Report for the exchange visit entitled "Plasmonic nanoparticles in energy applications"

1) Purpose of the visit

The ESF exchange grant funded my visit at the Institute of Electronic Structure and Laser (IESL) at the Foundation for Research and Technology - Hellas (FORTH). The purpose of the visit was to conduct research and networking in collaboration with the Technological Educational Institute of Crete (TEIC). The main objectives that were succesfully accomplished were a) to continue on-going research work with IESL, which will lead to at least one publication, b) to plan a future application for an International Training Network bid (ITN-FP7) and c) to attract potential PhD candidates/postdocs or undergraduates to visit/work in my research group.

2) Description of the work carried out during the visit

***Networking*:**

The visit in IESL and TEIC was extremely successful and allowed me to maximize my networking and strengthen my collaborations. As a result of this visit I was invited to give a major talk at a summer school in Chania [ICARUS/OREA 2012, (for more details please see http://orea2012.chania.teicrete.gr/Lecturers_%26_Teaching_Material.html)]. Apart from the dissemination of our joint work I was able to establish new contacts with colleagues from Europe, which will benefit further collaborative work.

Another outcome of my visit and networking was that I was invited to give a second talk at the COST Action 'Bioinspired technologies' that will happen in October in Crete. This invitation will allow me to further enhance my network and blended more with the community.

Apart from the scientific part which I will describe in the coming paragraphs another important aspect of the collaboration with IESL was that one of the undergraduates of the host institution (Ms. Stavroula Pyrgelakou) was attracted in my research area and she applied for a PhD degree in my group at Southampton. She is a strong candidate and currently her application is being considered by the School.

Research

The main research work that I conducted in IESL and TEIC was focused on three objectives:

a) to synthesize different types of gold nanoparticles and appropiately functionalize them for their implementation in active photovoltaic layers

b) To implement the newly formed nanoparticles in blends of organic active photovoltaic layers

c) To fabricate prototype photovoltaic devices and assess the role of the plasmonic particles in device characteristics.

This project was successful and the results are now drafted to a manuscript for a publication as well as a grant application is in preparation [FP7-NMP-2013-SMALL-7 (4.0-2 Innovative materials for efficient, stable and cheap organic photovoltaic cells)]. Some of these results will be discussed in the next section.

Apart from the main project, the ESF exchange grant helped us to initiate two new relevant projects. The first project concerns the synthesis of gold nanoparticles of different sizes and shapes using a combination of chemical and laser-based methods and the second one concerns the study of the interactions between graphene sheets and different types of gold nanoparticles. Both of these topics are complementary to the main project and will help us to maximize our research output and apply for one more European call to pursue further funding [FP7-NMP-2013-LARGE-7 (4.0-1 Graphene production technologies)].

<u>3) Description of the main results obtained</u>

During my stay in IESL we synthesized several different types of gold nanoparticles using chemical methods. In detailed we synthesized spherical gold nanoparticles of sizes 2-4 nm 5-8 nm and 13-15 nm, hollow gold nanoparticles (20-30 nm) and nanocages of a size of 80-90 nm, gold nanorods with dimensions ranging from 15x47 to 15x 160 nm and branched gold nanoparticles with sizes of 150-200 nm (see Figure 1). These particles were stabilized either with cetyl trimethylammonium bromide (CTAB), trioctylammonium bromide (TOAB) or citrate ions and they were kept for further use for the different projects. Although most of the protocols for nanoparticle synthesis are reported there are only few groups in the world that can make advanced monodispersed shapes of nanoparticles such as hollow gold nanoparticles and gold nanorods. Apart from using these materials in our experiments, the second aim was to transfer the knowledge of advanced nanoparticle synthesis at the host institution. The as-made nanoparticles were characterized by TEM, UV-Vis, DLS and zeta potential measurements.

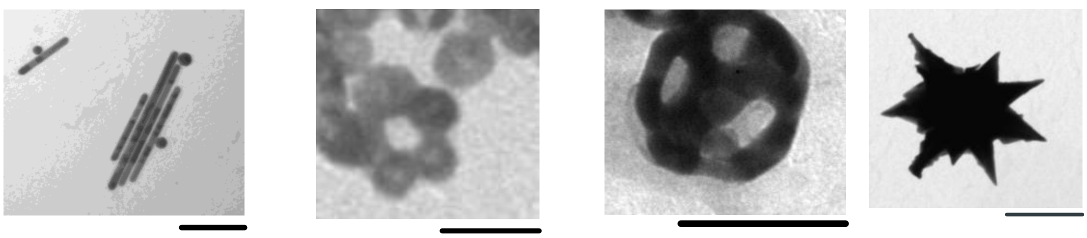

Figure 1. Examples of the different types of gold nanoparticles synthesized during my visit in IESL. Scale bars are 100 nm. Gold nanorods, hollow spheres, gold nanocages and branched gold nanoparticles.

