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RESEARCH ARTICLE

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Photovoltaic devices from CdSe nanocrystals and conjugated polymer composites

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Abstract The preparation of CdSe nanospheres (ns-CdSe) and their application as electron acceptor in conjugated polymer photovoltaic devices are reported. ns-CdSe with diameters of 5 nm were prepared through an organometallic method. The transmission electron microscopy (TEM), ultraviolet-visible (UV-Vis) absorption and photoluminescence (PL) spectra indicate that the CdSe nanocrystals (NCs) are monodispersed nanospheres with the first exciton absorption peak at around 625 nm and the emission peak at around 652 nm. The PL spectra of the ns-CdSe/polymer composite films show that the PL of the conjugated polymers is effectively quenched upon the addition of ns-CdSe. Photovoltaic devices were fabricated from the composites of ns-CdSe and poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) or poly(3-hexylthiophene) (P3HT). Under AM1.5 illumination (100 mW/cm^2), the short circuit current (I_{SC}), open circuit voltage (V_{OC}), fill factor (FF) and energy conversion efficiency (η) reached 1.56 mA/cm^2, 0.75 V, 34.5% and 0.40%, respectively for device from the ns-CdSe/MEH-PPV (15 : 1 by weight) and 1.93 mA/cm^2, 0.65 V, 38.4% and 0.48%, respectively for device from the ns-CdSe/P3HT (10 : 1 by weight).

Keywords CdSe nanocrystals, conjugated polymer, photovoltaic devices

1 Introduction

Solar energy is one of the important renewable and clean energy sources, while oil and coal are limited, and carbon dioxide from fuel burning is considered as a major source of global climate warming [1]. As one of the possible alternatives to the silicon solar cells, conjugated polymer photovoltaic devices have attracted more and more attention due to their low-cost, simple manufacture process, the potential for large-areas devices and the possibility to be realized on flexible substrate [2−4]. Although device from the conjugated polymer/C_{60} derivatives composite, which is the mostly studied system, has achieved an η of 5% at these days, it still needs to be further improved for the commercial applications [5]. There are mainly two reasons for the low η in polymer photovoltaic devices. First, the carrier mobility is low in polymers and C_{60} derivatives, the reported hole mobility (μ_h) of conjugated polymer is 10^{-1}−10^{-7} cm^2/(V s) and the electron mobility (μ_e) of C_{60} derivatives is 1.0×10^{-2} cm^2/(V s) [6,7], and the electrons and holes are prone to recombie during the transport process. Second, the spectral response of the conjugated polymer is mismatching with solar-terrestrial radiation [8]. The application of inorganic semiconductor nanocrystals (NCs) due to their high electron mobility in replace of C_{60} derivatives in polymer photovoltaic devices has attracted much research interest in recent years. CdSe [9,10], ZnO [11] and GaAs [12] NCs have been introduced into polymer photovoltaic devices.

CdSe is a very important II-VI compound semiconductor and its application has been expanded into the photovoltaic devices [9,10], light-emitting diodes [13] and biolabelling. As for its application in polymer photovoltaic devices, the past research mainly focused on 1-dimensional CdSe nanorods and branched tetrapods, and there was little research on nanospheres, for which the obtained η was very low (~0.1%) [14].

In this paper, high-quality CdSe nanospheres were prepared through an organometallic method [15], and photovoltaic devices were fabricated from the composites of ns-CdSe and conjugated polymers. The η for devices from the ns-CdSe/MEH-PPV and ns-CdSe/P3HT composites are 0.40% and 0.48% respectively.

2 Experimental

2.1 Chemicals and apparatus

Se powder (99.999%) and trioctylphosphine (TOP, 90%) were purchased from Alfa Aesar and Aldrich, respectively.

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Oleic acid (OA, 97%) and 1-octadecene (ODE, 90%) were purchased from Acros Organics. Polyethylene dioxythiophene (PEDOT) was purchased from Bayer AG. All chemicals were used without further purification. Analytical grade of solvents were used in this study.

