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Nanoscale characterisation of hybrid photovoltaic cells based on C_{61} capped CdSe QDs

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Abstract. Hybrid solar cells based on 1,2 methanofullerene (C_{61}) capped CdSe and poly (3-hexylthiophene) (P3HT) were been investigated through a range of techniques. High resolution transmission electron microscopy (HRTEM) was used to characterize size, morphology and crystal structure of as-grown and C_{61}-capped CdSe quantum dots. Cross sectional lamellar specimens were prepared from full photovoltaic devices using a focused ion beam milling approach. The sections were analysed by high angle annular dark field imaging in scanning TEM mode to determine the morphology of the device, in particular the intermixing of P3HT and capped quantum dots.

1. Introduction

In recent years organic photovoltaic cells based on semiconducting polymers have achieved good power conversion efficiencies, but an improvement of the devices has been demonstrated using polymer blended with fullerene derivates [1,2] or with quantum dots [3]. We have studied a ternary system that includes P3HT, methanofullerene and CdSe quantum dots (QDs). The ratios of C_{61}-capped CdSe to P3HT and C_{61} to CdSe were varied and the macroscopic optoelectronic properties were investigated in solution, using UV-VIS absorption and normalized PL spectra. It was found that incorporation of C_{61}-capped QDs into P3HT increases the total absorbance through the cumulative contributions of P3HT and CdSe. Photoluminescence measurements show that the C_{61} capping induces the quenching of the emission peak typical of CdSe QDs, which suggests a charge-transfer event which effectively competes with radiative recombination of electron and hole in the QD. This is an important prerequisite for photovoltaic behavior, as photo-generated electron-hole pairs can be transferred to the outer circuit through the interconnected carbonaceous network. Prototype solar cells were prepared on ITO coated glass substrates, and tested in a solar simulator. To complement the macroscopic characterization of this novel hybrid solar cell, we performed a detailed investigation of the active components of the device using a range of transmission electron microscopy techniques, aimed at verifying the nanoscale architecture.

2. Experimental methods

CdSe quantum dots were synthesized according to the procedure of *Peng et al.*[4]. QDs growth was carried out by colloidal chemical approach, using dihydrate cadmium acetate as precursor and the native capping agent was substituted with 1,2 methanofullerene C_{61} [5]. Methanofullerene (1,2 mg) was dissolved in 8 ml of 1,2 dichlorobenzene and the solution was added to the oleic acid capped CdSe. The mixture was held at 50 ^{o}C for 6 hours, stirred magnetically and sonicated. The exchange capping procedure was monitored by absorption and photoluminescence spectra. High resolution transmission electron microscopy (HRTEM) was used to characterize size, morphology and crystal structure of CdSe QDs and capped QDs, drop-cast from solution on holey carbon Cu grids. HRTEM images were taken using a JEOL 4000 EX (400 kV acceleration voltage).
Photovoltaic devices were prepared using drop casting method from a 1, 2 dichlorobenzene solution, on a clean ITO glass substrate in a nitrogen atmosphere, and Al contacts were deposited by thermal evaporation. The hybrid solar cells had the following configuration: ITO/TiO_2/P3HT-CdSe C_{61}/Al. A thin cross sectional sample of the solar cell was prepared by Ga ion focused ion beam milling in a FEI Helios FEG SEM/FIB microscope. A 200 kV FEI Tecnai F20 scanning transmission electron microscope (S)TEM was employed to characterize the x-sectional device.

3. Results and discussion

Figure 1(a) shows a typical high resolution TEM image of CdSe QDs. Fast Fourier Transform analysis of the QDs revealed that the CdSe crystallized in the zincblende structure. Some defects in the crystalline structure of CdSe, e.g. twinning, probably due to imperfect growth, are visible. The diameter distribution of CdSe QDs was measured from about 100 nanoparticles, and the resulting histogram is shown in Figure 1(b). From macroscopic absorption spectra obtained from QDs in solution, it is possible to determine the diameter average size of the QDs using the equation proposed by *Peng et al.* [4]. The absorption peak for the QDs was observed at 561 nm (2.21 eV). The two approaches give comparable results: $D_{HRTEM} = 3.12 \pm 0.48$ nm and $D_{Peng} = 3.28$ nm.

