*, Maria Victoria Martinez Diaz, Tomas Torres Brian O'Regan and James Durrant
Department of Chemistry, Imperial College London, Exhibition Road,
London SW7 2AZ, U.K. E-mail: a.listorti@imperial.ac.uk

Injection efficiency in excitonic solar cells is usually investigated via ultrafast transient spectroscopy; however the presence of a redox electrolyte leads to a significant retardation of the injection half-time. This provides a potentially cheaper and simple approach to monitor this process. Here the Single Photon Counting (SPC) approach is applied to the injection efficiency study of two different families of dyes. In the first example two porphyrins with different anchoring groups are investigated, the effect of extended conjugated system on injection dynamics and cell performance have been studied. The second example regards phthalocyanines (Pc) as dyes. A zinc-Pc and a Ruthenium-Pc are compared in order to understand the difference in those systems between a singlet and a triplet injection.

PB19

The Influence of Morphology on Thin Film Properties: Electron Traps and Adsorption Sites on Nanostructured Rutile Electrodes

Thomas Berger, and Roberto Gómez*
*Institut Universitari d'Electroquímica i Departament de Química Física, Universitat d'Alacant, Apartat 99. E-03080 Alacant (Spain), *Roberto.Gomez@ua.es*

Electron transport properties of nanoparticulate films are of utmost importance for their application in dye-sensitzed solar cells (DSCs) and in photocatalysis. Interestingly, electron diffusion coefficients in nanoparticulate films were found to be orders of magnitude smaller than in the case of single crystals. This slow transport is attributed to a high concentration of localized states, which act as electron trapping sites. The diffusion coefficient is strongly affected by both the number and the energy distribution of trap states. For nanoparticulate films the spatial location of transport limiting trap states is an important and controversial issue.

For monocrystalline TiO_2 electrodes capacitive currents are observed in the voltammogram at potentials that are negative enough to induce the filling of shallow traps below the conduction band edge and conduction band states, respectively. Nanoparticulate electrodes exhibit, apart from these currents, an additional pair of capacitive peaks at more positive potentials. We have taken advantage of the well-defined morphology and crystal structure of three different types of rutile electrodes to investigate the nature of these band gap states.[1] In particular, films composed of oriented nanowires (NWs), films of randomly distributed nanoparticles (NPs) and smooth single crystals have been used. The trap state concentration turns out to depend strongly on the morphological structure of the films. Based on results concerning the surface modification of the electrodes we propose a model with a location of these band gap states at grain boundaries.

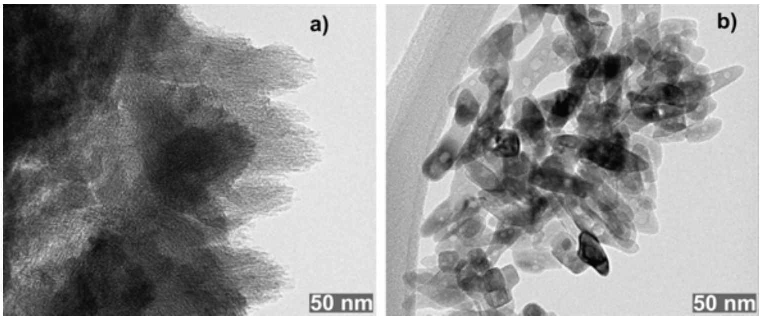


Figure 1. TEM images of rutile nanowires (a) and nanoparticles (b)

Particularly good photoelectrocatalytic properties were observed for NW films when compared to NP electrodes.[2] Both UV-Vis absorption and photoaction spectra evidence that the NWs are in the quantum confinement regime as the band gap is 0.27 eV larger than that of NPs. The high photocatalytic activity of NW films for the photooxidation of organic molecules was attributed to an increased reactivity of photogenerated electrons and holes as a direct consequence of the increased band gap and to a reduced recombination due to a very low concentration of grain boundaries.

The adsorption behaviour of nanoparticulate electrodes is of crucial importance for their application in DSCs. The electron injection efficiency as well as the photoelectrochemical stability of the dye molecules depend on the mode of adsorption. Also in photocatalysis, the surface structure of the nanoparticles has a strong influence on the performance of the oxide. We, therefore, performed ATR-IR spectroscopic studies to investigate the surface condition and the adsorption properties of the nanowire and nanoparticulate films. High signal intensities allowed for the investigation of the adsorption of organic model molecules (formic acid, oxalic acid) from aqueous acidic solutions.[3] The use of Au thin films (film thickness: 20 nm) deposited onto the ATR crystal as substrate for the rutile nanowire film enabled us, furthermore, to perform for the first time a photoelectrochemical study coupled to in-situ ATR-IR spectroscopic measurements. The results concerning the evolution of the photocurrent and the change of the adsorbate concentration during UV/Vis exposure will be discussed in the light of the unique morphological and electronic properties of the investigated films.

References

1. T. Berger, T. Lana-Villarreal, D. Monllor-Satoca, and R. Gómez, *J. Phys. Chem. C* 2007, **111**, 9936.
2. T. Berger, T. Lana-Villarreal, D. Monllor-Satoca, and R. Gómez, *J. Phys. Chem. C* 2008, **112**, 15920.
3. T. Berger, J.M. Delgado, T. Lana-Villarreal, A. Rodes, and R. Gómez, *Langmuir* 2008, **24**, 14035.

PB20

Studying electron recombination and transfer processes in TiO_2 nanoporous electrodes by combining open-circuit potential decay and cyclic voltammetry measurements

Damián Monllor-Satoca, Roberto Gómez
Institut Universitari d´Electroquímica i Departament de Química Física, Universitat d´Alacant, Apartat 99. E-03080 Alacant (Spain). E-mail: damian.monllor@ua.es

The photoelectrochemical behavior of nanoporous TiO_2 electrodes is receiving an increasing attention since the early 90s. This is partly due to the discovery of an efficient photoelectrochemical cell for the conversion of light into electricity based on an anatase nanoporous photoanode (dye-sensitized solar cell, DSSC). Charge carrier recombination,[1-3] which is thought to occur easily at the nanoparticle surface, needs to be minimized, especially if we take into account that the nanoporous thin films are thought to present a very high volumic density of surface and grain boundary traps that may behave as recombination centers.

In this contribution[4] we combine both open circuit potential decay measurements with cyclic voltammetry in the electron accumulation region as a means to obtain, without a priori assumptions, the decay rate for electrons in TiO_2 nanostructured thin films (Figure 1). Integration of the voltammogram allows us to determine the total electron concentration in the nanoporous film as a function of the electrode potential. We can then translate the open circuit potential into electron concentration in the film and obtain directly electron concentration vs. time decay curves.

Not only the average first-order rate constants for electron consumption are obtained in such a way but also the values of such constants as a function of the electrode potential (microcanonical rate constants). As an example, this method is applied to different titanium dioxide samples as to elucidate the effect of fluorination[5,6] on the rate of both electron recombination (with surface trapped holes) and electron transfer to dissolved oxygen. In both cases, but especially for recombination, there is, upon fluorination, a significant retardation of the electron consumption process in agreement with several photocatalytic studies found in the literature.

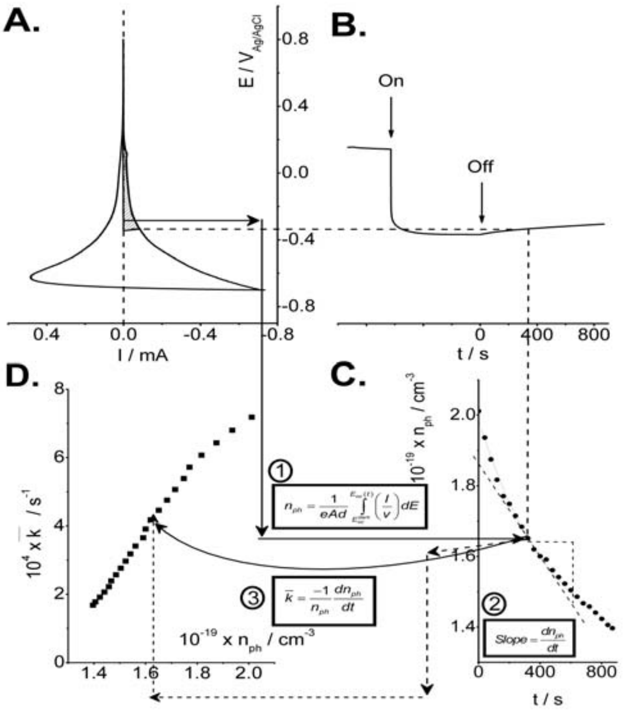


Figure 1. Scheme showing the pseudo-first order rate constants calculation algorithm. The electrode was a P25 nanostructured thin film in contact with a N_2-purged $HClO_4$ 0.1 M solution (electrode thickness, 7 μm; electrode exposed area, 1.54 cm^2; light intensity, 0.24 W) (A) Cyclic voltammogram obtained in the dark (10 mV/s), (B) (Photo)potential transient decay obtained after the electrode was illuminated, (C) Photogenerated electron concentration variation with time, obtained from (A) and (B) data, and eq. (1) , (D) Pseudo-first order rate constant variation with photogenerated electron concentration, obtained from (C) data and eq. (2) and (3).

