

Engineering of hybrid heterostructures from organic semiconductors and quantum dots for advanced photovoltaic applications

Sergey Dayneko^{*a}, Marine Tedoradze^b, Mikhail Artemyev^a, Igor Nabiev^{a,c}, Alexander A. Chistyakov^a

^aLaboratory of Nano-Bioengineering, Moscow, Russian Federation; ^bFrumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Moscow, Russian Federation;

^cEuropean Technology Platform "Semiconductor Nanocrystals", Institute of Molecular Medicine, Trinity College Dublin, Dublin 8, Ireland.

ABSTRACT

Semiconductor quantum dots (QDs) are characterized by high extinction coefficients adjustable by varying the nanoparticle size and a high quantum yield of charge generation. They have the advantage of efficient charge transfer from QDs to organic semiconductors. An advanced photovoltaic cell where a SnO₂/ITO electrode is covered with layers of CdSe QDs integrated in a polyimide (PI) organic semiconductor (about 100 nm thick) and Cu-phthalocyanine (20–40 nm thick) has been developed.

Laser-induced photoluminescence analysis has permitted the optimization of the QD concentration in the PI matrix. Special attention has been paid to the electrode surface quality, including the effect of oxygen-plasma treatment of the transparent SnO₂/ITO electrode surface on the heterostructure photoconductivity. The mechanisms of excitation and charge transfers from QDs to the organic semiconductor and their effects on the efficiency of solar radiation conversion to electricity are discussed. Photovoltaic study of the structures developed has been performed, and the effect of the Cu-phthalocyanine layer on their photoconductivity has been estimated. The photovoltaic efficiency of optimized PI–CdSe hybrid structures approaches that of the best performing systems based on the MEH–PPV organic semiconductor.

Incorporation of CdSe QDs in MEH–PPV has been demonstrated to increase the photovoltaic efficiency of the system by 50%, thus allowing the development of novel QD-based inorganic/organic hybrid materials with considerably improved photovoltaic properties.

Keywords: hybrid materials, nanocrystals, photovoltaics, photoluminescence, organic semiconductor, quantum dots, solar cells.

1. INTRODUCTION

Interest in CdSe and CdSe/ZnS semiconductor nanoparticles is mainly determined by strong dependence of their optical properties (the absorption and luminescence spectra) on their size¹. By controlling the sizes of the nanoparticles, one can obtain structures whose luminescence spectra cover the entire visible range². On the other hand, modern methods of colloidal chemistry make it possible to synthesize nanocrystal assemblies with a size variation no more than 5% and correspondingly narrow luminescence bands^{3,4}.

The possibility of incorporating nanoparticles into novel composite materials for optoelectronic devices^{5–7}, such as light-emitting diodes⁸ and photovoltaic cells^{9,10}, has been paid much attention recently^{11–14}. Nanoparticles incorporated in various matrices have been demonstrated to retain most their properties determined by size quantization¹⁵, which makes the use of nanocomposite structures based on organic semiconductors and nanoparticles a promising approach to the development of novel materials for optoelectronics¹⁶. In addition, organic semiconductors are inexpensive and highly processable; therefore, nano-organic hybrid materials that could help to solve the important problem of solar electric energy generation are not expected to cost much^{17,18}.

* s.daineko@gmail.com

Two materials, donor and acceptor, are required for efficient operation of an organic photovoltaic cell¹⁹. Note that the spectral sensitivity range of polymeric solar photovoltaic cells (SPVCs) can be substantially extended by selecting the acceptor component with a strong absorbance in the solar spectral region that overlaps with the optical gap of the conjugated polymer. Inorganic nanoparticles are good candidates for the role of such acceptors²⁰. By varying the size of nanoparticles, one can adjust the electron states and energies of frontier orbitals so as to ensure efficient absorption in the band gap of the polymer and charge separation, respectively, which considerably improves the photoelectric characteristics of nano-organic hybrid materials^{21,22}.

