JANUARY 2012

1st call awarded projects

nanophotonics for energy efficiency

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SEED COLLABORATIVE PROJECTS TO INCREASE ENERGY EFFICIENCY THROUGHT DISRUPTIVE NANOPHOTONICS

The projects awarded during the First Call for Seed Projects done by the N4E Nanophotonics for Energy Network of Excellence are the follwing:

ecoDOTs

NOVEL ECO-FRIENDLY LUMINOPHOR QUANTUM DOTS FOR ENERGY EFFICIENCY SOLID STATE LIGHTING

Partners

TUD, Technische Universitaet Dresden · Nikolai Gaponik
Bilkent University · Hilmi Volkan Demir
OSRAM GmBh · Berit Wessler

Na.NO.Tox.SO.C.

NON TOXIC NANOCRYSTAL SOLUTION PROCESSED SOLAR CELLS

Partners

ICFO, The Institute of Photonic Sciences · Gerasimos Konstantatos
TUD, Technische Universitaet Dresden · Stephen Hickey

GLH

GRAPHENE-BASED LIGHT HARVESTING

Partners

ICFO, The Institute of Photonic Sciences · Frank Koppens and Valerio Pruneri
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COQUASIHYB STRUCTURES

Colloidal quantum dot - Si Hybrid PV

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US, University of Southampton - Pavlos Lagoudakis
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This project is funded by the European Commission's Seventh Framework Programme for Research (FP7)

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Project context and objectives

The use of Cd-free quantum dots, their physics and uses in energy transfer hold a great promise for future environmental friendly applications. The aims of this project have been to design and develop radically new, environmentally friendly, nanostructured material alternatives to conventional phosphors for the future production of innovative color conversion LEDs that outperform today's phosphor based LEDs in terms of their photometric performance including color rendering index, color homogeneity and correlated color temperature with respect to high luminous efficacy of optical radiation. Today's traditional phosphors solely rely on the use of combinations of rare earth ions in a ceramic host. While this conventional type of phosphors is good at photon conversion with high quantum efficiency, there exist fundamental problems related to their photometric performance. Among them, photometric issues associated with their large emission bandwidth (and thus inevitable emission tail toward long wavelengths), combined with the problems of uncontrolled scattering due to undesirably large particle sizes (causing color coordinates to change over angle) are crucial. Also, the fact that China is the major holder and supplier (currently 95-97%) of rare earth ion resources (necessary for conventional phosphors) worldwide raises a strategically critical issue. Therefore, novel eco-friendly luminophor alternatives as proposed herein are essential to the solid-state lighting future of Europe.

Now scientific research is ready for a fundamental advancement to design and produce an entirely new generation of luminophor nanomaterials based on rational nanophotonic and photometric design. Such a scientific challenge is addressed and accomplished by combining innovative materials in the ecoDOTs project.

The basic innovative research approaches involve:

i) the development and use of Cd-free colloidal semiconductor quantum dots (nanocrystals – NCs) from environmentally friendly materials such as InP and ZnS as the colour converting units with large absorption cross-sections, and fine tuning of their emission,

ii) the enhancement of the coating performance by opportunely using high refractive index and low absorption metal oxide particles to achieve enhanced light extraction, and

iii) the state of the art modeling and verification of photometric performance of the materials and assemblies and their integration and validation on test LED devices along with photometric evaluation.

Brief description of the main results

In this project, we demonstrated the synthesis, characterization, and in film temperature dependent energy transfer study and emission kinetics among the different sized InP/ZnS quantum dots. Using different sized InP/ZnS dots in a mixed form in a film structure, we observed up to 80% FRET efficiency and donor lifetime modifications from 18 ns to 4 ns. The suppression of the nonradiative channels in the quantum dots as being cooled to cryogenic temperatures has been observed as well for the InP/ZnS quantum dots. The experimental lifetime modifications of the donor and acceptor quantum dots as a result of energy transfer are in good agreement with our theoretical approach based on the exciton-exciton interaction among the dots. We investigated metal oxide nanoparticles with the aim of enhanced light extraction with better colour mixing. We showed the enhancement of LED color-conversion coating film by opportunely using high refractive index and low absorption particles such as TiO2 nanoparticles of various sizes. We also verified photometric performance of the color-converting materials and assemblies on LED devices along with photometric evaluation.

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Final results, potential impact and use

To date the photometric performance of Cd-containing II-VI semiconductors could not be exceeded. Therefore, the development, optimization and application of Cd-free nanomaterials for colour conversion purposes, which are compatible to large-scale, environment-friendly manufacturing, is a main novelty of this seed-project. Furthermore, incorporation of these nanoluminophors into controlled scattering medium enables unprecedented colour homogeneity.