References

1. A. Zaban, M. Greenschtein, J. Bisquert, *ChemPhysChem*, 2003, **4**, 859.
2. J. Bisquert, A. Zaban, M. Greenshtein, I. Mora-Seró, *J. Am. Chem. Soc.*, 2004, **126**, 13550.
3. M. Bailes, P.J. Cameron, K. Lobato, L.M. Peter, *J. Phys. Chem. B*, 2005, **109**, 15429.
4. D. Monllor-Satoca, R. Gómez, *J. Phys. Chem. C*, 2008, **112**, 139.
5. C. Minero, G. Mariella, V. Maurino, E. Pelizzetti, *Langmuir*, 2000, **16**, 2631.
6. M. Mrowetz, E. Selli, *Phys. Chem. Chem. Phys.*, 2005, **7**, 1100.

PB21

Phenomenological Modeling of Dye-sensitized Solar Cells: a Transient Approach

Luísa Andrade, José Sousa, Helena Aguilar Ribeiro and Adélio Mendes*
Laboratory for Process, Environment and Energy Engineering (LEPAE), Faculty of Engineering of University of Porto, R. Dr. Roberto Frias, 4200-465 Porto, Portugal.

Dye-sensitized solar cells (DSCs) are very attractive and promising devices for photovoltaic (PV) applications. In fact, these devices are a cheap alternative to conventional PV cells since they are based on low-cost materials and fabrication processes, therefore having the potential for low-cost electricity production from sunlight. The general principle for direct energy conversion in a DSC assumes that the process of light absorption and charge transport are differentiated. In this way, since large band gap semiconductors are almost insensitive to the visible portion of the solar spectrum, light harvesting is accomplished by a monolayer of dye molecules, chemically bounded to the surface of the semiconductor, typically TiO_2. Photoexcited electrons of the dye are injected into the conduction band of the TiO_2 and percolate through the semiconductor network towards the transparent conducting oxide (TCO) coating and into an external circuit. The electrons are then returned to the cell through the counter electrode, where they take part in an iodide/triiodide redox reaction catalyzed by a platinum layer coated onto the TCO[1].

In the last two decades, several studies focused on theoretical approaches for insightful understanding of the basic working mechanisms of DSCs. Sodergren *et al.*[2] developed a steady-state phenomenological model based on electron diffusion through the porous semiconductor; Papageorgiou *et al.*[3] presented a comprehensive analysis on the relevance of mass transport in the steady-state operation of nanocrystalline photoelectrochemical solar cells and Ferber *et al.*[4] reported an electrical model for DSCs allowing the calculation of the internal properties of the cell as well as the charge carriers' density distributions. In 2001 Ferber *et al.*[5] modeled the electric fields within the TiO_2 semiconductor and within the redox electrolyte. The present work aims at contributing for the progressive understanding of the charge transfer mechanisms that govern DSC's mode of operation.

One of the most powerful characterization techniques of DSCs, the electrochemical impedance spectroscopy (EIS) involves transient probing. This way, a phenomenological transient modeling has the potential of a deeper understanding of the relevant phenomena occurring in a DSC and the ability to be related with such transient characterization methods. Thus, considering the DSC sketched in Figure 1, a one-dimensional transient phenomenological model was developed. It assumes that the injected conduction-band electrons may recombine only with the electrolyte redox species. Due to the small dimension of the titania particles, no significant electrical potential gradient is assumed, resulting only in a diffusive electrons transport. For modeling purposes, the mesoscopic porous structure, consisting of TiO_2 nanoparticles covered with light absorbing dye molecules and interpenetrated by the I^-/I_3^- redox mediator (electrolyte), is considered as a homogeneous nanocrystalline structure of thickness L. The continuity and transport governing equations are defined for the mobile species involved: the electrons in the TiO_2 conduction band and the I^-/I_3^- ions in the electrolyte. The TCO/TiO_2 boundary is modeled as an ideal ohmic contact, while the electrolyte/platinized TCO interface is described by a Butler-Volmer approach. With this model, we can calculate the concentration profiles (electrons and ions) and the theoretical current-voltage characteristics of the cell, and compare it with experimental data.

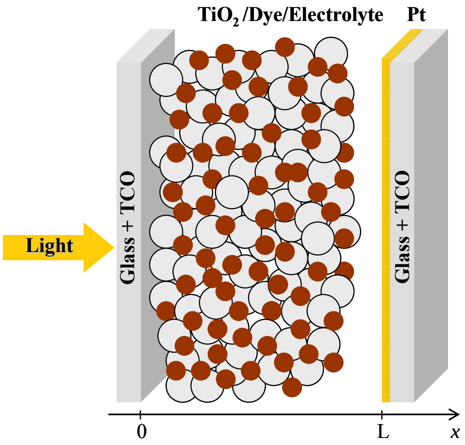


Figure 1 – Scheme of the modeled DSC.

References

1. B. O'Regan and M. Grätzel, *Nature*, 1991, **353**, 737-740.
2. S. Soedergren, A. Hagfeldt, J. Olsson and S.-E. Lindquist, *J. Phys. Chem.*, 1994, **98**, 5552-5556.
3. N. Papageorgiou, M. Grätzel and P. P. Infelta, *Sol. Energy Mater. Sol. Cells*, 1996, **44**, 405-438.
4. J. Ferber, R. Stangl and J. Luther, *Sol. Energy Mater. Sol. Cells*, 1998, **53**, 29-54.
5. J. Ferber and J. Luther, *J. Phys. Chem. B*, 2001, **105**, 4895-4903.

PB22

Lanthanide luminescent organic complexes: effect of N-based co-ligands on photophysical properties

A. Alessi, P. Biagini, S. Fanutti, N. Perin, M. Salvalaggio*, S. Spera and A. Tacca
Eni S.p.A., Research Center for Non-Conventional Energies "Istituto Eni Donegani", via Giacomo Fauser 4, I-28100 Novara (Italy)
*mario.salvalaggio@eni.it

The unique photophysical properties of lanthanide ions (long lifetimes and very sharp and narrow emission bands) have encouraged vigorous research activities in view of photonic applications such as tunable lasers, components of the emitting materials in multilayer organic light emitting diodes (OLED) and light conversion molecular devices[1]. It is well-known that the coordination of suitable ligands as highly absorbing "*antennae*" is required to overcome the very low absorption coefficients of the lanthanide ions. β-diketones are commonly used sensitizing antennae as they can efficiently transfer energy to Ln$^{(III)}$ ions and are able to form stable and strong adducts with all the metals of the lanthanide series[2]. Moreover, ancillary co-ligands such as bipyridines and phenanthrolines can impressively influence the emission intensity of these complexes[3].
The above considerations prompted us to synthesize and characterize various octa-coordinated lanthanide β-diketonate complexes of general formula: Ln(acac)$_3$(L) [where Ln= Eu, Sm, Tb, Dy; acac = 4,4,4-trifluoro-1-(2-naphtyl)-1,3-butanedionate or 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedionate; L = 2,2'-bipyridine, 1,10-phenanthroline, 5-nitro-1,10-phenanthroline, 3,4,5,7-tetramethyl-1,10-phenanthroline]. These Ln$^{(III)}$ complexes were characterized by NMR and FT-IR spectroscopy and their photophysical properties were studied by UV-Vis absorption and by steady state and time resolved photoluminescence spectroscopies, with the aid of cyclic voltammetry measurements.