Heterostructures containing nanocrystals of the CdSe and CdSe/ZnS types have recently been used to obtain nanostructured interfaces and simultaneously enhance photogeneration of carriers^{22,23}. These heterostructures may represent organic semiconductors with CdSe nanocrystals distributed within them or sandwich structures entirely consisting of semiconductor nanocrystal films²³. Nanocrystal films are comparatively easy to fabricate, and the technologies for producing structures based on organic semiconductors are well-developed²⁴. This allows inexpensive photovoltaic cells with an energy conversion efficiency as high as 4% to be manufactured²⁵. In general, semiconductor nanocrystals are promising for the use in SPVCs, because the so-called exciton multiplication effect²⁶ allows them to exceed the 30% Shockley–Queisser efficiency limit of p–n junction solar energy converters²⁷.

In developing SPVCs with a high energy conversion efficiency, special attention should be paid to the optimal selection of the nanocomponents of the heterostructure²⁸. The right choice of the quantum dot (QD)–organic semiconductor pair is crucial²⁹. The semiconductor macromolecules should facilitate the dissociation of the exciton formed in a QD upon absorption of a photon and ensure efficient charge (electron or hole) transfer from the QD to the molecule of the organic semiconductor³⁰. Poly(p-phenylene vinylene)s, e.g., poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV), and polythiophenes, e.g., poly(3-exylthiophene) (P3HT), are the most promising organic semiconductors to be used together with QDs of the CdSe type³¹. On the other hand, semiconductors of the polyimide (PI) type are of special interest because they are resistant to temperature and oxidation, which may considerably simplify the technology of fabrication of nanohybrid photovoltaic structures.

This study was the first to use a PI semiconductor for developing a photovoltaic cell based on a nano-organic hybrid heterostructure. We designed a photocell where an ITO electrode was covered with a 20- to 40-nm layer of Cu-phthalocyanine (CuPc) and a 100-nm layer of CdSe nanocrystals incorporated in PI organic semiconductor. After optimization, the photoefficiency of this hybrid structure proved to approach that of the best performing systems based on organic semiconductors of the MEH-PPV type known to date. We also demonstrated that incorporation of CdSe nanocrystals into the MEH-PPV organic semiconductor increases the photoefficiency of the system by 50%, thereby offering new possibilities for development of nano-organic hybrid systems with improved photovoltaic characteristics.

2. MATERIALS AND METHODS

We used CdSe nanoparticles whose surface had been covered with trioctyl phosphine oxide (TOPO) in the course of their synthesis from organometallic compounds by colloidal chemistry methods³². TOPO is a surfactant and is known to substantially decrease the efficiency of spatial charge transfer from QDs to the organic semiconductor³³. Therefore, nanocrystals thoroughly cleared of TOPO were used for obtaining nanocomposites. The nanocrystals were cleared of the surfactant as follows. The surfactant-covered nanoparticles were dissolved in 200 μ l of chloroform. After that, 800 μ l of ethanol was added to the solution, which caused precipitation of nanoparticles because they lost the surfactant molecules. To separate the dissolved surfactant from the precipitated nanoparticles, the solution was centrifuged at 10,000 rpm for 5 min. The supernatant containing TOPO was rejected, and the purification procedure was repeated. We empirically determined the number of the purification cycles after which the nanoparticles still could be dissolved after the sedimentation (two or three cycles were usually the optimal number). Thus, after several cycles of nanocrystal purification, we obtained a solution of nanoparticles without TOPO on their surface.

Nanocrystals were incorporated into an organic semiconductor matrix as follows. The nanoparticles cleared of the surfactant and sedimented as described above were dissolved in tetrachloroethane containing an organic semiconductor. The solution was sonicated to enhance the mixing of the nanoparticles and the organic semiconductor. We empirically adjusted the organic semiconductor concentration in the solution so that homogeneous matrices of the same thickness were obtained. This concentration proved to be several milligrams per milliliter.

