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Enhanced performance of hybrid solar cells using longer arms of quantum cadmium selenide tetrapods

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We demonstrate that enhanced device performance of hybrid solar cells based on tetrapod (TP)-shaped cadmium selenide (CdSe) nanoparticles and conjugated polymer of poly (3-hexylthiophene) (P3HT) can be obtained by using longer armed tetrapods which aids in better spatial connectivity, thus decreasing charge hopping events which lead to better charge transport. Longer tetrapods with 10 nm arm length lead to improved power conversion efficiency of 1.12% compared to 0.80% of device having 5 nm short-armed tetrapods:P3HT photoactive blends.

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Hybrid solar cells have been developed to combine the attractive attributes of both inorganic thin-film and organic bulk-heterojunction photovoltaics to achieve cost-effective manufacturing with competitive efficiency and potential for flexible device applications.^{1–3} Inorganic colloidal nanoparticles (NPs) can be engineered to have higher carrier mobility and better thermal stability than pristine organic semiconductors, with facile access to bandgap tunability. By controlling the shape and size of spherical quantum dots (QDs) and elongated nanorods (NRs), it has been reported that device performance can be improved.⁴ Perhaps one of the most attractive feature from a device fabrication point of view is that NPs can be fabricated using printing techniques as in QD light emitting diodes (QLEDs).⁵

Among colloidal NPs, intrinsic three-dimensional (3D) architecture of tetrapods (TPs) and hyper-branched NPs allows them to be excellent candidates as an electron acceptor with enhanced electron transport over organic materials.^{6,7} The preference of using TPs over QDs and NRs is due to the overall higher surface area to volume ratio which leads to more electrically desirable and connected paths, thus better electrical transport.^{8–12} Although it is difficult to synthesize more complex nanostructures reproducibly, recent advances have demonstrated low-cost chemical synthesis of TPs with high yields in shape selectivity and dimensional uniformity using surfactant cationic ligands.¹¹ Capitalizing on such advances, we investigate the impact of using two different sizes of cadmium selenide (CdSe) TPs on device performance along with the respective nano-scale morphology of the hybrid CdSe TPs:poly (3-hexylthiophene) (P3HT) layer.

Size-controlled CdSe TPs with selectivity of more than 90% were synthesized following previously published methods.¹¹ Oleic acid (OA) used in the synthesis binds to the TP

surface as a surface ligand coating, giving the TPs stability towards chemical degradation and enhancing colloidal stability in organic solvents. However, due to relatively long length of OA (~ 2 nm), such ligands must be exchanged with shorter ones in order to reduce the inter-particle distances, thereby enhancing the electronic transport of the resulting thin layer incorporating the TPs. In addition, judicious choice of the ligands must be made in order to allow better compatibility when mixed with a specific host polymer in a given solvent.¹³ For this purpose, a pyridine ligand exchange step was carried out prior to device fabrication.

The device structure and thickness of each layer are described in Fig. 1(a). Patterned indium tin oxide (ITO) onto glass substrates, manufactured by Thin Film Devices Inc., were cleaned by sequential ultra-sonication in baths of acetone, methanol, and isopropanol. Immediately prior to device fabrication, ultraviolet ozone (UVO) treatment was used to remove organic residues that might be present on the ITO surface. Hole injection layer of poly (3,4-ethylenedioxythiophene):poly (styrenesulfonate) (PEDOT:PSS, HC Starck Clevios P VP Al 4083) was deposited using spin coating, followed by a

FIG. 1. (Color online) (a) Schematic diagram of device structure and cross-sectional TEM images of hybrid solar cells having (b) Long-armed and (c) Short-armed CdSe TPs:P3HT photoactive layer.

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drying process at 150 °C for 30 min. Respectively, a photoactive layer of CdSe TPs:P3HT (purchased from Rieke Metals, Inc.) in chloroform:pyridine (9:1) solvent mixture was spin-coated and then heat treated at 150 °C for 30 min. Blended layers consisted of 90 wt. % CdSe TPs and 10 wt. % P3HT at 16 mg/ml concentration. In this work, we limited our study to compare hybrid solar cells using long-armed (arm width $\times$ length: ca. 4 nm $\times$ 10 nm) to that of short-armed (ca. 4.5 nm $\times$ 5 nm) TPs. After annealing under nitrogen atmosphere, the samples were loaded into a vacuum chamber, without exposure to ambient room environment. Lithium fluoride (LiF)/aluminum (Al) electrodes were then thermally evaporated at a base pressure of 1×10^{-7} Torr to result in an array of devices each having an active area of 20 mm². Cross-sectional transmission electron microscopy (TEM) images in Figs. 1(b) and 1(c) showed the various layers of our devices as described above.

Current density-voltage (J - V) characteristics were evaluated using a source measure unit (SMU, Keithley 237) and a solar simulator (Spectra Physics Oriel) under the condition of air mass 1.5 global (AM 1.5 G). The illumination intensity was adjusted to be 100 mW/cm² by using silicon photodiode reference cell (Hamamatsu) calibrated by the National Renewable Energy Laboratory. Characterizations of optical properties of ultra-thin photoactive layers with a nominal thickness of 60 nm were carried out using photoluminescence (PL, Horiba Jobin Yvon), absorption spectra (Varian Cary 5000 UV-Vis-NIR spectrophotometer), and quantum efficiency (QE, Optronic Laboratories) measurements. External (EQEs) and internal quantum efficiencies (IQEs) were analyzed in air using an excitation wavelength range of 350 to 700 nm at 10 nm intervals. Cross-sectional TEM samples were prepared on copper (Cu) grids by using focused ion beam (FIB, Philips Nova-200) and TEM imaging of such samples was acquired at 200 kV (Philips CM-200).