In the present project we concentrated our efforts on band-gap emitting InP NCs. Reproducible up-scaling of the synthesis of stable, processable (compatible with silicone or alternative sol-gel matrices) and simultaneously strongly emitting (with QY of >50%) InP NCs is still a challenging task, which is addressed in the ecoDOTs seed-project.

In *this project* the InP/ZnS quantum dots of different sizes has been used successfully to demonstrate the Forster type nonradiative energy transfer in which the experimental results match well together with the theoretical approach based on the exciton-exciton interaction among the donor-acceptor pairs. The experimentally observed lifetime modifications have been found to be well matched with the steady state photoluminescence measurements. Furthermore, the temperature dependent emission kinetics of the donor-acceptor species has also been studied to further have a better understanding of the emission kinetics. The results overall is believed to provide a better insight of the nonradiative energy transfer among quantum dots and the use of the Cd-free dots for innovative optoelectronics and biological applications based on FRET mechanism.

Fig. A shows the emission and absorption spectra of the quantum dots in solution together with the transmission electron microscopy (TEM) image, taken by FEI Tecnai G2 F30 equipment. The donor and acceptor quantum dot diameter is measured to be ~2.4-2.8 nm respectively with a certain size distribution which is also clear from their photoluminescence FWHM. This kind of size variation is common for such kind of III-V quantum dots. The absorption spectra is Stoke shifted from the photoluminescence spectra and the acceptor quantum dot is chosen to be around 100 nm away from the donor emission peak to prevent the emission overlap to some extent.

Our results indicate that the energy transfer efficiency is ~80% (See Fig. B) and is in good agreement with our theoretical model based on exciton-exciton interaction.

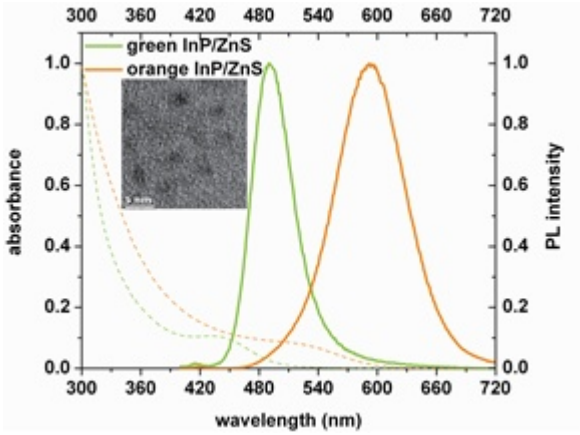

Figure A. Photoluminescence and absorption spectra of the donor and acceptor InP/ZnS quantum dots together with the transmission electron microscopy image (the

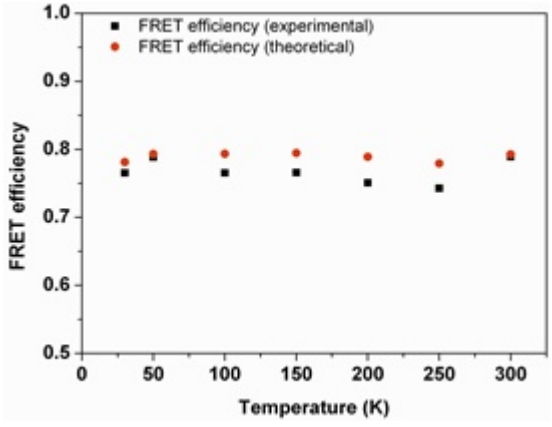

Figure B. Theoretical and experimental FRET efficiency as a function of temperature.

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NON TOXIC NANOCRYSTAL SOLUTION PROCESSED SOLAR CELLS

Partners

The Institute of Photonic Sciences · Gerasimos Konstantatos

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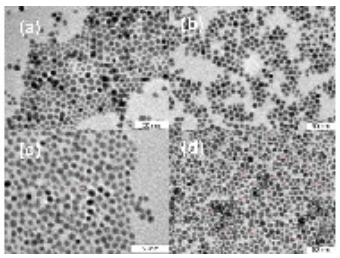
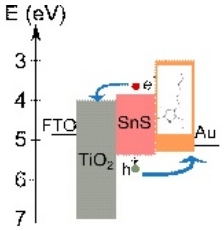
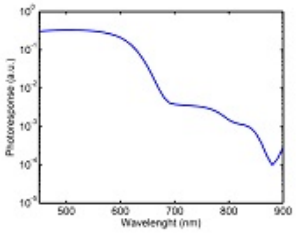
Tin sulfide (SnS) is a 1.4eV bandgap material, very close to the optimum of 1.1-1.3eV for single-junction solar cells, thus being especially suited to harvest to solar energy. Development on colloidal chemical routes for the synthesis of such material enabled its incorporation into roll-to-roll processing techniques such as spraycasting or inkjet printing, which can lower the equipment costs associated to the current photovoltaic technologies. We have incorporated colloidal SnS nanocrystals (NC) into some "traditional" NC-based device architectures, such as depleted or bilayer heterojunction. The former has been reported to exhibit the largest power conversion efficiency among this type of materials, where a porous layer of a large bandgap n-type semiconductor (i.e. titania) allows for the infiltration of the NCs that compose the active area. The latter approach was used to bring together SnS NCs with bismuth sulfide n-type NCs, focusing towards the first all-inorganic environmental-friendly colloidal-based solar cell where the two elements significantly contribute to the overall photocurrent. We have observed photocurrent contribution from SnS NCs in solid state solar cell structures which may open the way towards the development of an alternative material platform towards low-cost, non-toxic nanocrystal solar cells.



