THE FINAL PROJECT REPORT FOR EUROPAN SCIENCE FOUNDATION PROGRAMME (ORGANISOLAR)

BULK HETEROJUNCTION SOLAR CELLS BASED ON INORGANIC SEMICONDUCTORS

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THE PURPOSE OF VISIT

INTRODUCTION

Solar energy has a great importance among the renewable energy sources. Since sunlight can be transformed into electricity using solar cells, many researchers have been focused on this subject. First of all, conventional solar cells were built from inorganic materials such as silicon. The efficiency of inorganic based solar cells reached up to %24. However, fabrication process of such solar cells is quite expensive. In addition silicon based solar cell show low efficiency at high temperatures. Hybrid and photoelectrochemical (dye sensitized) solar cells have been the alternatives for conventional silicon solar cells. Hybrid solar cells consist of both organic and inorganic materials. Organic materials are inexpensive, easily obtainable and their functionality can be controlled by molecular designing. On the other hand, inorganic semiconductors can be manufactured as nanoparticles and inorganic semiconductor nanoparticles offer the advantage of having high absorpion coefficients and size tunability. By varying the size of the nanoparticles the bandgap can be tuned therefore the absorption range can be tailored. First of all O'Regan and Gra¨ tzel [1] were reported Dye-sensitized solar cells (DSSCs) based on TiO2 photoelectrode and Nazeeruddin et al. [2] reported high solar energy to electricity conversion efficiency, Z, up to 11% with ruthenium bipyridyl dyes.

Although efficiencies of 11% are reported the technological development is still hindered due to the leakage or evaporation of the electrolyte solution. The presence of an electrolyte solution in photoelectrochemical cells makes the manufacturing process difficult. Therefore, recent efforts in dye sensitized solar cell research are more focusing on replacing the electrolyte solution with a solid material to eliminate practical problems with sealing. A solid state cell exhibits a structure similar to the dye sensitized photoelectrochemical cells except for the replacement of liquid electrolyte with a p type semiconductor or “quasi solid” counterpart. Polymeric materials as replacement for the electrolyte solution are of practical interest since they are inexpensive and can be tailored chemically to fit a wide range of technological purposes [3].

THE AIM OF STUDY

The aim of this project is to fabricate and characterize different kinds of hybrid solar cells and also to understand the limiting factors for the effiency of these solar cells and to find solutions meeting all these limiting factors. An effective strategy for hybrid solar cell fabrication is to use blends of nanocrystals with semiconductive polymers as a photovoltaic layer. The basis of this is the bulk heterojunction concept. The usage of inorganic semiconductor nanoparticles embedded into semiconducting polymer blends are promising for several reasons such as high absorption coefficients and photoconductivity of inorganic semiconductor materials, variability of n- or p- type doping levels of the nanocrystalline materials and also band gap tuning in inorganic nanoparticles with different nanoparticle sizes. Charge transfer junctions with high interfacial area are formed by blending semiconductor nanocrystals into conjugated polymers. Operation of such solar cells is due to photocurrent generation at the interface of nanocrystal/polymer composite materials. In any donor acceptor bulk heterojunction solar cells nanomorphology is a key issue and seen as one of the limiting factors. Therefore, morphology of films prepared by blending semiconducting polymers and inorganic nanoparticles will be characterized by atomic force microscope (AFM). The effect of nanomorphology on the performance of hybrid solar cells fabricated using several different inorganic nanoparticles and polymers will be investigated. Another important parameter which limits the performance of hybrid solar cells is the surfactant around the nanoparticles which prevent further growth, agglomeration and also the oxidation of the nanoparticles. However, the surfactant around the nanoparticles hinders the charge transfer from the polymer to the nanoparticle acting as an insulating layer. The effect of different surfactants around the nanoparticles on the solar cell performance will be investigated.

In this study hybrid solar cells based on nanoparticles will be fabricated. The project will mainly focus on bulk heterojunction solar cells by blending inorganic semiconductor nanoparticles such as CdS, CdSe, CdSe/CdS (core/shell) and CdTe/CdS (core/shell) with semiconducting polymers such as poly (3-hexylthiophene) (P3HT). The nanoparticles which will be used in this project were synthesized by Dr. Mahmut Kus and co. workers with different synthetic pathways. Especially for CdS nanoparticles, some alkali or transition metals (Li, Na, Mn etc.) were doped during synthesis of nanoparticles in order to fill some crystal defect and from new energy level inside. By doping such metal ions to nanoparticles, it is expected that electron traps will be filled by these metal ions and current loss will be decrease.