2.2 Preparation of CdSe nanospheres

Synthesis of cadmium stearate: in a three-necked flask, 0.05 mol of sodium stearate was dissolved in 200 mL alcohol and refluxed, then 0.05 mol of cadmium nitrate dissolved in alcohol was drop-added into the flask and the mixture was kept refluxing for 3 h. The mixture was cooled down, and the white solid was washed by alcohol several times, filtered and dried under vacuum.

A typical synthetic procedure for CdSe nanospheres is as follows: first, 0.395 5 g (0.58 mmol) of cadmium stearate and 10 g of ODE were loaded into a 50 mL three-necked flask and heated to 240°C; then, 1 mmol Se powder dissolved in a mixture of 1.5 g of TOP and 2.5 g of ODE (prepared in a glove-box) was added rapidly into the reaction mixture. Subsequently, 1.16 mmol of OA diluted in 1 g of ODE was added immediately into the mixture. The mixture was stirred at about 220°C under the protection of nitrogen for 1 h. After reaction, the mixture was cooled down to 50°C and precipitated by adding acetone and centrifuged. The CdSe nanocrystals were extracted by hexane, precipitated by methanol and centrifuged for several times, then, the precipitation was transferred into a 250 mL round bottom flask and refluxed in pyridine for 24 h. The product was precipitated and washed by hexane several times, and then, the CdSe nanospheres without surface ligands were obtained.

2.3 Fabrication of photovoltaic devices

Photovoltaic devices were fabricated using a sandwich structure of ITO/PEDOT: PSS[poly(3,4-ethylene dioxythiophene)/poly-(styrene sulfonate)](~100 nm)/ns-CdSe: MEH-PPV (or P3HT) composite (~100 nm)/Al(~150 nm). ITO/PEDOT: PSS was used as the anode, and PEDOT was spin coated with a thickness of 100 nm onto a precleaned ITO substrate and dried by baking in vacuum at 80°C for 12 h. The 30 mg/mL ns-CdSe solution in chlorobenzene and 5 mg/mL MEH-PPV (or 17 mg/mL P3HT) solution in chlorobenzene were thoroughly mixed and spin coated onto the surface of PEDOT, with a thickness of 100 nm. The aluminum cathode with a thickness of 150 nm was subsequently thermally deposited at a pressure of $< 3.0 \times 10^{-4}$ Pa. Devices were encapsulated using epoxy resin in a N_2 atmosphere dry box (Vacuum Atmosphere Co.) and measured under ambient conditions.

2.4 Analysis and characterization

The size and morphology of the ns-CdSe were observed by transmission electron microscopy (TEM) (Hitachi H-7500). The crystal structure was characterized by X-ray powder diffraction (XRD). The absorption spectra were measured by an HP 8453 ultraviolet-visible (UV-Vis) spectrophotometer. The photoluminescence (PL) spectra were recorded on a fluorometer (Jobin-Yvon Fluorolog-3). Energy conversion efficiencies were measured under an AM1.5 solar simulator (100 mW/cm^2). The current-voltage (*I-V*) characteristics were measured with a Keithley 236 source-measure unit.

3 Results and discussion

CdSe NCs were prepared by using cadmium stearate as the precursor, OA as the surfactant and inert solvent ODE as the reaction medium. The TEM image, XRD pattern, UV-Vis absorption and PL spectra of the as-synthesized CdSe NCs are shown in Fig. 1. The samples exhibited a spherical shape with an average diameter of 5 nm, and the nanospheres assembled into regular arrays. The XRD pattern reveals that the sample consists of zinc blende structure, and the peaks at about $2\theta = 25.4°$, 42.0° and 49.7° correspond to the reflection of (111), (220) and (311) planes of CdSe. ns-CdSe exhibits clear absorption and emission features in the near infrared region, the first exciton absorption band is peaked at around 625 nm and the emission band is peaked at 652 nm with a FWHM (full width of half maximum) of 35 nm.