TEM images of colloidal Sns nanocrystals



Band diagram of investigated Sns NC based solar cells



Spectral response showing sensitization of polymer-based solar cells in the NIR due to incorporation of SnS NCs

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GLH

GRAPHENE-BASED LIGHT HARVESTING

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Thin metal films and metallic nano-structures exhibit the capability to confine optical fields far below the diffraction limit (surface plasmons: SP). Strongly driven by the recent developments in nanoscale device fabrication, SP-based devices have resulted in a wide variety of applications including light harvesting devices and methods to improve the efficiency of solar cells and biosensors, as well as a medium to tailor the long-range energy transfer between emitters and tailor strongly enhanced interactions between optical emitters and SPs.

Although several fabrication methods are now available for structuring metals at the nanoscale, an extremely high level of control is required to provide reproducible devices with a high level of control over strongly confined optical fields. Moreover the intrinsic properties of the metal are not in-situ tuneable, and the losses associated to strong scattering in metals are detrimental to the device efficiency and capabilities.

Here, we incorporate an atomic-layer of carbon (graphene) as an alternative material for carrying surface plasmon modes and as a medium for extremely efficient light harvesting and to tailor energy transfer between optical emitters. These significant advantages make graphene an excellent candidate for light manipulation and harvesting devices, which can be directly integrated with electronic circuits and PV cells. This project aims at making the first steps towards graphene nano-plasmonics, by studying the interactions between graphene and fluorescent emitters (quantum dots).

The goals of this project are two-fold:

1. We studied the transfer efficiency from the optical energy from quantum dots to graphene (Figure 1)
2. We studied novel type of device integration based on substrate induced doping of graphene

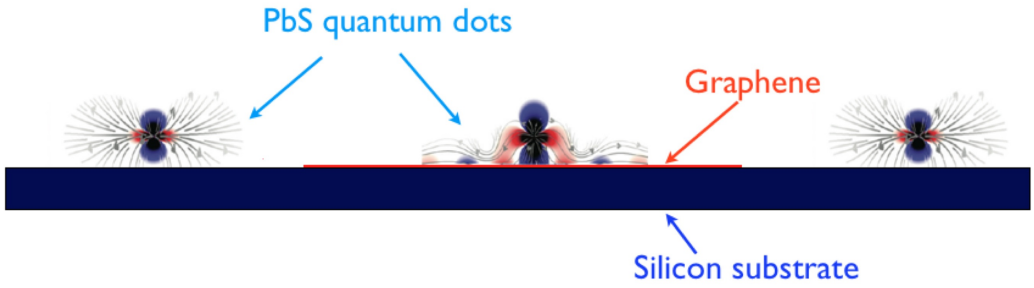

Figure 1: schematic representation of energy transfer from emitters to graphene. The gray lines represent the Poynting vectors. Strong energy transfer to graphene is expected due to the unique properties of graphene.

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Objectives and results

WP1 · Fabrication of high quality graphene devices with nanoscale electronic contacts and gates (Figure 2). The graphene flakes were prepared by the standard mechanical exfoliation technique of highly ordered pyrolytic graphite with tape and deposited on a SiO2 (285nm)/Si wafer. Contacts to graphene were defined by conventional electron beam lithography followed by evaporation of titanium and gold (5 nm / 100 nm). The mobility of the devices was about 1000-3000 cm2/Vs.

WP2 · The synthesis of high quality quantum dots and tuning of their optical properties to match optimal conditions for energy transfer (Figure 2).

PbS quantum dots have synthesized and thin films have been deposited on graphene. The quantum dots on graphene reveal a strong modification of the lifetime, elucidating energy transfer processes between quantum dots and graphene.

WP3 · Integrating graphene devices with ferroelectric materials in order to boost the doping to extremely high levels and suppress plasmonic losses.