EXPERIMENTAL SECTION

Materials:

PEDOT:PSS

PEDOT:PSS or Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (see figure 1) is a polymer mixture of two ionomers. One component in this mixture is made up of sodium polystyrene sulfonate which is a sulfonated polystyrene. Part of the sulfonyl groups are deprotonated and carry a negative charge. The other component poly(3,4-thylenedioxythiophene) or PEDOT is a conjugated polymer and carries positive charges and is based on polythiophene. Together the charged macromolecules form a macromolecular salt [4].

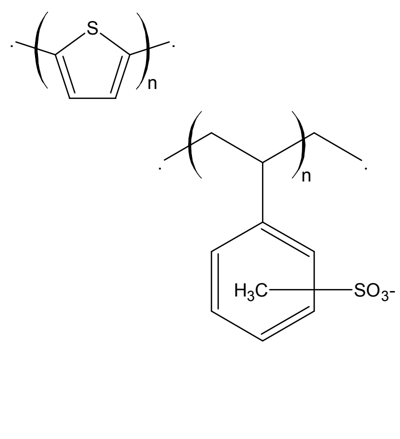


Figure 1 : Molecular composition of PEDOT:PSS

It is used as a transparent, conductive polymer with high ductility in different applications. For example, AGFA coats 200 million of photographic film per year with a thin extensively stretched layer of virtually transparent and colorless PEDOT:PSS as an antistatic agent to prevent electrostatic discharges during production and normal film use, independent of humidity conditions.

If high boiling solvents like methylpyrrolidone, dimethyl sulfoxide, sorbitol are added conductivity increases many orders of magnitude which makes it also suitable as a transparent electrode, for example in touchscreens, organic light-emitting diodes and electronic paper to replace the traditionally used indium tin oxide [4].

P3HT

Figure 2 shows the chemical structure of the frequently used organic semiconductor poly(3-hexylthiophene) (P3HT) for photovoltaic applications. Regioregular P3HT has been used in this work. P3HT is highly soluble in common organic solvents and has a broad absorption spectra with a maximum around 550 nm.

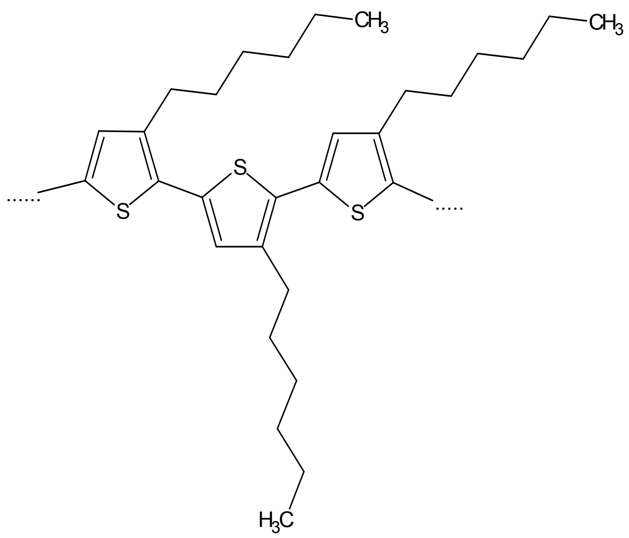


Figure 2 : Molecular structure of P3HT

PCBM:

Best-known PCBM compound. Effective n-type semiconductor soluble in organic solvents. Used for solar cells (OPVs), thin-film transistors (OFETs), and photodetectors [5-7]. Figure 3 shows the molecular structure of PCBM. PCBM has optical absorption in the visible region. This can lead to improved light-harvesting in OPVs, [8] especially in combination with large bandgap donors like MDMO-PPV.

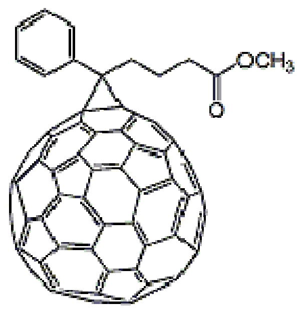


Figure 3: Molecular structure of PCBM

CdSe/CdS, CdTe and Na doped CdS nanoparticles:

CdSe/CdS nanoparticles are well known fluorescent nanoparticles. They shows different optical features depending on their particle size. Due to their tunable optical properties, they are used in many area such as light emitting diodes, solar cells, living cell imagining etc. In this study, different sized CdSe/CdS nanoparticles were used. Figure 4 shows the fluorescence spectra of nanoparticles which depend on their crystal size.