Compared with the TOPO (trioctylphosphine oxide) method, which uses trioctylphosphine oxide as the surfactant [16], the method in this paper possesses the following advantages: (1) the reaction temperature is significantly lowered down, the nucleation temperature can be lowered from 300°C

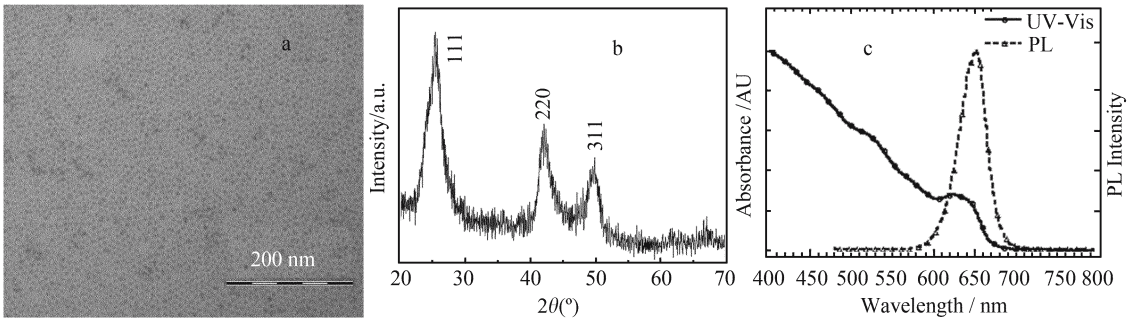

Fig. 1 (a) TEM image, (b) XRD pattern and (c) UV-Vis absorption and PL spectra (470 nm excitation) of CdSe NCs

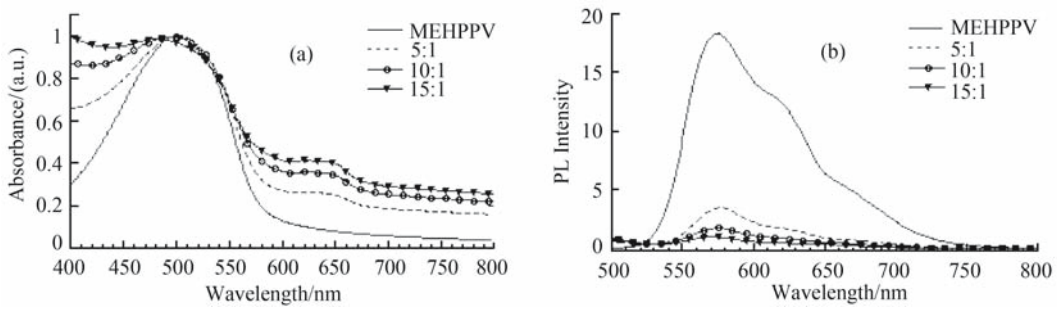

Fig. 2 (a) UV-Vis absorption and (b) PL spectra (470 nm excitation) of ns-CdSe/MEH-PPV composite films. The mass ratios in the spectra correspond to the ratios of ns-CdSe to MEH-PPV by weight in the composites

to 240°C or even lower, which favors the implementation of mass production; (2) the dosage of toxical organic phosphine is greatly reduced in this reaction system; (3) the synthesized NCs possess high quality; (4) the NCs can be dispersed very well in organic solvents such as toluene and chlorobenzene and form high-quality film easily, which is important for blending of NCs with conjugated polymer in the fabrication of photovoltaic devices.

CdSe NCs without surface ligands can be blended uniformly with conjugated polymers. Figure 2 shows the UV-Vis absorption and PL spectra of the composite films (with a thickness of 100 nm) of ns-CdSe and MEH-PPV, the PL intensity was corrected by the absorbance of MEH-PPV in the film of different composition.

