Research Article

Structural and Optoelectronic Properties of CdSe Tetrapod Nanocrystals for Bulk Heterojunction Solar Cell Applications

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Semiconducting CdSe tetrapod nanoparticles were prepared, and their structural and optical properties were examined. The surface capping molecule, octylphosphonic acid, was replaced with butylamine after the particles synthesis. The exchange of surface ligands changed the physical properties of the nanocrystals, which resulted in a slight decrease in the nanoparticles size. The effects of changing surface ligands of CdSe tetrapod nanocrystals on the structural and optoelectronic properties were investigated, and it was found that the surfactant of nanoparticles could affect the device performance by enhancing the charge carrier separation at the active layer interfaces. Power conversion efficiency of the bulk heterojunction solar cells having the structure of glass/ITO/PEDOT:PSS/(CdSe+PCPDTBT)/Al was improved from 1.21% to 1.52% with the use of ligand-exchanged nanoparticles.

1. Introduction

Bulk heterojunction solar cells (BHJ) based on blends of semiconducting nanocrystals (NCs) and conducting polymers have attracted considerable attention owing to their low cost, simple processing, and ability to dissolve each component to obtain composite layers optimized for solar energy conversion [1, 2]. Currently, polymer-fullerene solar cells and polymer solar cells have reached power conversion efficiencies (PCEs) of approximately 7.4% [3] and 8.62% [4], respectively. Solar cells with the fullerene replaced with semiconducting inorganic nanoparticles (NPs) as the electron acceptors are called hybrid BHJ solar cells [5]. Although the PCEs of hybrid BHJ solar cells are lower than those of fullerene-based BHJ cells, they have the potential to show better performance, because NPs have a high absorption coefficient, high intrinsic charge mobility, and can be synthesized into various shapes (sphere, rod, elongated sphere, tetrapod, etc.) with size of 3 to 100 nm, desirable exciton dissociation characteristics, percolation pathway development, and charge transport properties [6–11]. CdSe NPs are one the most selected materials owing to their well-established synthesis method [12, 13]. CdSe NPs also act as good electron acceptors in combination with the commonly used semiconducting polymers [14]. The effects of the various processing conditions, shapes of the nanocrystals, and surfactants used during synthesis as well as the semiconducting polymers selected were investigated intensively [15].

The first hybrid BHJ solar cells using mixtures of semiconducting polymer and inorganic nanocrystals were reported in 1996 by Greenham et al. [1], who found that the addition of CdSe nanoparticles to polymers in devices relied on the ability of the nanoparticles to disperse within the polymer to make larger interfacial surface area for carrier transfer between the two materials and to improve continuous pathways to the contacts. Hybrid BHJ solar cells based on blends of CdSe tetrapods and polymers have been reported to show the efficiency of 3.13% (Dayal et al.) [14], and their devices contained a low-band gap polymer, poly[(2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']-dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT), and CdSe nanocrystals. The improved cell efficiency of this world’s best CdSe hybrid BHJ solar cell was attributed to the enhanced sunlight absorption from the PCPDTBT polymer and improved charge collection by the CdSe tetrapod nanostructures. The effects of the surface ligand of CdSe
nanoparticles on the device performance have also been reported [16], which have been investigated to engineer the nanoparticle/polymer blend's morphology and phase separation behavior. Surface ligands on the nanoparticles can act as traps for charge carrier transport or can dominate the nanoparticles' electrical properties by occupying surface electronic states or acting as insulators that reduce charge transport [17]. The properties of surfactant could affect the cosolubility of CdSe/polymer blends in solvents and also affect the optoelectronic properties of the active layer.

This work discusses mainly the structural and optoelectronic properties of synthesized CdSe tetrapod nanocrystals. Furthermore, the effects of surface ligand modification on the physical properties of CdSe NPs and surface morphology of the CdSe/polymer active layer were investigated, and the improvement of the bulk heterojunction solar cell performance has been demonstrated as a result of the nanoparticles' surface ligand exchange.