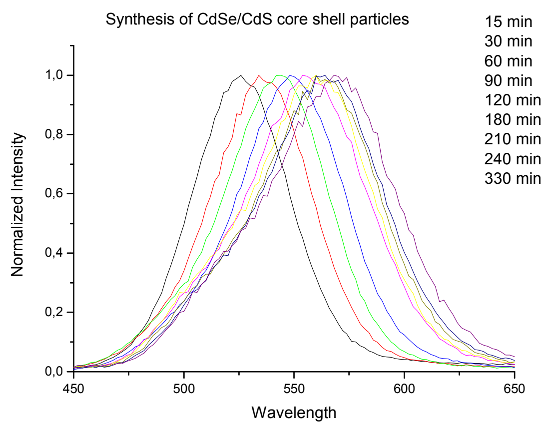


Figure 4: Fluorescence spectra of CdSe/CdS nanoparticles (Given time shows the duration of synthesis)

Nanoparticles used in this study were synthesized and characterized by Dr. Mahmut KUS and coworkers in their laboratories (Izmir Institute of Technology-Turkey). TOPO and oleic acid capped Nanoparticles were prepared and used. Figure 5 shows TEM images of one of TOPO capped CdSe/CdS sample.

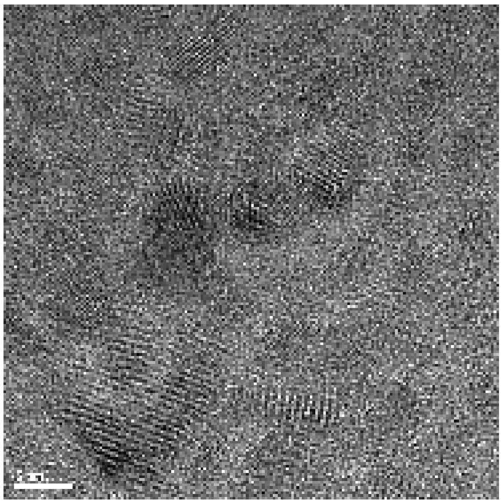


Figure 5: TEM images of TOPO capped CdSe/CdS nanoparticles

It is known that metal doping improves the optical properties of nanoparticles. Generally transition metal were used as dopant but here, an alkali metal Na is used. The fluorescence intensity increased and broadened by Na doping. Figure 6 shows the fluorescence spectra of Na doped CdS.

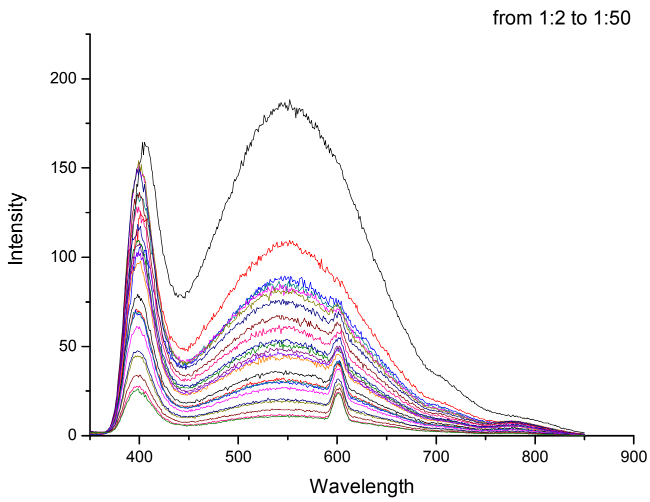


Figure 6: Fluorescence spectra of Na doped CdS nanoparticles.

Substrate Preparation

As substrates, glass sheets of 1.5x 1.5 cmP2P covered with ITO, from Merck KG Darmstadt, were used with an ITO thickness of about 120 nm and sheet sheet resistance < 15 ΩcmP-2P.

The ITO Merck KG Darmstadt was used in all experiments. ITO glasses were etched with an acid mixture of HClBkonzB:HNOB3konzB:HB2BO (4.6:0.4:5) for an hour. The scotch tape was used to protect the determined area of ITO from etching. After etching, the substrate was cleaned by using acetone, ethanol, iso-propanol and finally with distilled water in an ultrasonic bath.

Device Preparation

Solar Cell Preparation

Three types of bulk heterojunction solar cells based on inorganic nanoparticles were prepared. İnorganic nanoparticles which correspond to CdSe/CdS, CdTe, Na doped CdS were abbreviated to be QD.

Type1:

The layers in this type of solar cells are described to be ITO/PEDOT:PSS/P3HT:QD/LiF/Al.

ITO glasses were etched and cleaned. PEDOT:PSS were spin coated at 1500 rpm then dried at 70 C under vacuum overnight.

P3HT solution was prepared in chlorobenzene. The concentration was 10 mg/ml. QD solutions are also prepared in chlorobenzene. Since the amount of capping agent was not known it was difficult to calculate the concentratioın of QDs to be mg per ml. So we used optical density to fix our concentration. The optical density of QD solutions were 0.4.

