Synthesis of new nanocrystal-polymer nanocomposite as the electron acceptor in polymer bulk heterojunction solar cells

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Abstract

A hydroxyl-coated CdSe nanocrystal (CdSe-OH) and a CdSe-polymer nanocomposite were synthesized and used as the electron acceptors in polymer solar cells (PSCs). The CdSe-polymer composite was prepared via atom transfer radical polymerization (ATRP) of N-vinylcarbazole on functionalized CdSe quantum dots. Physical properties and photovoltaic characteristics of the CdSe-poly(N-vinylcarbazole) (CdSe-PVK) nanocomposite have been investigated. Thermogravimetric analysis (TGA) results displayed higher thermal stability for CdSe-PVK nanohybrid in comparison with the linear-type PVK polymer. Differential scanning calorimetry (DSC) studies indicated that CdSe-PVK had a lower glass-transition temperature (T_g) in comparison with PVK due to the branch effect of the star-shaped polymer hybrid. Cyclic voltammetric (CV) measurements were performed to obtain HOMO and LUMO values of PVK and CdSe-PVK. TEM and SEM micrographs exhibited CdSe nanoparticles were well coated with PVK polymer. Both CdSe-OH and CdSe-PVK were blended with poly(3-hexylthiophene) (P3HT) and used as the active layer in bulk heterojunction solar cells. Polymer solar cell based on CdSe-PVK as acceptor revealed that the photovoltaic properties can be significantly improved when PVK polymer chains were grafted on surfaces of CdSe nanocrystals. In comparison with the P3HT:CdSe-OH system, PSC based on P3HT:CdSe-PVK showed an improved power conversion efficiency (0.02 vs. 0.001%). Film topography studied by AFM further confirmed the better device performance was due to the enhanced compatibility between P3HT and CdSe-PVK.

Keywords: atom transfer radical polymerization; CdSe; nanocomposite; poly(N-vinylcarbazole); polymer solar cell
1. Introduction

Over the past decades, polymer solar cells (PSCs) based on conjugated polymers have attracted considerable attention because of their potential use for future cheap and renewable energy production [1-3]. Efficient polymer-based solar cells utilize donor–electron acceptor (D-A) bulk heterojunction (BHJ) films as active layers [1,2]. The donor is typically a kind of conjugated polymer, while the acceptor is generally a type of organic or inorganic molecule. The D-A BHJ structure enables availability of the acceptor molecules in close proximity to the electron donor polymers, and thereby facilitates charge transfer from excited polymer chains to the electron acceptor molecules. More recently, many bulk heterojunction solar cells based on blends of conjugated polymers and inorganic nanocrystals that offer high electron mobility or improved spectral coverage have been investigated [4-8]. Furthermore, it has been stated that semiconductor nanocrystals (colloidally synthesized quantum dots, QDs) have the potential to increase the efficiency of conversion of solar photons to electricity up to about 66%, and can overcome the efficiency limit caused by carrier thermalization in the conventional solar cells [9]. In particular, spherical semiconductor nanoparticles, such as CdSe quantum dots, have been the subject of extensive studies over the past decade because of their unique optical and electronic properties [10-12]. Since CdSe has high electron mobility, we believe there is much room for further improvement in device efficiency for hybrid CdSe/conjugated polymer photovoltaic devices.

Although CdSe/conjugated polymer solar cells have been studied in several groups [5,13-17], the efficiency of photovoltaic devices is majorly limited by the low compatibility between inorganic CdSe nanoparticles and the conjugated polymers. In other words, application of this CdSe/conjugated polymer nanocomposite in solar cells requires a good dispersion of the CdSe nanocrystals in the polymer donor phase
in order to create a large interfacial surface area for charge transfer between polymer and nanocrystals. On the other hand, several reported studies for the synthesis of CdSe nanocrystals used high toxic and high reactive dimethyl cadmium as the precursor and used hazardous and expensive trioctylphosphine (TOP) or trioctylphosphine oxide (TOPO) as the coordinating solvent. Therefore, it remains a challenge to produce CdSe nanocrystals via an economical and simple method. Herein, we have employed a cheaper and greener Non-TOP-Based approach for the synthesis of in-situ thiol-capped CdSe nanocrystals through a wet chemical route [18-19] in aqueous solution.