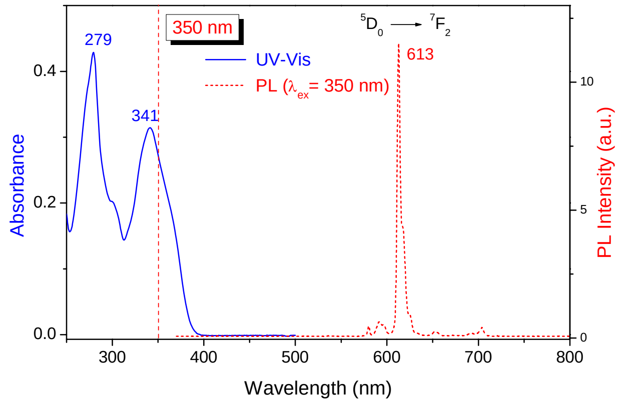


Figure 1.

Ligand-sensitized luminescence characteristic of the different Ln$^{(III)}$ centres are mainly based on β-diketonate ligand excitation around 350 nm. Otherwise, N-based bidentate ligand influence overall quantum yields evidencing different sensitization efficiencies[3] depending on β-diketonate ligand and rare earth centre. These co-ligands effects are discussed in terms of electron donor/acceptor character of the ligands.

References

1. J-C. G. Bünzli and C. Piguet, *Chem. Soc. Rev.*, 2005, **34**, 1048; A. de Bettencourt-Dias, *Dalton Trans.*, 2007, 2229; R. Hao, M. Li, Y. Wang, J. Zhang, Y. Ma, L. Fu, X. Wen, Y. Wu, X. Ai, S. Zhang and Y. Wei, *Adv. Funct. Mater.*, 2007, **17**, 3663.
2. J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1304; G.F. De Sa, O.L. Malta, C. de Mello Denega, A.M. Simas, R.L. Longo, P.A. Santa-Cruz and E.F. da Silva, Jr, *Coord. Chem. Rev.*, 2000, **196**, 165.
3. A.M. Klonkowski, S. Lis, M. Pietraszkiewicz, Z. Hnatejko, K. Czarnobaj and M. Elbanowski, *Chem. Mater.*, 2003, **15**, 656; C.R. De Silva, J.R. Maeyer, R. Wang, G.S. Nichol and Z. Zheng, *Inorg. Chim. Acta*, 2007, **360**, 3543.

PB23

The Electrochemical Properties of Tritoluylamine and Triphenylamine as Molecular Hole Transport Materials

Teresa Lana-Villarreal*, Irene Barceló, Néstor Guijarro, Roberto Gómez
Institut Universitari d´Electroquímica i Departament de Química Física, Universitat d´Alacant, Apartat 99. E-03080 Alacant (Spain). E-mail: Teresa.Lana@ua.es

Among the different configurations proposed for the fabrication of third generation solar cells, solid hybrid solar cells appear as promising devices. These cells combine the unique properties of one or more types of inorganic nanoparticles with a thin film of an organic hole transporting material.

In this contribution, we show that electrochemical experiments constitute a good strategy for the study of organic hole transporting materials. In fact, they allow us both to tune the material properties and to independently analyze them without the interference of other device components. To illustrate this approach, we have addressed the study of two model hole conductor materials, triphenylamine (TPA) and tritoluylamine (TTA), as thin film electrodes. Whereas TPA undergoes oxidative solid state electropolymerization, TTA units do not seem to suffer irreversible changes. The polymerization of TPA was evidenced not only by changes in successive cyclic voltammograms in 0.5 M $NaClO_4$ aqueous solutions, but also by in situ quartz crystal microbalance and UV-Vis spectroelectrochemical measurements. The same techniques were employed to electrochemically dope both materials at high enough positive potentials, as a function of the anion present in the solution. These experiments also provide information on the electronic structure of the materials, especially when they are combined with photopotencial measurements, which reveal that both behave as p-type semiconductors. In addition, it will be shown that the insertion of counterions and solvation of the organic thin film during doping and polymerisation also induce changes in the water contact angle and thin film morphology (Tapping Mode Atomic Force Microscopy). Finally, ideas will be given on how to take advantage of these studies to advance in the preparation of solid state devices, regarding especially quantum dot sensitised solar cells.

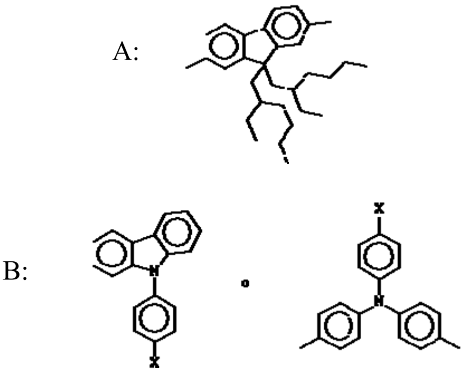
PB24

Alternating copolymers for optoelectronic applications: structure-property relationships

M. Caldararo, A. Pellegrino, N. Perin, R. Pò, M. Salvalaggio*, G. Schimperna and A. Tacca
Eni S.p.A., Research Center for Non-Conventional Energies "Istituto Eni Donegani", via Giacomo Fauser 4, I-28100 Novara (Italy)
*mario.salvalaggio@eni.it

Fluorenes, carbazoles and triarylamines are largely used in semiconducting polymers due to their peculiar properties: in particular, optimized carbazole derivatives can improve polymer hole mobility[1] and triarylamine moieties can act as donor materials[2], with an overall potentially positive effect in promoting charge-carriers transport of the polymers. As further specific example, 9,9-dialkylfluorene-triphenylamine copolymers can be used to prepare highly efficient hole extraction/electron-blocking layer in bulk-heterojunction solar cells[3]. The properties of these materials can be opportunely modulated by carbazole and triarylamine aromatic ring substitutions.

On the basis of the above observations, in order to investigate the influence of the electron-withdrawing and donating properties of carbazole and triarylamine units respectively, a series of alternating $(A\text{-}B)_n$ copolymers - where A is 9,9-dialkylfluorene and B is a carbazolic or a triarylaminic system - have been synthesized by Pd-catalyzed Suzuki coupling reaction of the various monomers with 9,9-bis-(2'-ethylhexyl)fluorene-2,7-diboronic acid:



X= H, CN, NO_2, OR

The so obtained copolymers have been characterized by UV-Vis absorption, ESR, steady state and time-resolved photoluminescence spectroscopies, with the aim to investigate structure-property relationships within the copolymer series by varying the accepting or donating character of the X substituent on the carbazole or the triphenylamine units.

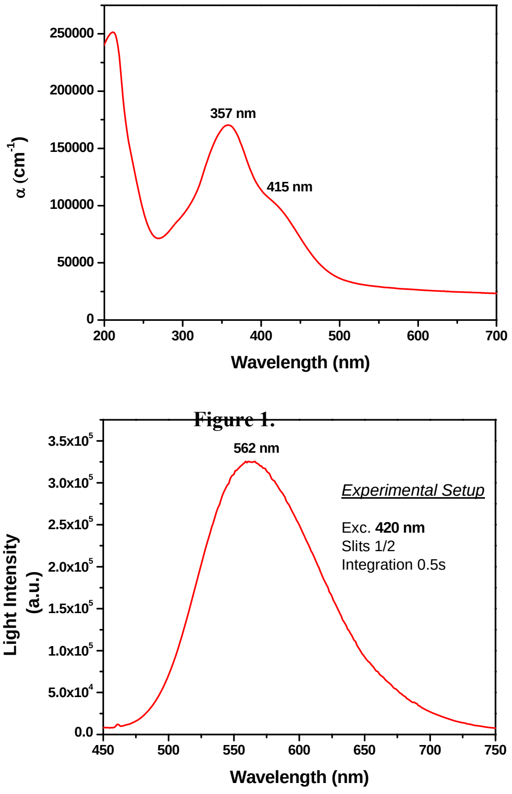


Fig. 1 – UV-Vis and PL spectra of $(A\text{-}B)_n$ with $x=NO_2$

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1 Leclerc, A. Michaud, K. Sirois, J.-F. Morin, M. Leclerc, *Adv. Funct. Mat.* 2006, **16**, 1694; N. Blouin, A. Michaud, D. Gendron, S. Wakim, E. Blair, R. Neagu-Plesu, M. Bellette, G. Durocher, Y. Tao and M. Leclerc, *J. Am. Chem. Soc.* 2008, **130**, 732;

2. Roquet, A. Cravino, P. Leriche, O. Alvque, P. Frre and J. Roncali, *J. Am. Chem. Soc.* 2006, **128**, 3459; Z.Q. Gao, Z.H. Li, P.F. Xia, M.S. Wong, K.W.Cheah and C.H. Chen, *Adv. Funct. Mat.* 2007. **17**, 3194.