The mixture of P3HT and QDs were prepared and spin coated onto PEDOT:PSS coated substrates. The ratio of P3HT and QDs were 10:20 10:10, 10:5, 10:2,5 respectively. Then LiF (0.6 nm) and Al (100 nm) were evaporated under vacuum onto substrates. Figure 7 shows the scheme of prepared solar cells.

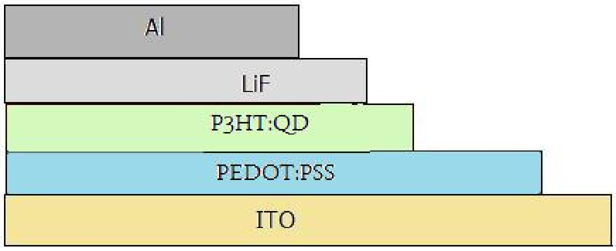


Figure 7: The scheme of solar cells based on P3HT:QD mixtures

Type2:

The layers in this type of solar cells are described to be ITO/PEDOT:PSS/PCBM:QD/LiF/Al.

All the procedures were same given above. Only PCBM was used instead of P3HT. The concentration of PCBM was 10 mg/ml. Figure 8 shows the scheme of prepared solar cells with PCBM.

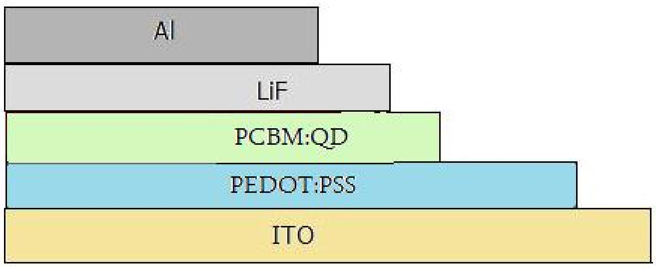


Figure 8: The scheme of solar cells based on PCBM:QD mixtures

Type 3:

The layers in this type of solar cells are described to be ITO/Compact TiO2/QD/P3HT/Au.

Compact TiO_2 layers were prepared according to ref [9] and were spincast under ambient conditions on top of the cleaned and patterned ITO substrates by using 8000 rpm resulting in approximately 100 nm thick films. After spin coating, the substrates were placed in an oven and sintered at 450 C for 30 minutes yielding insoluble compact layers.

CdTe quantum dots (optical density was 0.4 in water) were spin coated onto TiO2 layer at 1500 rpm and then dried under vacuum at 80 C.

P3HT with an average molecular weight of 58,000 (American Dye Source) was used as received. 10 mg P3HT was dissolved in 1 ml chlorobenzene. A P3HT film was covered on top of the Ruthenium coated TiO_2 electrodes. Finally, 100 nm gold electrodes were thermally evaporated. Figure 9 shows the scheme of hybrid solar cells consisting of CdTe nanoparticles.

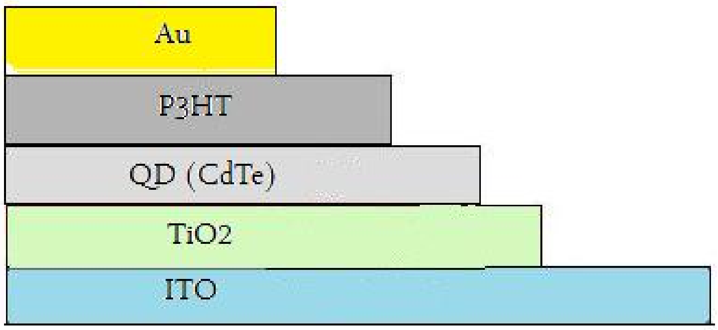


Figure 9: The scheme of solar cells consisting of CdTe nanoparticles

Light emitting diode (LED) preparation

Hybrid light emitting diode also prepared and characterized to determine the other features of QDs. Three types of hybrid LED were prepared as explained below.

Type1:

The layers in this type of hybride LEDs are described to be ITO/QD/LiF/Al or ITO/QD/Al

ITO substrates were etched and cleaned as described above. Then QDs (optical density was 0.4) were spin coated onto ITO substrates at 800 rpm. Then, LiF (0.6 nm)/Al (100 nm) or only Al electrode were evaporated.onto subtrate. Figure 10 shows the scheme of LEDs.

