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One pot synthesis of bi-linker stabilised CdSe quantum dots

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Abstract. In this study we exploited the classic Murray's synthesis for generating a hydrophilic CdSe quantum dot system in a single step procedure, with the aim of directly obtaining a material responding to the characteristic of polarity required in many end applications. 6-phosphonohexanoic acid was used as both ligand for generating the active monomer during the synthesis of the quantum dots and final stabiliser. Diffraction measurements identified the cubic phase of cadmium selenide. Energy dispersive spectroscopy analysis revealed non-stoichiometric quantum dots, being the Cd/Se ratio 60/40. This feature suggests a configuration in which Cd^{2+} ions are present on the nanocrystal surface. Diffuse reflectance infrared Fourier transform analysis was applied in order to investigate the structure of the quantum dot system: the results indicate a configuration in which the carboxylic function of 6-phosphonohexanoic acid establishes only a partial interaction with the quantum dot surface, being set in a pseudo-ester configuration.

1. Introduction

Semiconductor nanocrystals are attracting a relevant interest because of their potential applications in many domains, spanning from medicine to photovoltaics [1]. The most common synthetic approach relies on the fundamental works by Murray [2] and Peng [3], both based on the La Mer's theory [4] and exploiting a burst reaction in an oversaturated mixture of a cadmium precursor. This approach allows to obtain crystalline quantum dots (QDs) surrounded by an aliphatic shell. In view of end applications, often the native shell has to be substituted by a more suitable stabiliser by means of subsequent ligand exchange reactions. Since semiconductor QDs appear as very promising materials to be used as light harvesters in third generation solar cells [5], a bi-linker ligand ended by a carboxylic group is almost essential because of the capability of this group in interacting with metal oxide surfaces.

In this study we adapted the Murray's synthesis to perform a single step procedure to directly obtain a CdSe QD system stabilised by a bi-linker molecule, namely 6-phosphonohexanoic acid (HPA). The obtained CdSe nanocrystals were tested as light harvester in a solar cell device.

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2. Experimental

2.1. CdSe Quantum Dot synthesis

Standard airless techniques (Schlenk line) were used in the preparation of CdSe quantum dots. In a typical synthesis the Cd precursor is generated in a three-neck 25 ml flask by heating at 360 °C suitable amounts of CdO (4.10 x 10^{-4} mol) as cadmium source, 6-phosphonohexanoic acid (HPA) (8.20 x 10^{-4} mol) as ligand and trioctylphosphine oxide (TOPO) (9.80 x 10^{-3} mol) as coordinating solvent. The selenium precursor is generated under nitrogen atmosphere by stirring Se powder (8.20 x 10^{-4} mol) with trioctylphosphine (4.03 x 10^{-3} mol) and then injected into the reactor at a temperature of 280 °C. The raw material is purified by washing with anhydrous methanol and n-hexane. HPA-stabilised CdSe quantum dots were finally dried under vacuum at room temperature.

2.2. CdSe Quantum Dot characterisation

Diffuse reflectance infrared Fourier tranform (DRIFT) spectra were collected in a Bruker TENSOR 27 spectrometer (32 scans at a resolution of 2 cm^{-1}) and displayed in Kubelka-Munk units [6], [7]. Few milligrams of the sample were mixed with KBr powder and loaded in the accessory for diffuse reflectance (Harrick Scientific). KBr was used as a background. Transmission electron microscopy (TEM) observations were carried out with a Fei Tecnai F20 TEM with a Schottky emitter and operating at 200 keV. The instrument is equipped with an Edax EDS PV9761N SUTW Energy Dispersive X-ray spectrometer (EDX) for X-ray microanalysis. The QDs were dissolved in methanol and the solution dropped and evaporated at room temperature and atmospheric pressure on a copper grid with a holey carbon film for the analyses. The glancing incidence X-ray diffraction (GIXRD) pattern was collected by a Bruker D8 Advance diffractometer equipped by a Göbel mirror at a fixed incidence angle $\theta_i = 0.5°$. The Cu Kα line of a conventional X-ray source powered at 40 kV and 40 mA was used for the experiments. The average crystallite dimensions were evaluated by means of the Scherrer equation. Ultraviolet-visible (UV-Vis) measurements were carried out in a T80 PG instrument (quartz cells, optical path 1 cm).