3.W. Hains, T.J. Marks, *Appl. Phys. Lett.* 2008, **92**, 23504.33

PB25

Synthesis and characterization of poly(1-vinyl-3-alkylimidazolium) iodide polymers for quasi-solid electrolytes in dye sensitized solar cells

Eneko Azaceta[a], Rebeca Marcilla[a], Antonio Sanchez-Diaz[b], Emilio Palomares[b,c] and David Mecerreyes[a]*
[a], *New Materials Department, CIDETEC, Center for Electrochemical Technologies, Parque Tecnológico de San Sebastián , Paseo Miramón 196, Donostia-San Sebastián 20009, Spain.*
[b], *Institute of ChemicalResearch of Catalonia (ICIQ), Avda. Paisos Catalans 16, Tarragona 43007, Spain.*
[c] *ICREA, Spain.*

Dye sensitized solar cell (DSSC) is a type of photovoltaic device which yielded a light to electricity conversion efficiency of 11.1 % [1] using organic solvent based electrolytes. The problem of these innovative devices is the stability, mainly due to loss of electrolyte by leakage and the evaporation of the organic solvent. The loss by evaporation is overcome with the use of solvent free electrolytes based on ionic liquids (ILs) [2]. However, the leakage is still a problem that it is being addressed employing solid electrolytes [3].

We present here a new family of polymeric ionic liquids (PILs) that can be used to obtain quasi-solid electrolytes based on ILs. Similar polymers have showed to be excellent matrices to design quasi-solid electrolytes by dissolving them into conventional solvent systems or in combination with ionic liquids to develop “solvent free” electrolytes [4].

In this work, different PILs of poly(1-vinyl-3-alkylimidazolium) iodide with different alkyl derivatives such as methyl, propyl and perfluorodecyl were synthesized and characterized in terms of solubility, thermal stability, glass transition and crystallinity of the polymer (see Fig.1). Electrochemical characterization of the quasi-solid electrolyte prepared by mixing poly(1-vinyl-3-propylimidazolium) iodide with the ionic liquid 1-methyl-3-propylimidazolium iodide at different ratios, was carried out. Ionic conductivities were obtained by impedance spectroscopy and the values were in the range of 10^{-3}-10^{-7} S/cm, which strongly depended on the ionic liquid content. Furthermore, poly(1-vinyl-3-propylimidazolium) iodide was used to obtain quasi-solid electrolytes by mixing with a typical acetonitrile based electrolyte. Finally, this quasi-solid electrolyte was tested in a Dye Sensitized Solar Cell yielded a maximum efficiency of 3.73% [5].

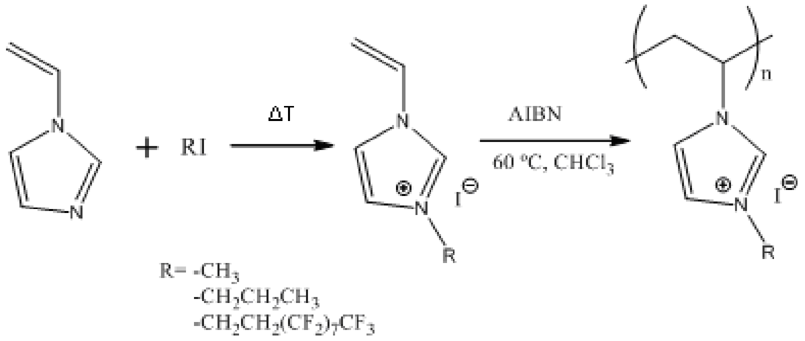


Figure 1.

References

[1] Y. Chiba, A. Islam, Y. Watanabe, R. Komiya, N. Koide, L.Y. Han, *Japanese Journal of Applied Physics Part 2-Letters & Express Letters* 45 (**2006**) L638–L640.
[2] Y. Bai, Y. Cao, J. Zhang, M. Wang, R. Li, P. Wang, S. M. Zakeeruddin, M. Graetzel, *Nature Materials* 7 (**2008**) 626-630.
[3] J. Wu, S. Hao, Z. Lan, J. Lin, M. Huang, Y. Hyang, P. Li, S. Yin, T. Sato, *J. Am. Chem. Soc.* 130 (**2008**) 11568
[4] a) R. Marcilla, F. Alcaide, H. Sardon, J. A. Pomposo, C. Pozo-Gonzalo, D. Mecerreyes, *Electrochemistry Communications* 8, (3), (**2006**) 482-488. b) M. Wang, Y. Lin, X. Zhou, X. Xiao, L. Yang, S. Feng, X. Li, Mat. Chem. Phys. 107 (2008) 61
[5] E. Azaceta, R. Marcilla, A. Sanchez-Diaz, E. Palomares, D. Mecerreyes *Electrochim. Acta* (**2009**), doi:10.1016/j.electacta.2009.01.058

PB26

THIN FILMS OF CARBON NANO BEADS AND THERE APPLICATION FO R PHOTOVOLTAICS

Shrikant Kawale[3], HarishKumar Dubey[1], B. Patil[1], S. Bharadwaj[1], A. Gupta[1], Goldie Oza[1], S. Pandey[1], P. Jagadale[2], N. Mishra[1], B. T. Mukherjee[4], D. Kshirsagar[2], Madhuri Sharon[5], C.H. Bhosale[3], Maheshwar Sharon[1]
1 Nanotechnology Research Center (NTRC), Birla College, Kalyan;
2 University of Genova, Italy;
3 Shivaji University, Kolhapur;
4 K.V. Pendharkar College, Dombivali, Maharastra, India;
5 Monad Nanotech Pvt. Ltd.
Corresponding e-mail: shri.physics@gamail.com

Plant derived precursor like camphor, mustard oil, turpentine oil and menthol were tried to deposit thin films of carbon material. Thermal Flash Vapor Deposition (TFVD) method was used for depositing thin films of carbon. Morphological Properties were studied by SEM, EDAX and electrical properties were studied by two probe resistivity method. Band gap of these films were calculated using spectrophotometric absorption study within the wavelength range 200nm to 1100nm. SEM image shows well dispersed carbon nano beads with diameter 30-50 nm. Film shows semi conducting behavior and Activation energy was found to be 0.014eV. These films after proper doping can be applicable for photovoltaic purposes. So far camphor was found to be best precursor for synthesis of carbon thin films.

Keywords: Camphor, TFVD, thin films.

PB27

Nb-doped TiO_2: from Hybrid Solar Cell working under inert atmosphere to nanostructured material for Dye Sensitized Solar Cells

Monica Lira-Cantu[a]*, **Mabube Khoda Siddiki**[a], **David Muñoz-Rojas**[b], **Natalia González-Pech**[a,c], **Irene Gonzalez-Valls**[a], **Judith Oro**[b].

c. *Centre de Investigaciò en Nanociencia i Nanotecnologia. Campus UAB, Edifici ETSE 2nd Floor. Bellaterra (Barcelona) Spain E-08193.* monica.lira@cin2.es
d. *Institut de Ciència de Materials de Barcelona (ICMAB). Campus UAB, Bellaterra E-08193, Spain.*
e. *Instituto Tecnologico y de Estudios Superiores de Monterrey (ITESM). Ave. Eugenio Garza Sada, 64640 Monterrey, N.L. (México).*

Photovoltaic response of Excitonic solar cells (XSCs) based on semiconductor oxides, has shown a dependence of oxygen in order to work properly: inert atmospheres decrease photovoltaic performance, while air (oxygen) improves their photovoltaic response but degrades organic semiconductors located at the interfaces.[1-3] The latter affects XSCs working under inert atmospheres or sealed conditions. As an effort to understand this working mechanism and to improve XSCs lifetime, we have synthesized semiconductor oxides doped with different amount of metal ions, and applied them in different types of solar cells. In this work, we present our most recent work on the application of Nb-doped TiO_2 fabricated as dense thin films and analyzed as electron transport material in a Hybrid Solar Cell (HSC). We analyzed and compare the photovoltaic response of the device under long-term irradiation conditions in Air and N_2 atmosphere (see Figure 1a). We then synthesized the material as nanoparticles to form nanostructured electrodes and applied it in Dye Sensitized Solar Cell (DSC) (see Figure 1b) obtaining power conversion efficiencies between 0.64 % and 0.86 % depending on dye and electrolyte applied.[4-6]