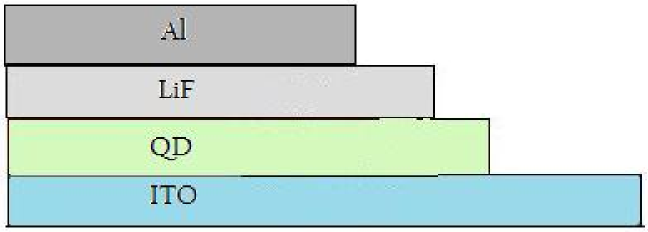


Figure 10: The scheme of single layer LED based on QDs.

Type2:

The layers in this type of hybride LEDs are described to be ITO/PEDOT:PSS/QD/LiF/Al or ITO/ PEDOT:PSS/QD/Al

ITO substrates were spin coated with PEDOT:PSS was spin coated onto ITO subtrates at 1500 rpm. Them dried under vacuum. QDs were also spin coated onto PEDOT:PSS at 800 rpm and dried. Finally LiF (0.6 nm)/Al (100 nm) or only Al electrode were evaporated.onto subtrate. Figure 11 shows the scheme of LEDs.

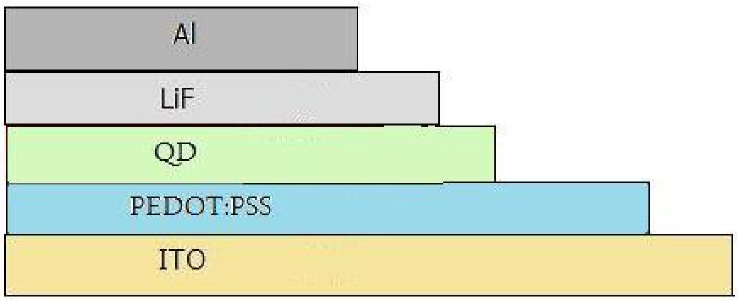


Figure 11: The scheme of polymer hybrid LED based on QDs.

Type 3:

The layers in this type of hybride LEDs are described to be ITO/PEDOT:PSS/QD:PVK/LiF/Al or ITO/ PEDOT:PSS/QD:PVK /Al

The mixture of PVK and QDs were prepared and spin coated onto PEDOT:PSS coated substrates. The ratio of PVK and QDs were 10:20, 10:10, 10:5, 10:2,5 respectively. Then, LiF (0.6 nm)/Al (100 nm) or only Al electrode were evaporated.onto subtrate. Figure shows the scheme of LEDs.

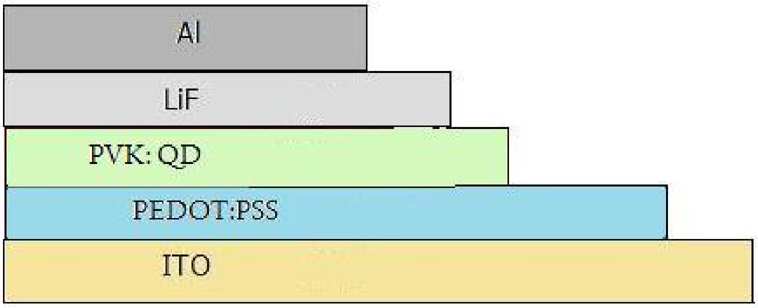


Figure 12: The scheme of polymer hybrid LED based on QDs

Device Characterization

The electrical characterization was carried out under inert argon environment inside a glove box system (MB 200 from MBraun). For solar cell characterization , a Keithley 236 sourcemeter was used.

For the characterization of the devices under light, a solar simulator (K. H. Steuernagel Lichttechnik GmbH) was used under AM 1.5 conditions. Devices were illuminated through the ITO coated glass. Solar cell efficiencies were calculated according to formula given below:

$$\eta = \frac{I_{sc} * V_{oc} * FF}{P_{in}}$$

where Isc is the short circuit current density, Voc is the open circuit voltage, FF is the fill factor and Pin is the incident light intensity.

For measuring the IPCE response between 300 and 900 nm the samples were illuminated under argon atmosphere inside a glovebox with light from a Xenon lamp passing a monochromator (FWHM ~4 nm, illumination intensity ranging between ~ 50 µW cmP-2P and ~200 µW cmP-2P) and chopped with a frequency of 273 Hz. Using an EG&G Instruments 7260 lock-in amplifier the photocurrent of the solar cell was related to the photon flux, determined with a calibrated Si detector. IPCE was calculated using the following formula:

$$IPCE(\%) = \frac{1240 * I_{sc}}{\lambda * P_{in}}$$

Where Isc is the short circuit current density (µA/cmP2P), λ is the incident photon wavelength (nm), Pin is the monochromatic light incidence (W/mP2P).

Charaterization of LEDs.