Recently, inorganic–polymer nanocomposites have continuously attracted much attention due to their unique size-dependent magnetic, optical, and material properties [20-23]. However, the exploitation of these properties requires a homogeneous dispersion of the inorganic particles in the polymer matrix. The use of atom transfer radical polymerization (ATRP) technique would conduct a controlled/”living” radical polymerization from the surface of an inorganic nanoparticle macroinitiator, yielding nanoparticles with an inorganic core and an outer layer of covalently attached, well-defined polymer chains. Through this modification, the compatibility of inorganic particles with the polymer matrix would be much enhanced. In this work, the CdSe-poly(N-vinylcarbazole) (CdSe-PVK) nanocomposite has been prepared by ATRP. The N-vinylcarbazole monomer was used and polymerized on the surface of CdSe nanoparticles due to the hole-transporting feature and the photoactivity of the carbazole sidegroup of the PVK polymer [24].

In a recently published report, we have described the synthesis of CdSe-PVK nanocomposite via ATRP approach [25]. In comparison with CdSe or PVK, this new nanocomposite possesses unique optical properties. Since this organic/inorganic nanohybrid is a potential electronic acceptor for photovoltaic devices, further effort
has been made to use this composite in the active layer of polymer solar cells. Herein, electrochemical properties and photovoltaic properties of the CdSe-PVK composite have been investigated. In addition, morphological studies by SEM, dark-field TEM, and AFM are also reported in detail.

2. Experimental section

2.1 Materials

2-Mercaptoethanol (ME, Aldrich), cadmium chloride (CdCl₂ · 2.5H₂O, Aldrich), selenium (Acros), sodium sulfite (Hayashi Chemicals), sodium hydroxide (Showa Chemicals), triethylamine (TEA, Acros), 1,2-dichlorobenzene (DCB), 4-(dimethylamino)pyridine (DMAP, Aldrich), N-vinylcarbazole (Aldrich) and poly(3-hexylthiophene) (P3HT, FEM Tech., MW=16900) were used as received. 2-Bromoisobutyryl bromide (BrIB, Aldrich), 1-bromoethyl benzene (BrEB, Aldrich) and tetrahydrofuran (THF, Tedia) were distilled before use. All other reagents were used as received.

2.2 Synthesis of hydroxyl-coated cadmium selenide nanoparticles (CdSe-OH)

At first, a 20 ml aqueous solution of sodium sulfite (0.06 mol) was prepared and then 0.02 mol of powdered selenium was added. With constant stirring, the mixture was heated and kept refluxing for 1 h. Upon filtration, sodium selenosulfate (Na₂SeSO₃) solution was purged with N₂ and stored in the dark. Next, a solution of 1.0 mmol of cadmium chloride and 2.5 mmol of the stabilizer (RSH; i.e. ME) in 250 mL of deionized water was adjusted to pH 11 with 1 M NaOH. The solution was placed in a three-necked flask fitted with a septum and valves and was deaerated with N₂ bubbling for 30 min. Under vigorous stirring, 5 mL (0.5 mmol) of the freshly prepared oxygen-free 0.1 M Na₂SeSO₃ solution was injected. The initial molar ratio
Cd\(^{2+}\)/Se\(^{2-}\)/RSH was therefore approximately 1:0.5:2.5. Subsequently, the mixture was cooled to 70 °C, and ethanol was added for flocculation; it was centrifuged and washed with absolute ethanol several times. The reaction is shown in Scheme 1.

2.3 Preparation of CdSe-PVK nanocomposite

A detail synthetic route and preparation procedure have been reported previously and shown in Scheme 1 [25].