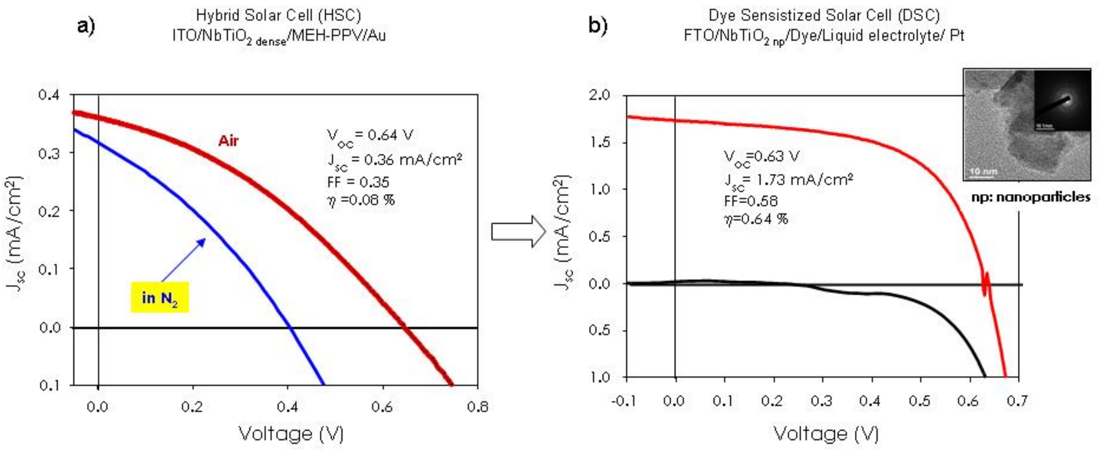


Figure 1. Nb-doped TiO_2 in Excitonic solar cells: a) Applied as dense thin film in a Hybrid Solar Cell (HSC) with MEH-PPV polymer and analyzed under ambient and N_2 atmosphere. b) Applied as nanostructured electrode made of nanoparticles in a Dye Sensitized Solar Cell (DSC). Measurements in air carried out at ~75 ºC, measurements under N_2 carried out at ~45ºC with a fixed gas flux, 1000 W/m^2 A.M.1.5. Active areas: 0.7 cm^2 for HSC and 0.25 cm^2 for DSC. Analyses performed at the photovoltaics laboratory at CIN2 (CSIC-ICN).

References

1. M. Lira-Cantu, K. Norrman, J.W. Andreasen, N. Casan-Pastor, and F.C. Krebs. *J. Electrochem. Soc.*, 2007. **154**(6), B508-B513.
2. M. Lira-Cantu and F.C. Krebs. *Sol. Eneg. Mater. Sol. Cells*, 2006. **90**(14), 2076-2086.
3. M. Lira-Cantu, M., K. Norrman, J.W. Andreasen, and F.C. Krebs. *Chem. Mater*. 2006. **18**(24), 5684-5690.
4. M. Lira-Cantu, M. K. Siddiki, D. Muñoz-Rojas, Natalia González-Pech, J. Oro. *Submitted*.

PB28

Performance comparison between organic and hybrid solar cells

S. Fernandez de Avila*, J.L. Alonso, J.C. Ferrer.
Departamento de Física y Arquitectura de Computadores, Área de Electrónica, Universidad Miguel Hernández, Avda. de la Universidad s/n 03202 Elx (Alicante), Spain.
*s.fdezavila@umh.es

In recent years, organic solar cells have attracted considerable interest as a cheap alternative for conventional inorganic solar cells[1]. In particular, those devices fabricated from organic or polymeric solutions that can be easily processed by simple techniques, such as different printing technologies, drop-casting or spin-coating among others, using any kind of substrates, including flexible ones. However, the efficiency of such organic solar cells is still low and they suffer a fast degradation process[2] that has only been stopped with encapsulation of devices.

Hybrid photovoltaic devices[1,3], consisting of a combination of both organic and inorganic semiconducting material, have been suggested as a route to overcome those difficulties. On one hand, inorganic semiconductors are more stable than organic materials, and might help to delay degradation of the solar cells. On the other hand, inorganic semiconductors have usually higher mobilities than polymers or organic molecules, and if they are manufactured as nanoparticulate colloids, their band gap can be tailored to maximize absorption and also, multiple exciton generation (MEG) can be reached, helping to increase efficiency.

To check the expected advantages brought by the incorporation of inorganic nanoparticles, it is common to compare the performance of different hybrid photovoltaic devices with respect to the reference organic photovoltaic device. However, in order to reach accurate conclusions, several factors have to be taken into account to be sure that both type of devices are comparable. Even spin-casting both active layers (the polymeric and hybrid one) in the same conditions from solutions with the same concentration, the presence of two phases (polymer and nanoparticles) with different density in hybrid layers may lead to a different thickness, avoiding the possibility to present a precise comparison of performance between both devices.

Figure 1 shows I-V curves of several hybrid photovoltaic (PV) devices made from poly(3-hexylthiophene) (P3HT) combined with PbS nanoparticles at different percentages in weight with respect to the polymer. The I-V curve of the P3HT polymer PV device (solid line in fig. 1) fabricated at exactly the same conditions is also shown for reference. From this graph we could guess that inclusion of inorganic nanoparticles leads to a lower efficiency but this result needs to be checked carefully.

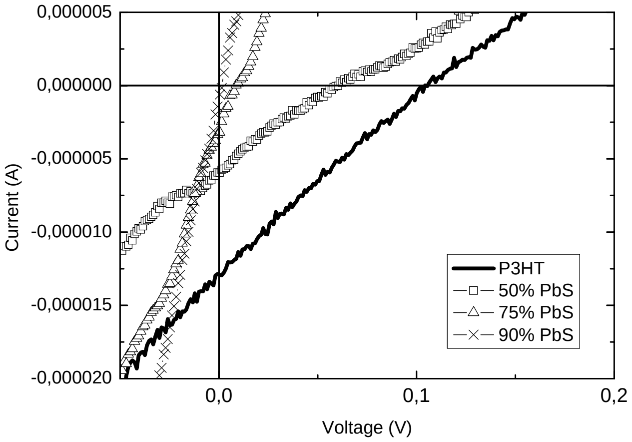


Figure 1. Comparison of I-V curves for a series of solar cells.

References

1. S. Günes, H. Neugebauer and N.S. Sariciftci. Chem Rev. , 2007, **107**, 1324.
2.]K. Kawano, R. Pacios, D. Poplavskyy, J. Nelson, D.D.C. Bradley, J. Durrant. Sol. Energy Mat. & Solar Cells, 2006, **90**, 3520.
3. B.R. Saunders, M.L. Turner. Adv. Coll. Interf. Sci. , 2008, **138**, 1.

PB29

Random walk numerical simulation for hopping transport: electron diffusion coefficient and transport energy approximation

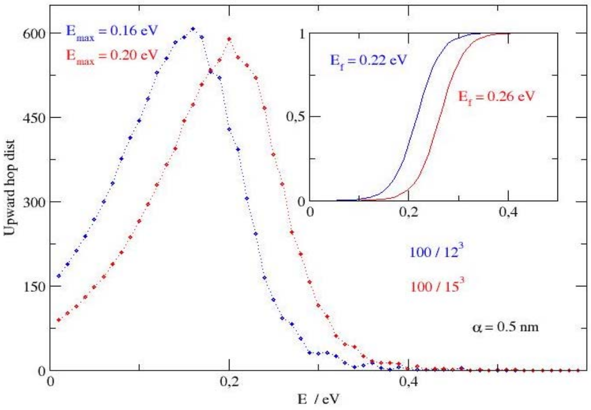
Juan A. Anta[a], Juan Bisquert[b],J.P. Gonzalez-Vazquez*[a],

a, Departamento de Sistemas Físicos, Químicos y Naturales, Universidad Pablo de Olavide, 41013 Sevilla, Spain.

b, Photovoltaic and Optoelectronic Devices Group, Departament de Física, Universitat Jaume I, 12071 Castelló, Spain.