The electrical characterization was carried out under inert argon environment inside a glove box system (MB 200 from MBraun). A Keithley 236 sourcemeter was used to investigate I-V charateristics. Stepwise voltage was applied for each volt to determine the broken point of LEDs.

Electromluminesans measurements were done with a ccd camera equipped with fiber optic system. First of all current was increased with respect to voltage then wise versa.

Results

Solar Cells

Three types of solar cells were fabricated in this study. The first concept was using P3HT/QD mixture on PEDOT:PSS coated ITO (Type1). P3HT/QDs mixture was prepared with different ratios from 10:20 to 10:2,5. Figure 13 shows I-V characteristics of type 1 solar cells (P3HT:QDs 1:1).

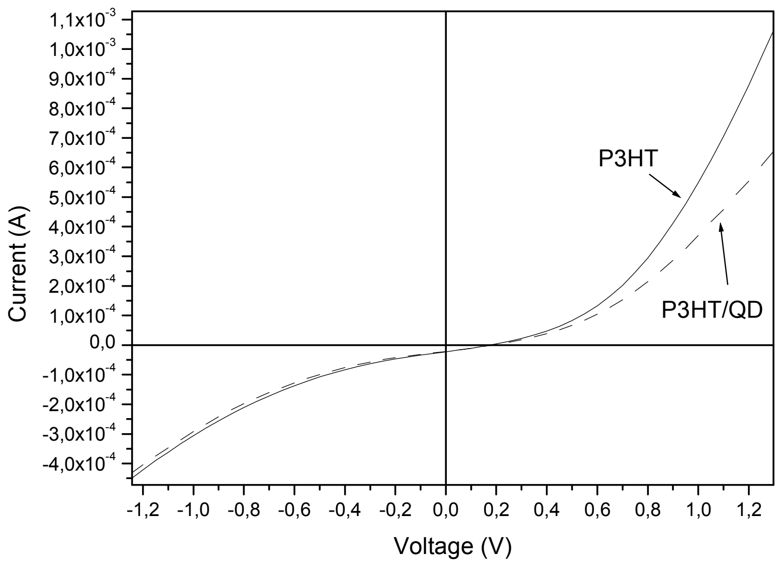


Figure 13: I-V characteristics of type 1 solar cells (P3HT:QDs 1:1 and only P3HT).

According to the results type1 cells do not work. Many of alternative ways were tested such as tuning the film thickness but no result was found for these types of solar cells. So we decided to use PCBM instead of P3HT.

We obtained interesting results with type2 solar cells (PCBM:QD). Voc values increased with PCBM:QD system in comparison with only PCBM cells. Voc increased from 200 mV to 400 mV while Isc was constant in both devices. Table 1 shows the data of solar cell characterization.

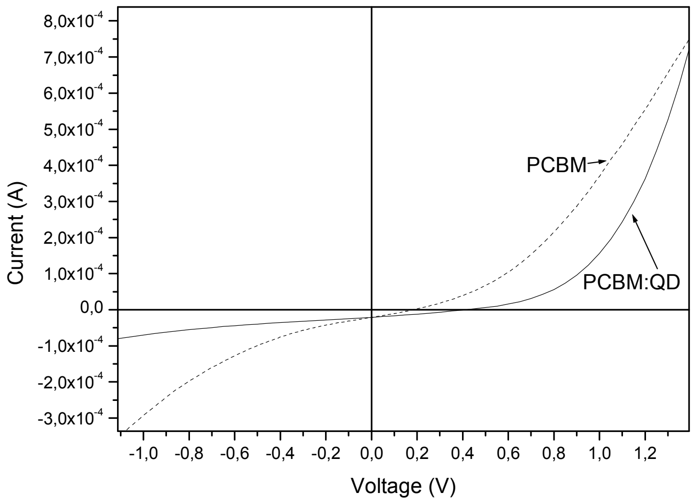
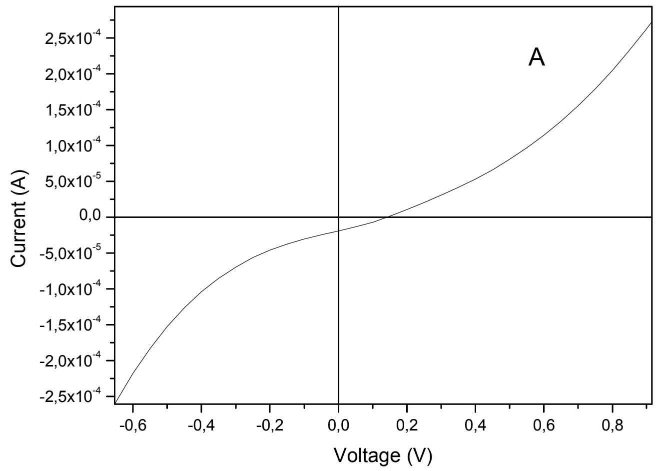


Figure 14: I-V characteristics of type 2 solar cells (PCBM:QDs 1:1 and only PCBM).