The organic semiconductor solution was prepared in advance, because it took several days to dissolve the substance completely. The main organic semiconductor used in the study was PI, whose structural formula is shown in Figure 1A.

for by the transfer of electrons or holes from QDs to organic semiconductor molecules. Thus, the quantum yield of luminescence characterizes the efficiency of the spatial charge transfer in the nanocomposite. It should also be noted that intense laser radiation is suitable for exciting luminescence with such a low quantum yield; therefore, the use of a YAG:Nd³⁺ (2 ω) laser allowed us to obtain and process luminescent signals with a sufficiently high signal-to-noise ratio. This was further facilitated by the excitation of nanocrystals precisely to the first level of size quantization with a relatively long-wave radiation ($\lambda = 532$ nm), because it induced only weak background luminescence of the polymeric matrix. Figure 3 shows the normalized luminescence spectra of films of organic semiconductors (PI and MEH-PPV) and QDs (CdSe nanoparticles). Since the luminescence spectra of MEH-PPV and QDs overlap, subsequent spectral luminescence experiments were performed with PI-based hybrid nanocomposites.

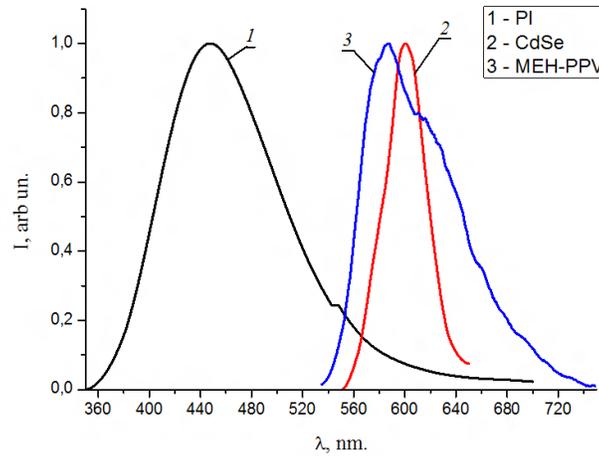


Figure 3. Normalized luminescent spectra of a polyimide (PI) film at an excitation wavelength of 266 nm, poly[2-methoxy-5-(2-ethyl-hexyloxy)-1,4-phenylenevinylene] (MEH-PPV) film at an excitation wavelength of 532 nm, and CdSe nanoparticles at an excitation wavelength of 532 nm.

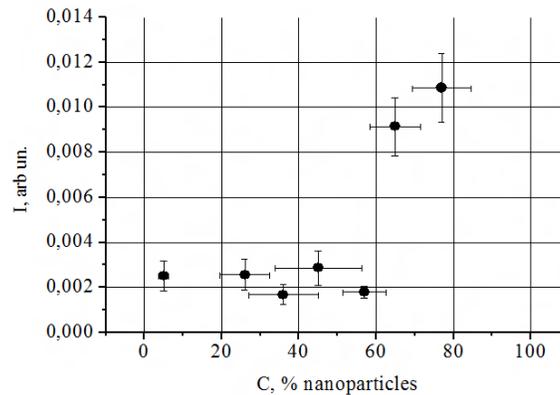


Figure 4. Dependence of the CdSe nanoparticle luminescence intensity per unit concentration of the nanoparticles on their absolute concentration in the polymeric matrix (excitation wavelength, 532nm).

Figure 4 shows the dependence of the relative quantum yield of nanoparticle luminescence on their concentration in the PI semiconductor matrix. The QD luminescence quantum yield remained constant as the nanoparticle concentration increased to ~60% and drastically rose with further increase in their concentration. The rise of the quantum yield at high nanoparticle concentrations, unexpected though it might seem, may be explained by a tendency towards clustering of nanoparticles (cleared of surfactant) when they were still in the solution from which the composite was formed. Our data

on light scattering under the same conditions as in this experiment³⁴ support this explanation. The quantum yield of luminescence of nanoparticle clusters is close to that of films, which, as noted above, is two orders of magnitude higher than the quantum yield of CdSe nanoparticles in an organic semiconductor matrix. Thus, clustering of even a small proportion of nanoparticles in the organic semiconductor matrix may considerably increase the mean quantum yield of CdSe nanocrystal luminescence mainly because of a decrease in the efficiency of electron or hole transfer from the nanocrystal to the organic semiconductor.