2. Experimental

CdSe tetrapods were synthesized using the method reported elsewhere [14]. In detail, 0.7 g of cadmium oxide (CdO), 5.2 g of trioctylphosphonic acid (TOP), and 2.14 g of octylphosphonic acid (OPA) were heated to 300°C in a two-necked flask under a nitrogen (N₂) flow. When the color of the cadmium solution turned colorless, the heat was removed and the solution was kept under a nitrogen flow. The selenium precursor was prepared by mixing 0.84 g of selenium (Se) with 2.54 g of tributylphosphine (TBP) in 0.6 mL of toluene and cooled in a refrigerator for 20 min prior to the injection. After 48 hrs, the cadmium precursor was reheated to 300°C, and the selenium precursor was injected rapidly at 300°C. The tetrapods were grown at 250°C for 50 min. The synthesized CdSe tetrapods were washed 5 times with a mixture of toluene and ethanol to remove the excess capping ligands and centrifuged 5 times. After the synthesis, the OPA ligands of as-synthesized OPA-capped CdSe tetrapods were replaced with butylamine (BA) ligands using a liquid-liquid exchange procedure.

The ultraviolet-visible spectroscopy (UV-vis), photoluminescence (PL), X-ray diffraction (XRD), and transmission electron microscopy (TEM) were used to characterize the structural and optical properties of the CdSe nanotetrapod particles. FT-IR spectra of ligand-capped CdSe tetrapod nanoparticles were obtained using 1.0 cm path length quartz cells. The samples were prepared by dispersing the nanoparticles in ethanol before the measurements. The photoluminescence (PL) was measured using a custom-made PL system at room temperature using 488 nm (argon laser) as the excitation source. The nanocrystal structure was measured using powder X-ray diffraction (XRD) on an MPD PANalytical, using CuKα radiation. The size and shape of the nanocrystals were estimated with a high-resolution transmission electron microscope (HR-TEM, H-7600).

Active layer for BHJ solar cells was formed from the blends of tetrapod NPs and semiconducting polymers. ITO-coated glass substrates were cleaned sequentially with trichloroethylene (TCE), acetone, and methanol for 10 min in an ultrasonic bath. They were then treated in a nitrogen plasma chamber at 50 W for 10 min to improve the surface properties. A thin (~70 nm) layer of poly(ethylene dioxythiophene) doped with poly(styrene sulfonic acid) (PEDOT:PSS, Sigma Aldrich) was spin-coated on the cleaned ITO-glass substrates at 4000 rpm for 30 s and dried at 100°C for 30 min. The CdSe nanoparticles (with different surface ligands) and PCPDTBT blends were first prepared in chlorobenzene. Approximately 150 ± 5 nm thick photoactive CdSe/PCPDTBT layers were deposited by dropping the blends and spin coating them onto the substrates at 4000 rpm for 30 s. The films of (ITO/PEDOT:PSS/(CdSe+PCPDTBT)) were treated thermally for 10 min on a hot plate in a nitrogen glove box at 150°C. The structural properties and surface morphology of the active layers were investigated systematically using a range of techniques including atomic force microscopy (AFM) and scanning electron microscopy (SEM). The bulk heterojunction solar cells having glass/ITO/PEDOT:PSS/(CdSe+PCPDTBT)/Al structure were fabricated. A 100 nm thick Al electrode was added to the top of the photoactive layers by thermal evaporation to complete the device structure. The current density-voltage (I-V) characteristics were investigated under AM1.5G illumination by a solar simulator (Keithley 699II).

3. Results and Discussion

Figures 1(a) and 1(b) show TEM and HR-TEM images of the as-synthesized CdSe nanocrystals (NCs). A large fraction of branches was obtained without selective precipitation, which shows that the tetrapods had been formed. The tetrapod limbs were approximately ~26 nm long and ~7 nm thick. Figure 1(b) shows the lattice fringes of the CdSe tetrapods with fringe spacing of 0.34 nm, corresponding to the (002) planes for the wurtzite structure of CdSe [18].