PCBM:QD ratio for the best performance was found to be 10:10. The obtained data was hopeful. Since the obtained Isc values are too low, some improvements must be done on these types of solar cells. We attributed the low Isc values that the capping agents (TOPO and Oleic acid) on QDs' surface, which are electrically insulator, prevent the current. In this point of wiev, we tested the water soluble CdTe nanparticles in TiO2 based hybride solar cells. CdTe nanoparticles were capping with mercapto propyonic acid in order to supply water solubility.

Voc values were reached up to 850 mV in type 3 solar cells. Figure 15 shows the I-V characteristic of type 3 solar cells.



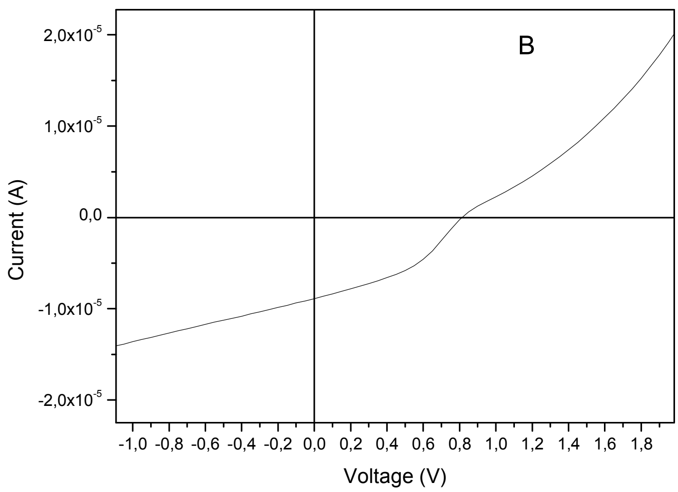


Figure 15: I-V characteristic of type 3 solar cells. (A) only P3HT and (B) QD/P3HT layer.

Table 1: I-V characteristics of solar cells

Device	Isc [mA]	Voc [mV]	FF %	MPoweroutput [mW]	Vmp [mV]	Imp [mA]
ITO/PEDOT:PSS/P3HT/LiF/Al.	0.022	200	24	0.001	100	0.011
ITO/PEDOT:PSS/P3HT:QD (CdSe/CdS)/LiF/Al.	0.022	150	30	0.001	100	0.01
ITO/PEDOT:PSS/PCBM/LiF/Al.	0.022	200	24	0.001	100	0.011
ITO/PEDOT:PSS/PCBM:QD(CdSe/CdS)/LiF/Al.	0.022	400	28	0.002	200	0.012
ITO/TiO2/P3HT/Au	0.019	150	24	0.001	100	0.007
ITO/TiO2/QD (CdTe)/P3HT/Au	0.037	800	41	0.012	500	0.025

Polymer Hybrid LED characterization

Polymer hybrid led devices of nanoparticles were also carried out. In this part of study we prepared 3 types of hybrid LED. ITO/QD/Al, ITO/PEDOT:PSS/QD/Al and ITO/PEDOT:PSS/PVK:QD/Al devices were prepared and characterized. Type 1 LEDs showed resistor like characteristic and no electroluminescence was observed. Type 2 LEDs showed diode characteristic and low electroluminescence. The switch on voltage was around 5 volts. Figure 16 shows I-V characteristic of ITO/PEDOT:PSS/QD (CdSe/CdS)/Al device.

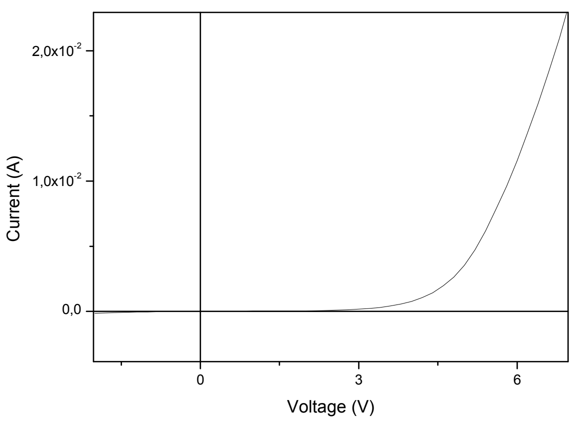


Figure 16: I-V characteristic of ITO/PEDOT:PSS/QD (CdSe/CdS)/Al device.