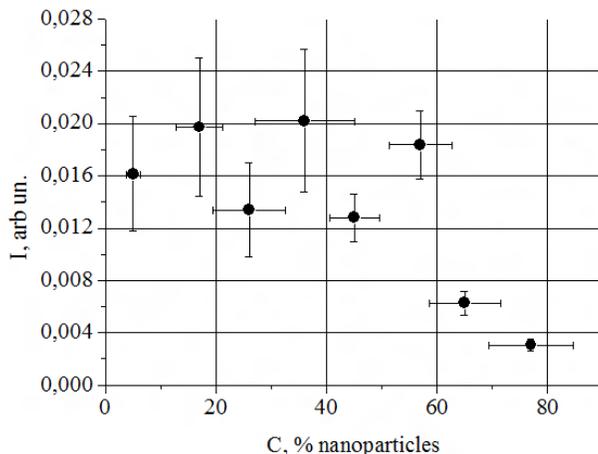


Figure 5. Dependence of the polyimide (PI) luminescence intensity per unit concentration of PI on the CdSe nanoparticle concentration (excitation wavelength, 266 nm).

Figure 5 shows the dependence of the relative quantum yield of PI luminescence excited with 266-nm laser radiation on the nanoparticle concentration. This quantum yield also remained constant as the nanoparticle concentration increased to ~60%, but it dropped at a higher concentration. Indeed, excitation of an organic semiconductor consists in the formation of excitons with a characteristic free path of about 10 nm, QDs serving as dissociation and nonradiative recombination centers for them. When the nanoparticle concentration in the organic semiconductor matrix reached ~60%, the mean distance between QDs was shortened to ~10 nm; hence, the probabilities of dissociation and nonradiative recombination of excitons increased, which was expressed in a decreased luminescence quantum yield. Clustering of nanoparticles also increased the efficiency of nonradiative processes. In addition, note that the mechanical properties of films containing CdSe nanoparticles are substantially deteriorated at a nanoparticle concentration higher than 60%, which makes them unsuitable for the heterostructures in question. Thus, a nanoparticle concentration of about 60% in matrices of organic semiconductors of the PI type is optimal for photovoltaic cells.

4. CONDUCTIVITY AND PHOTOCONVERSION

In the ITO/CuPc/PI:CdSe/Al photovoltaic cell developed in this study, the intermediate CuPc layer plays a crucial role in the transport of holes from the PI semiconductor containing QDs to the transparent electrode. In the case of MEH-PPV, this layer merely increases the current by ~10%; however, a PI-based photovoltaic cell cannot operate at all without this layer.

Table 1 shows the short-circuit currents and open-circuit voltages during irradiation of the designed structures from a source of light with a spectrum similar to the solar one at a power density of 10 mW/cm².

Table 1. Performance parameters of the designed structures irradiated with light whose spectrum is similar to the solar one at a power density of 10 mW/cm².

Photovoltaic cell	I_{sc} , μA	V_{oc} , V
ITO/CuPc/PI:CdSe/Al	0.08	1.4
ITO/CuPc/MEH-PPV/Al	0.15	1.4
ITO/CuPc/MEH-PPV:CdSe–ZnS/Al	0.15	1.4
ITO/CuPc/MEH-PPV:CdSe/Al	0.23	1.4

The values of short-circuit current show that the photovoltaic characteristics of the cells based on PI are similar to those of the cells based on MEH-PPV. Incorporation of CdSe/ZnS (core/shell) nanoparticles into the structure based on MEH-PPV does not increase the photocurrent, which indicates that the ZnS shell prevents charge transfer. Note that incorporation of CdSe nanocrystals in the organic semiconductor MEH-PPV considerably improves its photovoltaic properties. Thus, QDs are promising not only for extending the range of organic semiconductors suitable for solar cells, but also for substantially improving the photovoltaic properties of the materials that have been successfully used in this field for a long time.

5. CONCLUSION

We have developed a photocell where an ITO electrode is covered with a 20- to 40-nm layer of CuPc and a 100-nm layer of CdSe nanocrystals incorporated in PI organic semiconductor. The photoefficiency of this optimized hybrid structure is close to that of the best currently available systems based on organic semiconductors of the MEH-PPV type.

We have also demonstrated that incorporation of CdSe nanocrystals in the organic semiconductor MEH-PPV, the best organic semiconductor used in photovoltaics thus far, increases the photoefficiency of the system by 50%. This offers new possibilities for development of nano-organic hybrid systems with substantially improved photovoltaic properties.

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