**, Departamento de Sistemas Físicos, Químicos y Naturales, Universidad Pablo de Olavide, 41013 Sevilla, Spain*

The random walk numerical simulation (RWNS) method is used to compute electron diffusion coefficients and to test the validity of the transport energy concept for materials characterized by exponential distributions of trap energies and hopping transport. The Miller-Abrahams jumping rates are used to compute the hopping times in the random walk simulation. To test the theoretical assumptions the jump diffusion coefficient is computed as a function of Fermi level and temperature. It is observed that there is indeed a characteristic energy for which the probability of hopping reaches a well-defined maximum. As a consequence of this the diffusion coefficient exhibits a similar behaviour with respect to the Fermi energy and temperature as that found in the multiple trapping model.



References

1. J. A. Anta, I. Mora-Sero, T. Dittrich, et al., Physical Chemistry Chemical Physics, 2008, 10, 4478.
2. J. Bisquert, Journal of Physical Chemistry C, 2007, 111, 17163.

PB30

Systematic studies of organic solar cells based on a combinatorial approach

Ton Offermans,* **Guillaume Basset, Jörg Schleuniger, Giovanni Nisato, Carsten Winnewisser**
CSEM BASEL, Section Polymer Optoelectronics, CSEM Centre Suisse d'Electronique et de Microtechnique SA, Mattenstrasse 22, CH-4016 Basel, Switzerland

A novel, fully automated, fabrication and characterization apparatus for polymer solar cells and light-emitting diodes has been developed. This high throughput apparatus allows the fabrication of 49 devices with a controlled variation of essential parameters like material, material composition, blend concentration, layer thickness, and annealing temperature. Up to now, due to a lack of elaborate design tools, extensive experimental effort is required in order to optimize novel materials, material combinations and device structures for polymer based solar cells. Our apparatus provides an extensive dataset which can be used for device optimization and a profound device modeling offering a deeper theoretical understanding of underlying device physics in organic solar cells.

PB31

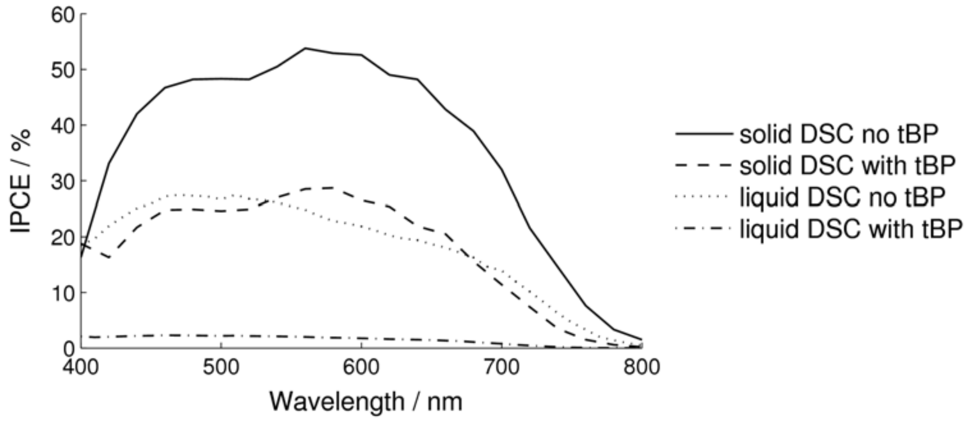
A Purple Perylene Sensitizer for Solid State Dye-Sensitized Solar Cells

Ute B. Cappel,[a]* Martin H. Karlsson,[a] Neil Pschirer,[b] Felix Eickemeyer,[b] Jan Schöneboom,[b] Peter Erk,[b] Gerrit Boschloo,[a] Anders Hagfeldt[a]
a, Department of Physical and Analytical Chemistry, Ångström laboratory, Uppsala University, Box 259, 751 05 Uppsala, Sweden.
b, BASF SE, Speciality Chemicals Research, D-67056 Ludwigshafen, Germany
*ute.cappel@fki.uu.se

Sensitizers employed in solid state dye-sensitized solar cells using the hole conductor 2,2'7,7'-tetrakis-(*N*,*N*-di-*p*-methoxyphenyl-amine)-9,9'-spirobifluorene (spiro-MeOTAD) usually also function well in combination with the iodide /tri-iodide redox couple. Here, we present a new perylene sensitizer, ID176, which works well in solid state DSCs but not in liquid electrolyte ones.[1] The sensitizer was characterized by UV-visible spectroscopic techniques,[2] cyclic voltammetry, incident photon to current efficiency (IPCE) and current-voltage measurements.

ID176 has a broad absorption spectrum with an absorption onset at 730 nm in DCM solution and adsorbed toTiO_2, which can be further red-shifted in the presence of lithium ions. The HOMO level is sufficiently positive to enable regeneration by both spiro-MeOTAD and iodide, while the LUMO is only marginally more negative than the TiO_2 conduction band. In complete devices, solid state DSCs showed a two times higher IPCE than DSCs using the iodide/tri-iodide redox couple when *tert*-butyl pyridine (tBP) was not used as additive to either spiro-MeOTAD or the liquid electrolyte (Figure 1). In presence of tBP, the IPCE values for solid state DSCs were even 10 times higher than the IPCE values for electrolyte DSCs. Together with an open-circuit voltage improvement, solar cell efficiencies were up to 3 times higher in solid state DSCs than in liquid DSCs, reaching over 3 % when the volatile additive tBP was not used. These results suggest a different mechanism in injection and regeneration in solid state DSCs compared to ones using the iodide/tri-iodide redox couple.

Figure 1. IPCE spectra of ID176.



References

1. U. B. Cappel, M. H. Karlsson, N. Pschirer, F. Eickemeyer, J. Schöneboom, P. Erk, G. Boschloo, A. Hagfeldt, *submitted to JACS.*
2. U. B. Cappel, E. A. Gibson, A. Hagfeldt, G. Boschloo, *J. Phys. Chem. C,* 2009, available online.

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Lanthanide luminescent organic complexes: effect of N-based co-ligands on photophysical properties

A. Alessi, P. Biagini, S. Fanutti, N. Perin, M. Salvalaggio*, S. Spera and A. Tacca
Eni S.p.A., Research Center for Non-Conventional Energies "Istituto Eni Donegani", via Giacomo Fauser 4, I-28100 Novara (Italy)
*mario.salvalaggio@eni.it

The unique photophysical properties of lanthanide ions (long lifetimes and very sharp and narrow emission bands) have encouraged vigorous research activities in view of photonic applications such as tunable lasers, components of the emitting materials in multilayer organic light emitting diodes (OLED) and light conversion molecular devices[1]. It is well-known that the coordination of suitable ligands as highly absorbing "*antennae*" is required to overcome the very low absorption coefficients of the lanthanide ions. β-diketones are commonly used sensitizing antennae as they can efficiently transfer energy to $Ln^{(III)}$ ions and are able to form stable and strong adducts with all the metals of the lanthanide series[2]. Moreover, ancillary co-ligands such as bipyridines and phenanthrolines can impressively influence the emission intensity of these complexes[3].

The above considerations prompted us to synthesize and characterize various octa-coordinated lanthanide β-diketonate complexes of general formula: $Ln(acac)_3(L)$ [where Ln= Eu, Sm, Tb, Dy; acac = 4,4,4-trifluoro-1-(2-naphtyl)-1,3-butanedionate or 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedionate; L = 2,2'-bipyridine, 1,10-phenanthroline, 5-nitro-1,10-phenanthroline, 3,4,5,7-tetramethyl-1,10-phenanthroline]. These $Ln^{(III)}$ complexes were characterized by NMR and FT-IR spectroscopy and their photophysical properties were studied by UV-Vis absorption and by steady state and time resolved photoluminescence spectroscopies, with the aid of cyclic voltammetry measurements.

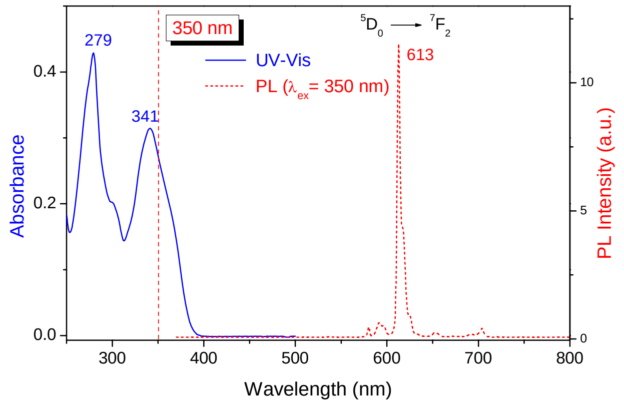

Figure 1.