Among the strong expertise of the IESL is the use of femtosecond laser to prepare nanoparticles via laser ablation. This is a technique where a gold surface is ablated by a laser pulse in a media to produce mostly spherical colloidal nanoparticles. While this method produces particles of high dispersion it has the unique charcteristics that the as-prepared colloids are pollycrystaline and do not have any surfactants on their surface. Such characteristics can not be easily obtained by chemical methods, however they are critical to the physicochemical behaviour of the nanoparticles. For these reasons, I was trained and synthesized spherical gold nanoparticles (4-15 nm) by laser ablation.

In TEIC, I gained experience in the preparation of organic photovoltaic devices (OPV) and in the measurement of the basic device characteristics including power convertion of the prototype devices. Initially, and in order to learn the process, the active layers of the device were made by a mixture of polythiophenes and the fullerene derivative [6,6]-phenyl-C61-butyric acid methyl ester. In organic solar cells this fullerene derivative plays the role of an electron acceptor transporting the charges from the exciton dissociation to the electorode. On the other hand, the hole transportation is carried out by the semiconductor polymer (in this case –thepolythiophenes (P3HT).

The main reason for blending gold nanoparticles in the active layer was to increase the number of excitons by scattering of the light. However, from our results it seems that the gold nanoparticles play an additional role that we will analyze at the following paragraphs.

For these experiments we decided to utilize the most simplistic types of gold particles. These are the nanospheres made by laser ablation (4-15 nm) and the nanospheres made by the classical Brust method using TOAB as the surfactant (5-8 nm). The main difference between these two types of particles (apart from the variation in size distribution) was that the nanoparticles made by laser ablation did not have any surfactant on their surface.

These two types of particles were separately mixed with P3HT:PCBM and photovoltaic devices were prepared. The I-V curves of a series of experiments involving these two types of particles are shown in the figure 2. From this figure, we can conclude that while the particles blended in the active layers are of similar concentrations and sizes, the devices prepared with the bare gold nanoparticles (made by laser ablation) are almost 30-40% more efficient than the devices prepared with the TOAB-coated gold nanoparticles. Running a series of control and calibration experiments where we add the TOAB surfactant to laser ablated nanoparticles and we premix P3HT with TOAB-coated nanoparticles in order to replace the TOAB to the nanoparticle surface, we draw the following conclusions. A) the bare gold nanoparticles (made by laser ablation) are almost 30-40% more efficient than the TOAB coated gold nanoparticles, B) if the TOAB-coated gold nanoparticles or the laser ablated nanoparticles are premixed with P3HT prior to the addition to PCBM, the derived devices are 20-40% more efficient (this happens because the P3HT covalently binds to the nanoparticles (releasing TOAB) prior to mixing with PCBM, thus changing the stereochemical structure of the final blend), C) The gold nanoparticles act as additives (independent to their type), and critically influence the stereochemical configuration of the P3HT:PCBM blend affecting the power conversion characteristics of the device. These results are of great interest because they highlight the dual role of the nanoparticles, not only as light scatterers, to increase the number

Active Layers		Jsc (mA/cm^2)	Voc (V)	Fill factor	Power Conversion (%)
P3HT:PCBM (control 1)	1	8.29	0.60	0.54	2.66
P3HT:PCBM +ToAB (control 2)	2	8.27	0.61	0.53	2.65
(P3HT:PCBM + bareAuNPS)+ToAB	3	9.45	0.60	0.57	3.20
(P3HT+bare AuNPs)+PCBM	4	10.54	0.59	0.59	3.66
(P3HT+AuToAB)+PCBM	5	8.77	0.60	0.52	2.72
P3HT:PCBM+ bare AuNPs	6	9.75	0.61	0.60	3.52
P3HT:PCBM+ AuToAB	7	7.69	0.57	0.45	1.97