In Fig. 2 the absorption peak at about 500 nm originates from the π-π* transition of MEH-PPV, the peak at about 640 nm is the characteristic absorption of CdSe NCs, and the absorption spectrum of the hybrid is the superposition of the two components. Compared with the pure MEH-PPV, the absorption spectra of the hybrids are extended to the near infrared region due to the presence of ns-CdSe. The PL of MEH-PPV can be effectively quenched upon the addition of CdSe NCs. When the mass ratio of ns-CdSe/MEH-PPV is 15 : 1, more than 95% of the PL of MEH-PPV is quenched. The UV-Vis absorption and PL spectra of ns-CdSe/P3HT hybrids are similar to those in Fig. 2. When the mass ratio of ns-CdSe/ P3HT is 10 : 1 or higher, the PL of P3HT is almost completely quenched.

The exciton diffusion length of conjugated polymers is typically about 10 nm [17], sufficient interfaces between the donor and acceptor phases are necessary in order to achieve efficient charge separation. Otherwise, the singlet exciton could decay radiatively to the ground state before reaching the interface and efficient charge separation could not happen. Because the size of the NCs is very small and the specific area is very large, it is possible to form sufficient interfaces between the NCs and the polymers and facilitate highly efficient charge separation. The effective quenching of the PL of the polymers in the above hybrids demonstrates that the excitons separate efficiently at the interfaces between the polymer and NCs, electron transfers rapidly to the NCs, and the hole retains in the polymers.

It is demonstrated that for the ns-CdSe/MEH-PPV composite photovoltaic devices, the best device performance is $I_{sc} = 1.56$ mA/cm^2, $V_{oc} = 0.75$ V, $FF = 34.5\%$ and $\eta = 0.40\%$, respectively, when the mass ratio of ns-CdSe/MEH-PPV is 15 : 1. For the ns-CdSe/P3HT composite photovoltaic devices, the best device was made from the film with mass ratio of ns-CdSe/P3HT = 10 : 1, the I_{sc}, V_{oc}, FF and η are 1.93 mA/cm^2, 0.65 V, 38.4% and 0.48%, respectively. Figure 3 shows the current-voltage characteristics of these devices in the dark and under AM1.5 illumination at an intensity of 100 mW/cm^2.

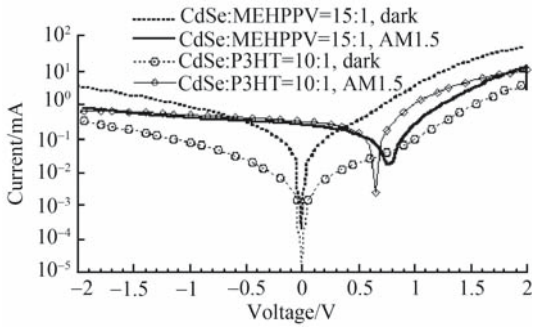

Fig. 3 Current-voltage characteristics of ns-CdSe/MEH-PPV (15 : 1 by weight) and ns-CdSe/P3HT (10 : 1 by weight) composite photovoltaic devices in the dark and under AM1.5 illumination at an intensity of 100 mW/cm

Greenham et al. [14] reported the application of CdSe nanospheres in polymer photovoltaic devices and showed an η of about 0.1%. Much higher energy conversion efficiency in this study might be due to that, oleic acid as the surfactant combines weakly with the surface of the NCs, so it is easy to remove from NCs surface. While in the past reports, the CdSe NCs were prepared by using TOPO as surfactant, the TOPO combined strongly with the surface of the NCs, and it was difficult to be removed completely. The residual TOPO at the NCs surface could reduce the efficiency of charge separation and transport. Although the η here is higher than that in the past report, it is still much lower than devices made from blend of MEH-PPV and CdSe tetrapods ($\eta = 2.1\%$ [18]). Studies for the preparation of CdSe nanorods or branched CdSe NCs by using oleic acid or other surfactants which are bounded less weakly with the CdSe NCs surface is in progress, and results will be reported in forthcoming papers.

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