Ligand-sensitized luminescence characteristic of the different $Ln^{(III)}$ centres are mainly based on β-diketonate ligand excitation around 350 nm. Otherwise, N-based bidentate ligand influence overall quantum yields evidencing different sensitization efficiencies[3] depending on β-diketonate ligand and rare earth centre. These co-ligands effects are discussed in terms of electron donor/acceptor character of the ligands.

References

1. J-C. G. Bünzli and C. Piguet, *Chem. Soc. Rev.*, 2005, **34**, 1048; A. de Bettencourt-Dias, *Dalton Trans.*, 2007, 2229; R. Hao, M. Li, Y. Wang, J. Zhang, Y. Ma, L. Fu, X. Wen, Y. Wu, X. Ai, S. Zhang and Y. Wei, *Adv. Funct. Mater.*, 2007, **17**, 3663.
2. J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1304; G.F. De Sa, O.L. Malta, C. de Mello Denega, A.M. Simas, R.L. Longo, P.A. Santa-Cruz and E.F. da Silva, Jr, *Coord. Chem. Rev.*, 2000, **196**, 165.
3. A.M. Klonkowski, S. Lis, M. Pietraszkiewicz, Z. Hnatejko, K. Czarnobaj and M. Elbanowski, *Chem. Mater.*, 2003, **15**, 656; C.R. De Silva, J.R. Maeyer, R. Wang, G.S. Nichol and Z. Zheng, *Inorg. Chim. Acta*, 2007, **360**, 3543.

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Increasing efficiency by introducing a one dimensional photonic crystal in DSC

Silvia Colodrero[1], Anders Hagfeldt[2], Hernán Míguez[1,]*
1 Instituto de Ciencia de Materiales de Sevilla (CSIC), Américo Vespucio, 49, 41092 Sevilla, Spain
2 Department of Chemistry, Center of Molecular Devices, The Royal Institute of Technology,
Teknikringen 30, S-100 44 Stockholm, Sweden
hernan@icmse.csic.es

Dye sensitised solar cells (DSC) are devices that combine a solid wide band gap semiconductor with a liquid ionic conductor, and constitute an interesting alternative to solid state semiconductor photovoltaic devices, mainly due to their low cost of production. One way to enhance the cell efficiency is to modify its optical design in order to improve its optical absorption. In this way, a porous and highly reflecting one-dimensional photonic crystal[1] (1DPC) is implemented in solar cells to enhance the efficiency. The periodic structure is built by alternating layers made of different types of nanoparticles that allow us to obtain a wide and intense Bragg reflection peak. The photonic crystal, with a thickness of just half-micron, is able to efficiently localize incident light within the nc-dyed TiO_2 electrode in a targeted wavelength range. So, significant optical absorption amplification in a wide spectral range occurs in these structures that combine the presence of a highly reflecting photonic crystal and a layer of absorbing material, [2,3] being therefore enhanced the photogenerated current. Average power conversion efficiencies are improved between 15% and 30% with respect to the reference value attained for standard electrodes[4].

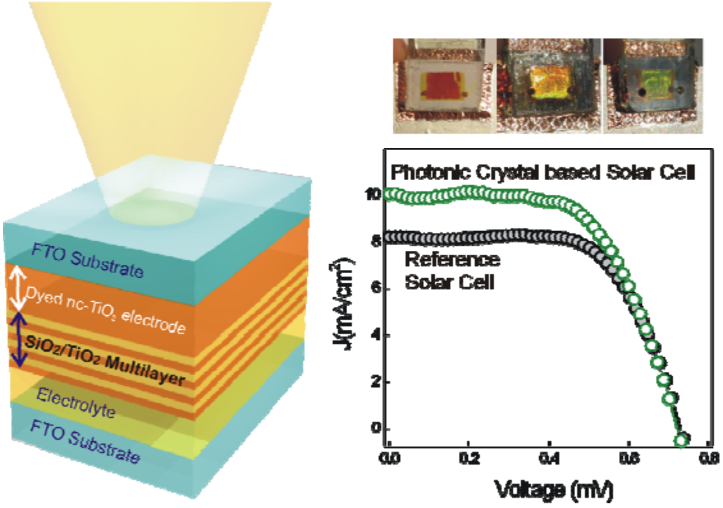

Figure. *Left*: Design of a dye-sensitized solar cell coupled to a porous nanoparticle based 1D photonic crystal exposed to frontal illumination. *Right:* Pictures showing different reference and photonic crystal based dye sensitized solar cells. The nanoparticle multilayer behaves as a one dimensional photonic crystal which provides the cell with a brilliant metallic reflection (top). IV curves for both a standard electrode made of titanium dioxide nanoparticles and the same electrode coupled to a 1D photonic crystal (bottom).

References

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[1] Colodrero, S., Ocaña, M., Míguez, H. *Langmuir,* 2008, **9**, 4430.
[2] Mihi, A.; Míguez, H. *J. Phys. Chem. B*, 2005, **33**, 15968.
[3] Colodrero, S., Mihi, A., Anta, J.A., Ocaña, M., Míguez, H. *J. Phys. Chem. C,* 2009, **4**, 1150.
[4] Colodrero, S., Mihi, A., Häggman, L., Ocaña, M., Boschloo, G., Hagfeldt, A., Míguez, H. *Adv. Mater.* 2009, **7**, 764.

List of Participants HOPV10

Prof	Abderrazzak	Douhal	University of Castilla la Mancha	ES
Mr	Abel	Sainz	Iberlaser	ES
Prof	Agustín R.	Gonzalez-Elipe	Institute of Materials Science of Seville	ES
Dr	Alejandro	Ansón-Casaos	Instituto de Carboquímica, CSIC	ES
Mr	Alejo	Sastre	Actia Servicios MCR	ES
Dr	Alexandre	Ndobe	ISMN-CNR	IT
Miss	Amparo	Forneli	ICIQ	ES
Dr	Ana	Borras	EMPA (Thun)	CH
Miss	Ana Rosa	Lagunas	CENER	ES
Prof	Anders	Hagfeldt	Uppsala University	SE
Mr.	Andrea	Listorti	Imperial College	GB
Prof	Angel	Barranco Quero	Institute of Materials Science of Seville	ES
Dr	Andreas	Bartelt	Helmholtz-Zentrum Berlin	DE
Miss	Anna	Reynal Verdà	Institut Catalá D'Investigació Quimica	ES
Prof	Anna	Vinattieri	Department of Physics	IT
Miss	Anais	Medina	Universidad Autonoma de Madrid	ES
Dr	Anton	Kiriy	Leibniz Institute of Polymer Research Dresden	DE
Mr	Antonio	Sánchez-Díaz	I.C.I.Q.	ES
Dr	Antonio	Urbina	Universidad Politecnica de Cartagena	ES
Prof	Arie	Zaban	Bar ilan university	IL
Mr	Armando	Izquierdo	Iberlaser	ES
Miss	Banu	Aydin	Universitat jaume I	ES
Prof	Beat	Ruhstaller	Zurich Univ. of Appl. Sciences	CH
Prof	Bernabé	Mari	Universidad Politecnica de Valencia	ES
Prof	Curtis	Berlinguette	University of Calgary	CA
Prof	Bisquert	Juan	Universitat jaume I	ES
Prof	Craig	Grimes	Penn State University	US
Dr	Chris	McNeill	University of Cambridge	GB
Mr	Christoph	Waldauf	Ikerlan	ES
Mr	Christophe	Defranoux	SOPRALAB	FR
Dr	Daniel	Ruiz Molina	CSIC	ES
Dr	David	Curiel	Universidad de Murcia	ES
Dr	David	Fermin	University of Bristol	GB
Dr	David	Gutiérrez-Tauste	LEITAT Technological Center	ES
Dr	David	Martineau	Sopralab	CH
Dr	DONGCHAN	LIM	Korea Institute of Materials Science	KR
Miss	Elena	Guillén	Universidad Pablo de Olavide	ES
Miss	Eleonora	Petrolati	University of Rome Tor Vergata	IT
Dr	Elizabeth	Gibson	Uppsala University	SE
Dr	Emilio Jose	Palomares Gil	ICIQ	ES
Mr	Eneko	Azaceta	CIDETEC	ES
Dr	Eric	Cloutet	LCPO-CNRS	FR
Dr	Eugenia	Martinez Ferrero	Institut Catala d'Investigacio Quimica ICIQ	ES
Dr	Eva	Barea	University Jaume I	ES
Miss	Eva	Unger	Uppsala University	SE
Mr	Fabian	Werner	FAU Erlangen-Nürnberg / ICIQ	DE
Prof	Fernando	Langa	Univ. Castilla-la Mancha	ES
Dr	Francisco	Fabregat	UJI	ES
Miss	Francesca	Setaro	Universidad Autonoma de Madrid	ES
Dr	Francisco	Montilla	Universidad de Alicante	ES
Mr	Frank	Schnell	Robert Bosch GmbH	DE
Mr	Fabrizio	Giordano	C.H.O.S.E. - University of Rome Tor Vergata	IT
Dr	Filippo	De Angelis	CNR-ISTM	IT