OPA-capped CdSe nanoparticles (NPs) were first synthesized, and the NPs' ligands were replaced from OPA to butylamine. The various cappings of the CdSe NPs with different surface ligands were confirmed by FT-IR spectroscopy as in Figure 2. The intense symmetric C–H stretching vibrations of the –CH₂– groups at 2948 and 2848 cm⁻¹ and a shoulder band of asymmetric stretching of the terminal –CH₃ group at 2956 cm⁻¹ can be associated with the alkyl chain of OPA as illustrated in Figure 2(a). The IR bands at 1456 and 1402 cm⁻¹ can be assigned to the –CH₂– bending vibration and the C–O–H bending vibration [19, 20]. The band at 1017 cm⁻¹ is indicated as the P–O–H bond, which is similar to the FT-IR analysis of OPA ligand [21]. However, the peaks at 2956 and 1017 cm⁻¹ of the OPA ligand were non-existent in Figure 2(b), meaning that the OPA ligand was replaced by the BA ligand after the ligand exchange process. The presence of butylamine is shown by the peak at ~3700–3781 cm⁻¹, which corresponds to the N–H stretching vibration modes [8, 22]. The structure of CdSe tetrapods (Tpods) was confirmed by X-ray diffraction as shown in Figure 3. Comparison of the XRD patterns of as-synthesized nanocrystals with those of...
Figure 1: (a) Transmission electron microscopic image and (b) high-resolution transmission electron microscopic image of CdSe tetrapod nanocrystals.

Figure 2: FT-IR spectra of (a) OPA-capped CdSe tetrapods (T pods) and (b) BA-capped CdSe T pods.

bulk CdSe crystals showed that the as-synthesized CdSe had a hexagonal wurtzite structure (ICDD-JCPDS: CdSe #00-019-0191) [23] with the arms elongated in the (002) direction. The diffraction peaks due to the reflections from (103), (100), and (101) were assigned as wurtzite phase related peaks. The (103) diffraction peak is significantly broader than the (100) and (101) peaks. This is consistent with the XRD data from the bulk tetrapod nanocrystals [24–27], which showed a more intense and narrow diffraction peak at the 2θ values of ~24 and ~27°, that is, consistent with the tetrapod limb in the c-axis direction of the wurtzite phase.

Figures 4(a) and 4(b) show the optical properties of the OPA-capped CdSe tetrapods determined by UV-vis and PL measurements. The CdSe nanocrystals were dispersed in ethanol prior to the spectroscopic measurements. The absorption edge of the UV-vis spectra was ~547 nm, and the emission peak of the PL spectra was ~593 nm (band gap energy ~2.09 eV). The effects of ligand exchange on the optical properties of the nanoparticles were investigated by UV-vis and PL, and the results are shown in Figures 5(a) and 5(b). After the ligand exchange from OPA to butylamine, the absorption edge of the UV-Vis spectra was shifted to a shorter wavelength from 547 to 542 nm, as shown in Figure 5(a), and the intensity of the emission peak of the PL spectra was decreased and shifted towards a higher energy from 2.09 to 2.14 eV, as shown in Figure 5(b). The shifting of the absorption edge and emission peak toward a shorter wavelength is often called a “blue-shift,” which may be due to the quantum confinement effect caused by the decrease in nanocrystal s’ size [28, 29]. The luminescence intensity from the smaller nanocrystals is likely to be much stronger, because smaller-sized nanocrystals possess a larger
surface-to-volume ratio than larger-sized nanocrystals, and most of the photo-generated charge carriers undergo recombination at the surface vacancies. The sizes of the nanoparticles before and after the ligand exchange were measured by HR-TEM, and it was found that the size of the BA-capped CdSe tetrapods was smaller than the OPA-capped ones (data not shown here). This result is consistent with the peak shifts of UV-vis and PL spectra.