In addition, similar results were observed with ITO/PEDOT:PSS/QD (Na doped CdS)/Al device. The intensity of electroluminesance was too low and not stable. So it was not possible to measure electroluminescence of type 2 devices. Then we prepared type 3 devices (ITO/PEDOT:PSS/PVK:QD/Al) to increase the light intensity. It must be noted that LiF layer showed no significant change in electrical characteristics, so, here, we considered the devices without LiF layer. Type 3 LEDs showed diode caharacteristic and electroluminescence. Especially Na doped CdS showed white light emission. Figure 17 shows I-V characteristic of hybrid led based on PVK:Na doped CdS devices.

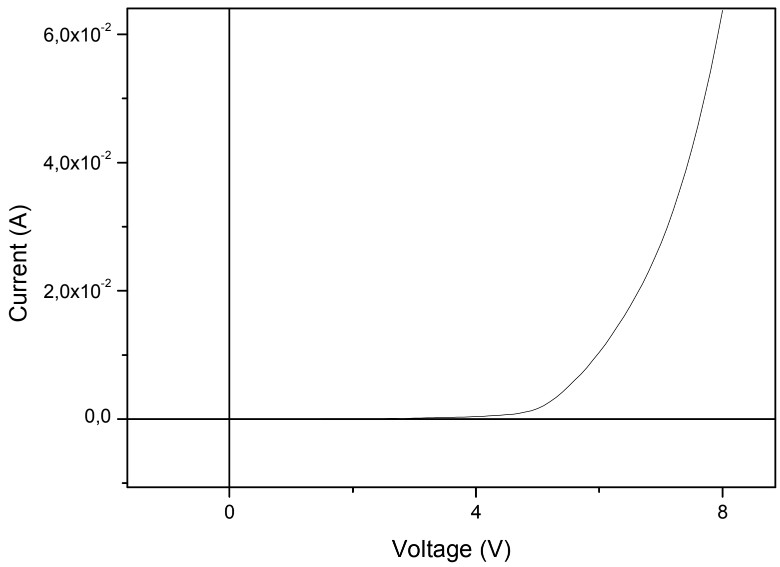


Figure 17: I-V characteristic of hybrid led based on PVK:Na doped CdS devices.

The swich on voltage was calculated to be around 6 volts for (ITO/PEDOT:PSS/PVK:QD (Na doped CdS)/Al). The light intensity was improved in comparison with type 2 LEDs (ITO/PEDOT:PSS/QD/Al) but still not enough for a reliable electroluminescence measurement. Nevertheless, we tried to measure the electroluminescence by applying voltage with respect to current and figure 18 shows the electroluminescence of white light emitting hybride diode (ITO/PEDOT:PSS/PVK:QD (Na doped CdS)/Al).

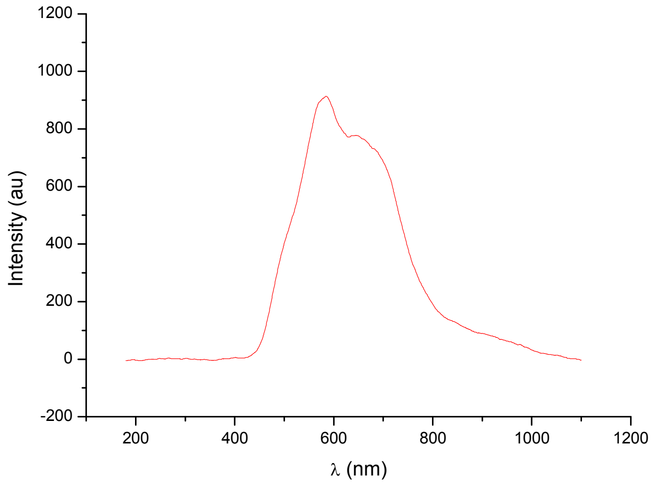


Figure 18: Electroluminescence of hybrid led based on PVK:Na doped CdS (at 8 V.).

Conclusions

In this study, quantum nanoparticles capped with different surfactants such as TOPO, oleic acid and mercapto propyonic acid were studied in hybrid solar cells and light emitting devices. The results showed that nanoparticles capped with water soluble surfactant are more proper then oil soluble ones for solar cell application. So we decided to synthesize a serial of water soluble nanoparticles for future application. Especially, long wavelength absorber nanoparticles with water soluble surfactants are planned to synthesize and test in solar cells. On the other hand light emitting devices also maybe improved because Na doped CdS gives white light emission. It was planned that different hole transport materials instead of PVK can be tested in such devices to improve the light density.

As a result, after some additional studies and improvements, we plan to publish the results.

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