Typical J - V characteristics are shown in Fig. 2. The power conversion efficiencies (PCEs) of hybrid solar cells based on long and short-armed TPs are 1.12% and 0.80%, respectively. Devices having long-armed TPs exhibit greater

FIG. 2. (Color online) Current density-voltage (J - V) characteristics of CdSe TPs (90 wt. %):P3HT (10 wt. %) hybrid solar cells (long-armed TPs: black solid line with circles and short-armed TPs: red dotted line with squares). Device parameters are shown in inset.

FIG. 3. (Color online) HREM cross-sectional images (500 kX) of (a) Long (ca. 4 nm $\times$ 10 nm) and (b) Short (ca. 4.5 nm $\times$ 5 nm) CdSe TPs:P3HT photoactive blends. The insets of (a) and (b) show the schematic illustrations of long and short TPs in P3HT matrix.

short circuit current density (J_{sc}) and fill factor (FF) than those of short-armed TPs. These results are consistent with previous reports indicating that longer NRs lead to enhanced PCE due to decreased charge hopping probability.³ Moreover, devices based on long TPs shows a factor of six lower series resistance ($\sim 19.8 \Omega \text{cm}^2$) than that of short TPs ($\sim 121.2 \Omega \text{cm}^2$), strongly supporting that the longer arm length favors better carrier transport pointing to a higher degree of continuous electrical path connectivity than shorter arm TPs. This is further supported by higher open circuit voltage (V_{oc}) of devices having shorter TPs. The higher V_{oc} of short-armed TPs (0.86 V) indicates a possible vertical phase separation or higher degree of aggregation of the short TPs in the blend than that of the longer ones.^{14,15} To further support this notion, high-resolution electron microscopy (HREM) was used. In Figs. 3(a) and 3(b), the TEM image of short TPs shows uniform distribution of nano-scale aggregates and closely positioned lattices as opposed to better connectivity and dispersion in the blends of the longer arm TPs.

Comparison of optical absorption in blended films of long and short-armed TPs with P3HT allows further understanding of the origin of the larger photocurrent generated from devices based on long-armed TPs. Figure 4(a) shows the absorption spectra of mixed TPs:P3HT layers. Blended film having long-armed TPs shows stronger absorption than short TPs over a broad range. The more photons absorbed in the active layer, the larger the photocurrent that can be generated. Annealed P3HT has been reported to contribute effectively to light absorption due to better crystallinity and/or increment in crystalline domain size.¹⁶ The stronger absorption of blends based on long-armed TPs is a possible indicator of a better P3HT ordering and larger domain structure in the blended layer. Furthermore, normalized absorption shows that long-armed TPs have relatively higher absorption than short-armed TPs over the spectral range of 350 to 470 nm in Fig. 4(b). Therefore, larger J_{sc} observed in devices based on long TPs can be attributed, in part, to the increased optical absorption due to morphological reasons aided by the increased length of the TPs.

As depicted in Fig. 4(c), the EQE of short-armed TPs:P3HT blend is lower than that of long-armed TPs. This is consistent with the corresponding absorption spectra. To exclude the influence of optical interference, the IQE is obtained by normalizing the EQE data. The IQE of device based on short-armed TPs:P3HT is lower than that of device

FIG. 4. (Color online) (a) Absorption spectra of blends of CdSe TPs (90 wt. %) and P3HT (10 wt. %). (b) Normalized absorption in blends of long/short TPs:P3HT, P3HT (blue dashed line), and pristine long/short TPs (black solid line/red dotted line). (c) External (EQEs) and (d) IQEs of devices based on CdSe TPs (90 wt. %) and P3HT (10 wt. %). (Black solid line with circles is for long TPs, where red dotted line with squares is for short TPs:P3HT blends.)

made using long-armed TPs:P3HT device in Fig. 4(d), indicating that charge carrier transport is less efficient in short-armed devices. Lower charge transport efficiency decreases not only the QE, but also the FF. The calculated FF of device having short-armed TPs (40%) is less than that of long-armed TPs (46%), which could result possibly from the presence of more recombination pathways and less efficient charge extraction process as evidenced by the higher Rs of short TPs. The aggregated and discontinuous morphology will also decrease the exciton diffusion and dissociation of short-armed TPs:P3HT devices, thus leading to loss in conversion efficiency.

Investigating further the morphological effects on charge transport, we can conclude that smaller TPs experience more hopping chances than longer TPs. Average number of interparticle hopping in long and short-armed TPs between PEDOT: PSS and LiF/Al cathodes are 8.0 ± 0.9 and 10.0 ± 0.8 , respectively. These values are calculated by counting projected TPs from TEM cross-sectional images of real devices shown in Figs. 1(b) and 1(c). Reducing the hopping due to a band-like transport of charges enhances the electron transport of large NPs.⁸ As seen in Fig. 3, long-armed TPs present longer percolation pathway and larger domains of P3HT, than those of shorter arm TPs:polymer blends. This allows for a more favorable hole drift and diffusion in order to minimize exciton recombination events along the charge transport pathways. Isolated and discontinuous clusters of P3HT in short TPs:P3HT blends shown in Fig. 3(b) hinder efficient hole transport towards the ITO electrode, leading to reduced currents.

In conclusion, the arm size of CdSe TPs and the spatial distribution of CdSe TPs:P3HT morphology are critical factors to improve optical and electrical properties of photovoltaic devices. Longer arms of TPs contribute to lower probability of charge hopping and increase the photo-spectral response. The PCE of devices having long-armed TPs is higher than those of short arms. The lower charge transport losses at interfaces

resulting from the formation of continuous percolation pathways in the longer armed devices contribute to enhanced J_{sc} and FF. This implies that controlling 3D morphologies and contact interfaces can be aided by the proper choice of the size of TPs and may lead to better device characteristics.

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