The effects of the surface ligand exchange of the CdSe tetrapods on the morphological properties of the CdSe/polymer film for bulk heterojunction solar cell applications were also investigated. The poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[1,2-b:3,4-b’]-dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT) was used as a light-absorbing and electron-donating material. The semiconducting OPA- or BA-capped CdSe nanoparticles were used as electron acceptors. Figures 6(a) and 6(b) show the SEM images of the surface of a composite film of OPA- or BA-capped CdSe and PCPDTBT with a loading of 5 mg/mL and the CdSe tetrapod concentration of 70 wt.%. The surface of the film with a BA ligand was much smoother than that with the OPA ligand. Figures 6(c) and 6(d) show the AFM images of the surface morphology of the composite films. The surface roughness of the composite films was both smooth and homogeneous, and the surface roughness of the film with BA-capped CdSe (∼1.69 nm) was smoother than that of the OPA-capped CdSe (∼2.52 nm). A smoother surface of the film with the BA-capped CdSe tetrapods was believed to be caused by the smaller particle size of the BA-capped CdSe tetrapods and the positive effects of butylamine in the dispersion characteristics of the nanoparticles in the solvents [30]. The rough surface was considered to be the self-organization signature of the polymer, and the solar cell devices generally showed higher efficiency on a smooth surface than on a rough surface [31].

The J-V curves of BHJ solar cells fabricated by using the CdSe nanoparticles capped with various surface ligands
with the optimal composition of 70 wt.% CdSe in the CdSe/PCPDTBT composite layers were recorded and shown in Figure 7 along with the device parameters. Power conversion efficiency ($\eta$) was improved by changing the surfactant from OPA ($\eta \sim 1.21\%$) to BA ($\eta \sim 1.52\%$) mainly due to the increase of current density ($J_{sc}$: 2.73 (OPA) to 3.41 (BA)), improvement of the surface morphology (RMS) from OPA-sample ($\sim 2.52\,\text{nm}$) to BA-sample ($\sim 1.69\,\text{nm}$), and increase of charge carrier separation at the polymer/nanoparticle interface which is observed in the quenching of photoluminescence intensity [8, 32]. Efficient separation of charge carriers prevents radiative recombination and thus quenches the photoluminescence of the nanoparticles and polymer components. The blue-shifting of the photoluminescence was also recorded when OPA was replaced by butylamine, which could be a potentially useful method of increasing charge carrier separation at polymer/nanoparticle interface in the BHJ solar cells. The BHJ solar cells made of CdSe with BA-capping ligand showed the best performance ($J_{sc} \sim 3.41\,\text{mA/cm}^2$, $V_{oc} \sim 0.72\,\text{V}$, $FF \sim 61.8\%$, and $PCE \sim 1.52\%$). The power conversion efficiency of BHJ solar cells fabricated in this study was, however, still relatively low compared with that of world record BHJ solar cells made with tetrapod-shaped CdSe nanocrystals and PCPDTBT polymer [14]. This is possibly attributed to the poorer charge collection due to unoptimized surface morphology and thermal treatment, which might lead to poorer interfacial properties between the polymer and CdSe nanocrystals, creating a phase separation within the active layers. We thus believe that the findings of this study with the PCE values obtained open a new route to improving the BHJ solar cell performance by utilizing another kind of ligands for the CdSe nanoparticles.

4. Conclusions

High-quality CdSe tetrapod nanoparticles were synthesized in this study. A large fraction of branches was obtained without selective precipitation, and the hexagonal wurtzite structure was confirmed. After the ligand exchange from OPA to the BA ligand, the size of the nanoparticles decreased, and the band gap energy increased from 2.09 up to 2.14 eV. The surface roughness of the BA-capped CdSe/PCPDTBT active layer was smoother than that of the OPA-capped CdSe one. The BHJ solar cell performance was significantly improved, showing the power conversion efficiencies of up to 1.52%
Figure 7: $J$–$V$ curves for the devices with OPA-capped and butylamine-capped CdSe tetrapod nanocrystals (CdSe/(CdSe+PCPDTBT) ~ 0.7).

$J_{sc} \sim 3.41 \text{ mA/cm}^2$ under AM1.5G simulated solar irradiation.

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