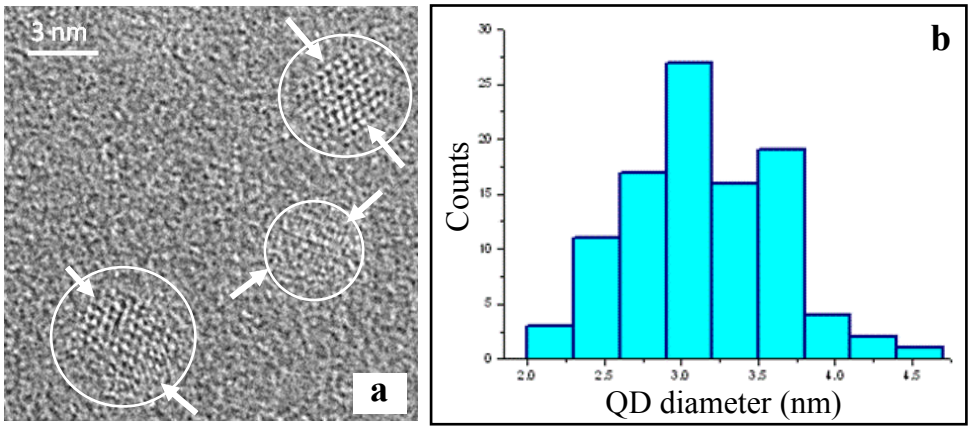

Figure 1. a) Inverted contrast HRTEM image of CdSe QDs, b) Particle size distribution calculated from about 100 QDs.

Figure 2(a) shows a high resolution TEM image of the capped CdSe QDs. The presence of fullerenes is evident on the surface of CdSe QDs. The diameter distribution measured from HRTEM images is displayed in Figure 2(b). The difference between average diameter CdSe QDs and capped CdSe QDs (Fig. 1(b) and 2(b)), is 0.70 nm, which is comparable with the diameter of a C_{60} molecule, and also compatible with (twice) the length of the 1,2 methanofullerene radical. As seen from the photoluminescence spectra in Figure 2(c), CdSe QDs show an emission peak at 571 nm, while capped CdSe QDs do not show any emission, confirming that radiative recombination is suppressed by the capping. This suggests that charge transfer has taken place.

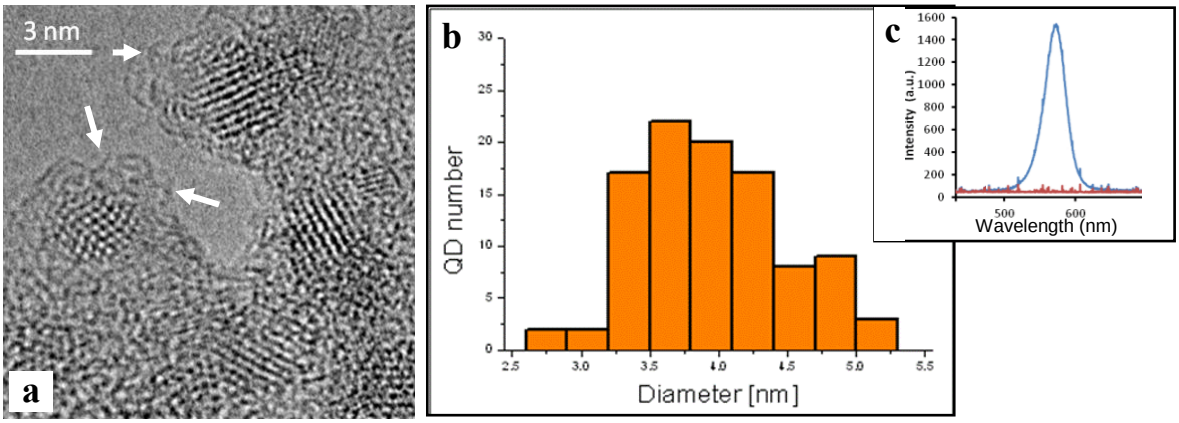

Figure 2. a) HRTEM image of the capped CdSe QDs, with white arrows highliting some of the fullerene molecules, b) Particle size distribution, and c) PL spectra of CdSe QDs and C_{61} capped QDs.

To verify the dispersion of QDs in the polymeric blend, a cross section of the device was prepared by FIB milling. The lamella was mounted on an Omniprobe grid, and thinned to a final thickness of about 150 nm, using low Ga ion currents to reduce Ga implantation. The section, shown at low magnification in Figure 3, was investigated using HAADF STEM imaging. The thickness of the various layers was measured at multiple locations along the section, and the average values are given in Table 1.

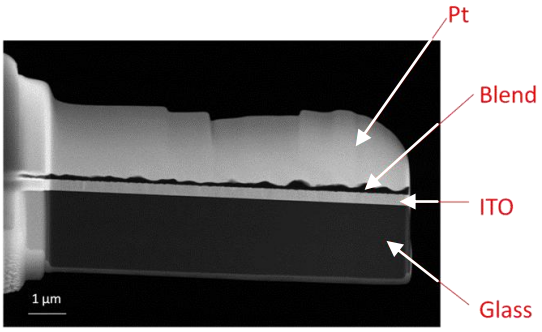

Figure 3. FIB lamella obtained from a complete hybrid solar cell. The Pt layer was deposited to protect the device from the Ga ion beam.