We successfully deposited graphene on transparent substrates which show modification of the intrinsic doping of graphene, revealed by transport measurements. Future experiments will elucidate the effects of doping on the near-field interactions between quantum dots and graphene.

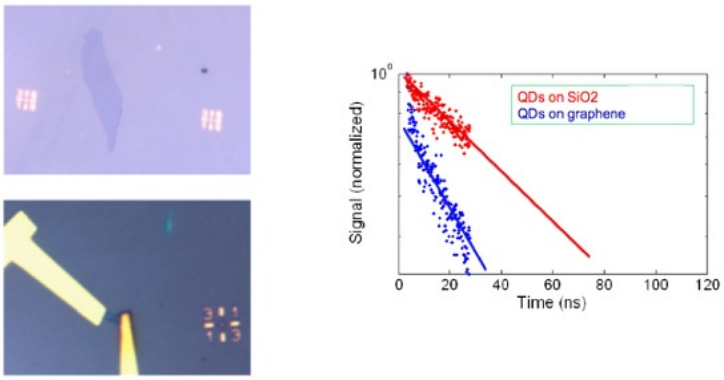

Figure 2: (left) Contacted graphene flakes. (right) Emission lifetime of PbS quantum dots on graphene and silicon

Integration

We have performed lifetime and fluorescence measurements (performed by partner 1) revealing the non-radiative energy processes from quantum dots (synthesized by partner 2) to graphene by excitation of electron-hole pairs in graphene. Theoretical work (by partner 4) elucidated the very rich physics due to the massless character of the charge carriers, the two-dimensionality, and the ability to tune the system from semiconductor to metal. Unusual scaling laws of the transfer processes have been observed. This system is therefore an ideal and novel testbed for studying in-situ tunable energy transfer processes to a unique and tunable system.

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COQUASIHYB STRUCTURES

Colloidal quantum dot - Si Hybrid PV

Partners

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Silicon is one of the most well studied and widely used semiconductors for development of photovoltaic cells. However, as an indirect band gap semiconductor it is characterized by low light absorption and low exciton efficiency. The power conversion efficiency of the commercial photovoltaic modules achieved to date does not exceed 15%. To overcome the existing limitations we follow a hybrid approach, which combines different materials for efficient solar absorption and carrier extraction. Such a hybrid photovoltaic device would be a potentially inexpensive scheme for achieving high-efficiency and low-cost solar-cell platforms.

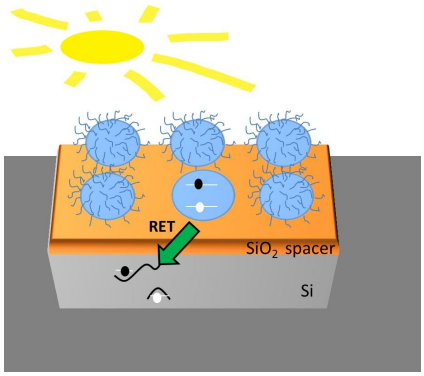

Figure 1: Schematic description of RET mechanism from PbS NCs to bulk silicon substrate

The main objective of this project is to develop and demonstrate a hybrid photovoltaic device, by taking advantage of the optical properties of semiconductor nanocrystals (SNCs) and the mature technology of bulk semiconductors. This device exploits the absorption of solar photons and the creation of excitons from the PbS SNCs to a silicon p-n junction. PbS SNCs exhibit a tunable absorption spectrum, which can be matched to the solar radiation and thus enhance the amount of the collected solar energy. In such devices, SNCs can be used as solar absorbers and their electronic excitation can be transferred from the SNCs to the bulk silicon by means of Resonant Energy Transfer (RET).

We used time resolved measurements for studying the dynamics of PbS NCs and the efficiency of RET from PbS SNCs to bulk silicon. The efficiency of the RET mechanism between the PbS SNCs and silicon is modulated by varying the distance between them. Recent results undoubtedly indicate the occurrence of RET from colloidal SNCs to bulk silicon. Temperature measurements also show that the RET efficiency remains high across a range of temperatures, with a value of 44% at room temperature. Furthermore, we have also fabricated simple prototype devices in order to confirm electrically energy transfer from the PbS SNCs to silicon. Preliminary results show an increase of 12% in photocurrent due to RET at room temperature and are very promising with a view to eventually realizating high efficiency light harvesting devices in a time of ever increasing energy consumption.

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Expected final results and their potential impact and use

The results of this project provide compelling experimental evidence that RET is an efficient mechanism in PbS/Si hybrid configurations with reported efficiency of 44% at room temperature. In collaboration with Q-CELLs such hybrid configurations are now being pursued in completed p-i-n fully nanotextured heterostructures. Any improvement reported on such configurations is expected to impact on the efficiency of x-Si PVs.

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