2.3. Solar cell fabrication and device characterization

A film (3 μm thickness) of TiO_2 nanoparticles (Solaronix) of nominal diameter of 13 nm was deposited by tape casting onto a SnO_2-F glass and fired at 450 °C for 30 minutes in atmospheric ambient. HPA-stabilised CdSe QDs were dissolved in methanol and the solution dropped and evaporated on the photoanode. QD-sensitised cells were prepared using the I^-/I_3^- redox couple and a Pt/ITO coated glass counterelectrode. The functional properties of the cells were investigated under simulated sun light irradiation using an ABET 2000 solar simulator at AM 1.5G irradiation with intensity 100 mW/cm^2, tunable with mechanical filters of different transmittance.

3. Results and discussion

The DRIFT spectrum of the as prepared CdSe QDs is perfectly superimposable to that of the tri-n-octylphosphine oxide used as reaction medium (Figure 1 (a)). A procedure of purification was then carried out in order to eliminate the residual solvent. After the purification the IR spectrum completely changes (Figure 1 (b)) and the profile is more similar to that of HPA. Phosphonic acids are characterised by three adjacent bands in the region from about 1070 to 933 cm^{-1} ascribable to several vibration modes of the $-PO_3H_2$ group, in particular the asymmetric and symmetric stretching modes of $-PO_3^{2-}$ are visible at 1035 and 1005 cm^{-1}, respectively, while the contribution at 968 cm^{-1} is due to P-OH stretching (Figure 1 (b)). The characteristic P=O stretching mode in HPA is visible as a rather, though well distinguished, weak peak at 1211 cm^{-1}. The very intense and sharp peak centred at 1710 cm^{-1} is, instead, characteristic of the C=O stretching mode of the carboxylic group of HPA (Figure 1 (b)). The analysis of the DRIFT spectrum recorded on the purified HPA-stabilised CdSe QDs reveals that the peak due to P=O stretching is disappeared while the whole group of P-O stretching modes results broadened and more defined. Moreover, a shift of ν_{asym} and ν_{sym} of P-O modes is well evident:

the vibrational modes are now centred at 1170 and 1088 cm^{-1}, respectively. These changes suggest a multidentate coordination of the phosphonate group to the CdSe QDs. Concerning the carboxylic function in the spectrum of the purified HPA-stabilised CdSe QDs, besides the band centred at 1710 cm^{-1} due to the stretching of C=O group which is perfectly superimposable to the analogous in HPA, an other contribution at 1548 cm^{-1} is noteworthy. This last signal can be ascribed to the asymmetric stretching vibration of the -C(O)O group. No peaks appear in the quantum dot spectrum due to symmetric mode of -C(O)O group.

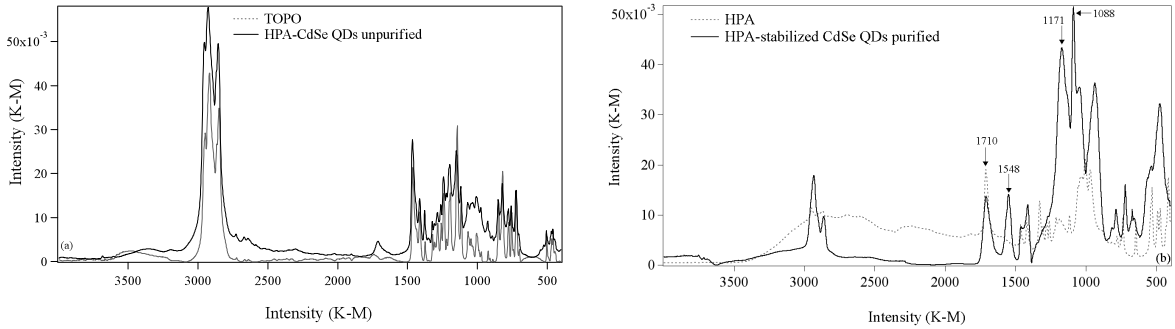

Figure 1: comparison between DRIFT spectra of (a) TOPO (dashed line) and unpurified HPA-stabilised CdSe QDs (solid line) and (b) HPA (dashed line) and purified HPA-stabilised CdSe QDs (solid line).

The obtained results suggest that HPA binds the surface Cd^{2+} ions by means of the phosphonate group: this hypothesis is supported by the re-organization and the global red shift of the vibrational modes of phosphonate group (Figure 1 (b)). On the other hand, the carboxylic function shows the stretching mode of carbonyl unaltered with respect to peak shape and position after coordination and the appearance of the asymmetric vibration of the –C(O)O group, while the O-H stretching mode is almost completely lost, only a shoulder being visible as a minor contribution in the region above 3000 cm^{-1}. When acting as a monodentate ligand, carboxylate group takes an ester-like configuration. In such a kind of configuration, the symmetry of carboxylic function RC(O)O is broken and the infrared spectrum would show the contribution from the stretching of C=O and an asymmetric vibration of the whole group [12]. We then suggest that the HPA molecules allocate all around the nanocrystal in a configuration like that shown in the inset of Figure 2 (c).