Table 1. Average thickness of the different layers measured from the cross section of the solar cell.

Layer	Thickness (nm)
ITO	300 ± 3
TiO_2	20 ± 2
Blend	140 ± 44

In this type of hybrid photovoltaic cell, CdSe and P3HT are used to absorb light and generate excitons, while a C_{61} network provides a conduction path for the electrons (holes are transported by the P3HT). The distribution and concentration of the nanoparticles within the P3HT matrix play a fundamental role in the functioning of the cell. The best compromise between carrier generation and transport was estimated for the ratios: CdSe:C_{61} 1:3 and CdSe@C_{61}:P3HT 1:1.

Figure 4(a) shows a high magnification HAADF STEM image of the active area of the solar cell obtained for these concentrations. The atomic number (Z) contrast allows us to identify the CdSe QDs easily. The QDs are quite uniformly dispersed in the polymer, with an average distance between particles of 5.57 nm measured in the 2D projections. By evaluating the maximum intensity of the HAADF signal for the QDs in Figure 4(a), we can estimate the projected CdSe thickness within the section, and therefore calculate the number of overlapping CdSe particles in this projection, as shown

in Figure 4(b-c). QDs are assumed to have the same average atomic number. It is interesting to notice that, assuming the lowest intensity corresponds to a single quantum dot of diameter D_{HRTEM}, the highest intensities correspond at most to the overlap of two QDs (2 x D_{HRTEM}) over the thickness of the lamella, which confirms an excellent dispersion of QDs within the polymer matrix.

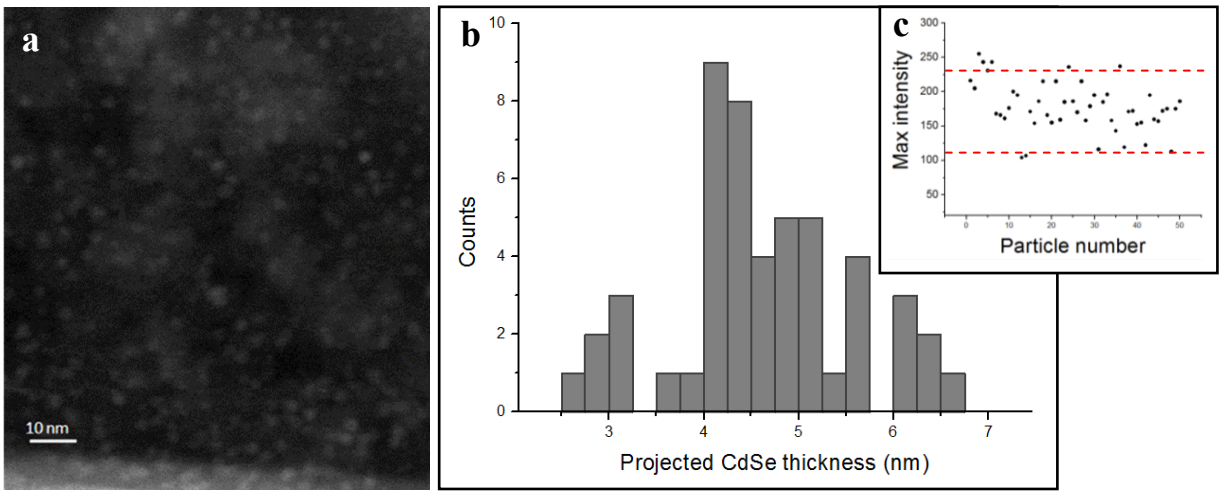

Figure 4. a) HAADF (S)TEM image of the ternary system CdSe/C_{61}/P3HT b) histogram of projected thickness obtained from the intensity distribution of CdSe in the HAADF image, shown in (c).

4. Conclusions

The incorporation of CdSe QDs in a conjugated polymer improves light absorption, as demonstrated by the presence of two absorption peaks in UV - VIS spectra for the composite. Charge transfer processes occur at the interface QDs/ C_{61} and P3HT/C_{61}, as suggested by the quenching effect shown by PL spectra. (S)TEM images demonstrate that individual zincblende CdSe QDs are effectively coated in fullerenes and uniformly dispersed in P3HT, which represents a good compromise between creating large contact area, promoting photon absorption, and aiding charge transport through the device. Recombination processes are not fully understood yet, due to the complexity of the system. Further studies are required to optimized the efficiency of the devices and to improve the knowledge of the physical mechanisms that determine the photovoltaic behaviour of this kind of nanocomposite.

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