Dr	Gavin	Tulloch	Dyesol Limited	AU
Dr	Germa	Garcia-Belmonte	UJI	ES
Dr	Gerrit	Boschloo	Uppsala University	SE
Prof	Graetzel	Michael	EPFL	CH
Prof	Hayase	Shuzi	Kyushu Institute of Technology	JP
Dr	Hernan	Miguez Garcia	ICMSE	ES
Dr	Helena	Aguilar	Universidade do Porto	PT
Dr	Hongxia	Wang	Bath University	GB
Mr	Idan	Hod	bar ilan university	IL
Miss	Ikerne	Etxebarria	IKERLAN, S.Coop	ES
Miss	Inés	Nieto Carvajal	Universidad de Murcia	ES
Miss	Irene	Barceló	University of Alicante	ES
Mrs	Irene	Gonzalez-Valls	Centre d'Investigacions en Nanociéncia i Nanotecnol	ES
Miss	Irene	Schimilinski	Fraunhofer Institute for Biomedical Engineering	DE
Mr	Ismael	Lopez Duarte	UAM	ES
Dr	Ivan	Mora-Sero	Universitat Jaume I	ES
Mr	Jairo	Nolasco	URV	ES
Prof	James	Durrant	Imperial College London	GB
Dr	Javier	Padilla	Polytechnic University of Cartagena	ES
Dr	John	Clifford	ICIQ	ES
Mr	Jon	Ajuria	Ikerlan	ES
Mr	Jose	Abad	Universidad de Murcia	ES
Dr	José	Herrero	CIEMAT	ES
Mr	José Luis	Alonso Serrano	UMH	ES
Mr	Jose Miguel	Navarro	CENER	ES
Mr	Jose Pablo	Gonzalez Vazquez	Universidad Pablo de Olavide	ES
Mr	Josep	Albero	ICIQ	ES
Dr	Josep	Pallares	Universitat Rovira i Virgili	ES
Dr	Juan Antonio	Anta	Universidad Pablo de Olavide	ES
Dr	Juan Carlos	Ferrer	Universidad Miguel Hernández	ES
Prof	Kang-Jin	Kim	Korea University	KR
Miss	Kee Eun	Lee	McGill university	CA
Dr	Kyu Hwan	Lee	Korea Institute of Materials Science	KR
Dr	Laurence	Lutsen	IMEC	BE
Prof	Laurence	Peter	University of Bath	GB
Miss	Lola	González	Institute of Materials Science of Seville	ES
Dr	Lucia	Bonoldi	ENI REFINING & MARKETING	IT
Dr	Lucia	Cavigli	Universita di Firenze	IT
Miss	Luisa	Andrade	Universidade do Porto	PT
Prof	María Teresa	Martíez	Instituto de Carboquímica, CSIC	ES
Mr	Marios	Neophytou	ikerlan	ES
Dr	Mario	Salvalaggio	ENI - CRENC - Istituto Eni Donegani	IT
Mrs	Marlene	Rivas	Actia Servicios MCR	ES
Miss	Márquez	Lourdes	Universidad Jaume I	ES
Dr	Martijn	Lenes	University of Valencia	ES
Dr	Mauricio	Calvo Roggiani	ICMSE CSIC	ES
Mr	Mathias	Nyman	Abo Akademi University	FI
Dr	Mathieu	Urien	Saint-Gobain Recherche	FR
Mr	Menny	Shalom	Bar Ilan university	IL
Miss	Merchan	Loles	UJI	ES
Mr	Miguel	García Iglesias	UAM	ES
Mr	Miquel	Planells	ICIQ	ES
Mr	Miquel	Nieto	Telstar Instrumat, S.L.	ES
Mr	Montero	José M.	Universitat Jaume I	ES
Dr	Monica	Lira-Cantu	Centre d'Investigacions en Nanociència i Nanotecnol	ES
Dr	Moritz	Riede	Institut fuer Angewandte Photophysik	DE
Prof	Mukundan	Thelakkat	University of Bayreuth	DE
Miss	Nagore	Imaz	Fundación Inasmet	ES
Mrs	Natalia	Gonzalez-Pech	Centre d'Investigacions en Nanociència i Nanotecnol	ES
Mr	Néstor	Guijarro Carratalá	University of Alicante	ES

Dr	Nieves	Espinosa	UPCT	ES
Dr	Nils A.	Reinke	Institute of Computational Physics	CH
Dr	Nuria	Garro	Universitat de Valencia	ES
Mr	Pablo	Martí-Ramos	ETSIT, University of Valladolid	ES
Mr	Pablo	Perez Boix	UJI	ES
Prof	Peng	Wang	CAS Changchun Institute of Applied Chemistry	CN
Prof	Perla	Wahnón	Universidad Politécnica de Madrid	ES
Miss	Phuong Tuyet	Nguyen	Roskilde University Center	DK
Dr	Pilar	De la Cruz	UCLM	ES
Mr	Pini	Luca	AUTOLAB	NL
Mr	Prasittichai	Chaiya	Northwestern University	US
Prof	Prashant	Kamat	Univ. of nOtre Dame	US
Mr	Rafael	García-Valverde	Universidad Politécnica de Cartagena	ES
Dr	Ramon	Tena-Zaera	CIDETEC	ES
Dr	Rebeca	Marcilla	CIDETEC	ES
Miss	Rebecca	Jensen	Northwestern University	US
Dr	Reza	Fallahpour	University of Zurich	CH
Mr	Robert	Steyrleuthner	Universitat Potsdam - Institut für Physik und Astr	DE
Dr	Roberto	Gómez	University of Alicante	ES
Dr	Roberto	Pacios	IKERLAN	ES
Mr	Roger	Hausermann	ZHAW	CH
Dr	Roger	Hiorns	Université de Bordeaux	FR
Miss	Sandra	Feldt	Uppsala University	SE
Dr	Sergei	Bereznev	Tallinn University of Technology, Department of Ma	EE
Mr	Shay	Yahav	Bar Ilan University	IL
Dr	Shogo	Mori	Shinshu University	JP
Prof	Shozo	Yanagida	Center for Advanced Science and Innovation	JP
Miss	Silvia	Colodrero	Institute of Materials Science	ES
Dr	Simona	Fantacci	CNR-ISTM	IT
Mr	Simon	Sandén	Abo Akademi University	FI
Dr	Sixto	Giménez	Universitat Jaume I	ES
Miss	Sophia	Buhbut	Bar-Ilan university	IL
Dr	Soriano	Alejandra	Universidad de VAlencia	ES
Dr	Susana	Fernandez de Ávila	Universidad Miguel Hernandez	ES
Miss	Stephanie	Narvey	Sopralab	CH
Mr	Sylvia	Paul	University of Potsdam	DE
Miss	Tannia	Marinado	Royal institute of technology	SE
Prof	Taro	Toyoda	The University of Electro-Communications	JP
Dr	Teh Lay	Kuan	Robert Bosch (SEA) Pte Ltd	SG
Dr	Teresa	Lana Villarreal	University of Alicante	ES
Miss	Tina	Li	Northwestern University	US
Dr	Thomas	Berger	Universidad Pablo de Olavide	ES
Dr	Ton	Offermans	CSEM Basel	CH
Dr	Torben	Lund	Roskilde University	DK
Dr	Ulgut	Burak	Gamry Instruments	US
Miss	Ute	Cappel	Uppsala University	SE
Dr	Volkmar	Hopfe	Fraunhofer IWS	DE
Mr	Walther	Benjamin	Robert Bosch GmbH	DE
Dr	Wei	David	Everlight Europe BV	NL
Dr	Yantao	Shi	Tsinghua University	CN
Dr	Youhai	Yu	Centre d'Investigacions en Nanociéncia i Nanotecno	ES
Mr	Zion	Tachan	Bar-Ilan University	IL