Evaluation of particles sizes was performed by means of TEM measurements (Figure 2 (a)), by the full width of half maximum (FWHM) of the XRD peak (Figure 2 (b)) and by the position of the first excitonic peak [8] (Figure 2 (c)). An optimum agreement was found between XRD (2.4 nm) and UV-Vis (2.7 nm) evaluation, whereas the presence of the stabiliser, visible in the micrograph as an amorphous material, could induce the TEM overestimating (5.4 nm) the nanocrystal sizes.

Selected area electron diffraction (SAED) analysis reveals the cubic structure of CdSe (a= 0.6077 nm, S.G: F-43m), also confirmed by XRD measurements. EDX analysis indicates that the quantum dots are non-stoichiometric, showing a molar ratio Cd/Se of 60/40. This finding is coherent with data previously reported by other authors: Moreels [9] and Taylor [10] found indeed similar ratios between the metal M and the counterion E in analogous systems. Recently, Owen [11] proposed a sphere-like structure for these materials, in which Cd^{2+} ions are present on the QD's surface, thus justifying the non stoichiometry. In such a configuration, metal ions can easily interact with the molecules of ligand shell by coordination, thus contributing in stabilising the system.

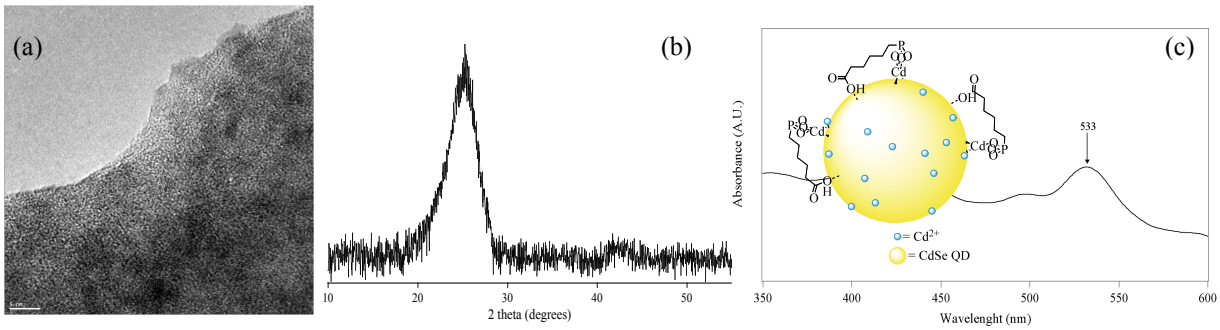

Figure 2: (a) TEM image (scale bar = 5 nm) and (b) XRD and (c) UV-Vis spectrum of HPA-stabilised CdSe quantum dots. (c) Proposed structure of HPA- stabilised CdSe quantum dots. HPA coordinates as a multidentate ligand by employing both the phosphonate and the carboxylate groups.

Preliminary measurements on a QD-sensitised solar cell showed short-circuit current density of 0.75 mA/cm^2 and open-circuit voltage of 0.43 V when illuminated with 100 mW/cm^2 simulated AM 1.5 spectrum, while an optimum Fill Factor was determined (0.64).

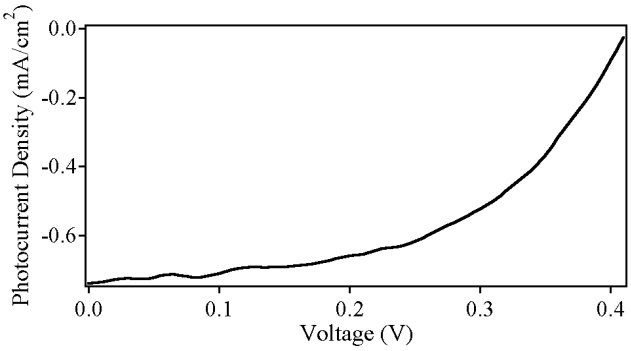

Figure 3: Current-voltage characteristics of QD-sensitised solar cell measured under simulated air mass (AM) 1.5 sun light (100 mW cm^{-2}).

4. Conclusions

The classic Murray's approach to generate crystalline CdSe quantum dots can be easily adapted to the one pot preparation of bi-linker stabilised system, which resulted soluble in polar solvents. Preliminary measurements on QD solar cells showed promising results.

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