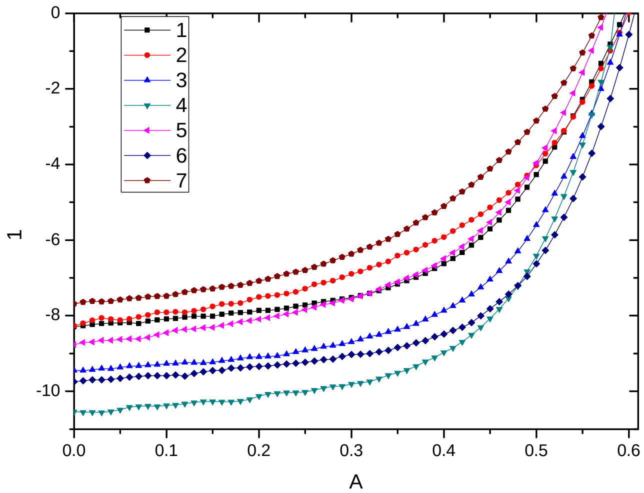

Figure 2. I-V curves, fill factor and power conversion of prototype devices including active layers of different compositions (See table). Bare AuNPs are referred to the particles made by laser ablation, AuToAB is referred to the particles made by chemical methods coated with TOAB.

of excitons but also as additives, destorting the structure of the active blend (P3HT:PCBM) for the transportation of the carriers.

These conclusions, together with detailed experimental evidence will be discussed at the manuscript that we currenlty drafting together with Dr. Emmanuel Stratakis (IESL) and Dr. Emmanuel Kymakis (TEIC).

Complementary to this main project we initiated two more projects. Firstly we explored ways to synthesize anisotropic nanoparticles by laser ablation with the aim to use surfactantless anisotropic particles in the active blends and secondly we started exploring the interactions of different size and shapes of nanoparticles with graphene. Graphene is a good potential candidate that could act as an additive in active blends of photovoltaic devices. The fucntionalization of graphene with gold nanoparticles is a good candidate to enhance the scattering properties and strongly influence the stereochemical configuration of the blends.

Control of nanoparticle anisotropy using laser ablated techniques has not bee shown so far. Currently, we work in this direction by combining chemical manipulation of the laser ablation of the gold surface. These experiments are in progress and they are very promising. Our initial experiments suggest that nanoparticle anisotropy can be controlled via laser ablation using active precursors dissolved in solution during the ablation process. Our work indicates that we can control the synthesis of branched gold nanoparticles using laser ablation. Such surfactantless nanoparticles will be used as active components in photovoltaic devices. It is well known that gold nanostars can scatter light more efficienlty than small spherical nanoparticles. Once the experimental part is completed we also plan to publish this work.

As mentioned earlier, in IESL we prepared a series of surfactant-coated nanoparticles (hollow gold nanoparticles, gold nanorods, branched gold particles, gold nanospheres). Currenlty, we try to covalently functionalize these particles to graphene sheets and characterize the properties of the new hybrid material. For this purpose we use a long dithiol that will be first functionalized to graphene and then to the different types of gold nanoparticles (the affinity of gold to thiols is well established). These experiments are also underway and we seek for seed-funding to accellarate our work.

4) Future collaboration with host institution (if applicable)

The outcomes of the work are very encouraging and we plan to exchange two more student visits to conduct joint work and gain multidisciplinary research experience. The student from Southampton will gain experience in the fabrication and characterization of photovoltaic devices while the visitor from IESL to Southampton will gain further expertises to syntheis and functionalization of nanoparticles. We actively look for futher mobility and seed-funding grant schemes (i.e. ESF programme, Royal society intrnational collaboration grant, IRSES) to sustain our collaboration until we win a major research fund that will allow us to establish a permanent collaborative relationship.

5) Projected publications/articles resulting or to result from your grant

From the joint research work that was enabled with the ESF exchange grant we will publish three papers in the three research areas that I mentioned in the above paragraphs. The manuscript on plasmonic nanoparticles for energy applications is already in preparation while the two others will be written after the completition of the experimental work.
It is planned that our experimental results will be disseminated to international conferences (i.e. MRS Spring 2013).

6) Other comments (if any)

We would like to thank the ESF scheme for the funds that enabled us to solidify our collaboration. We will strongly pursue more funding to further progress aspects of our work.

None of these actions (joint publications, grant applications, networking) would have been possible without this funding.