2.4 Characterization

Number average (\(\bar{M}_n\)), weight average (\(\bar{M}_w\)) molecular weights and polydispersity index (PDI, \(\bar{M}_w/\bar{M}_n\)) were determined by gel permeation chromatography (GPC) using Young Lin Acme 9000 liquid chromatograph equipped with a 410 RI detector and a \(\mu\)-Styragel columns with THF as the carrier solvent. The CdSe cores of the hybrid materials were etched with aqueous HCl solution to afford the neat polymers for GPC analysis. Thermogravimetric analysis (TGA) experiments were carried out using a TA Instruments SDT-2960 analyzer. The samples were heated from 50 to 800 °C under nitrogen at the heating rate of 20 °C/min. Differential scanning calorimetry (DSC) thermograms from 40 to 150 °C were obtained with a TA Instruments modulated DSC 2920 analyzer at a heating rate of 5 °C/min under a dry nitrogen purge. Cyclic voltammetric (CV) measurements were performed in 0.1M tetrabutylammonium perchlorate solution using a PGSTAT30 electrochemical analyzer (AUTOLAB Electrochemical Instrument, The Netherlands). A three-electrode cell assembly was utilized with an Ag/AgCl electrode as reference. Platinum wire was used as a counter electrode. An ITO-coated glass of area 1 cm\(^2\) was used as the working electrode. The morphology and energy dispersive spectroscopy (EDS) analyses of the synthesized samples were examined with
scanning electron microscope (SEM) (JEOL 5610, Japan). Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) pattern were taken with a JEOL JEM-1230 transmission electron microscope.

2.5 Fabrication of polymer solar cells and characterization

The employed device structure was ITO/PEDOT:PSS/P3HT:CdSe-OH or P3HT:CdSe-PVK/Al. Before device fabrication, the glass substrates coated with indium tin oxide (ITO) were first cleaned by ultrasonic treatment in acetone, detergent, de-ionized water, methanol and isopropyl alcohol sequentially. The ITO surface were spin coating ca. 80 nm layer of poly(3,4-ethylene dioxythiophene): poly(styrene) (PEDOT:PSS) to modify the ITO surface. The substrate was dried for 10 min at 140 °C in air, and then moved into the nitrogen-filled glove-box to spin coating the active layer. Two blend solutions (P3HT:CdSe and P3HT:CdSe-PVK) were prepared with 1:1 weight ratio (10 mg/mL P3HT) in 1,2-dichlorobenzene (DCB) as the active layer. Devices were spin fabricated by spin coating at 800 rpm for 30 s on top of the PEDOT:PSS layer. The devices were completed by evaporation of metal electrodes Al with area of 6 mm² defined by masks. The J-V curves were measured using a Keithley 2400 source meter, under illumination from a solar simulator. The intensity of solar simulator was set with a primary reference cell and a spectral correction factor to give the performance under the AM 1.5 (100 mW/cm²) global reference spectrum (IEC 60904-9). The film topography images of active layers were recorded with a Digital Instruments Dimension 3100 atomic force microscope (AFM) in tapping mode under ambient conditions.

3. Results and discussion

3.1 Structure design and synthesis of CdSe-PVK nanocomposite
The structure design and synthetic route were carried out in the following sequence. At first, CdSe-OH was prepared via wet chemical route. A Na$_2$SeSO$_3$ precursor was firstly synthesized according to the solution growth approach reported by Ma et al [26]. Next, a thio-group containing mercaptoethanol was used as the organic ligand and hydroxyl-coated CdSe nanocrystals (CdSe-OH) were prepared in the presence of mercaptoethanol by the in-situ reaction of cadmium and selenide ions. Since mercaptoethanol was coordinated to CdSe nanocrystals, hydroxyl-coated CdSe nanocrystals were formed. The electron-deficient atoms of cadmium on the surface of CdSe nanocrystals served as binding sites to anchor organic ligands and to hinder the further growth of crystal grains. Hence, the particle size of the CdSe nanocrystal was affected by the concentration of cadmium and selenide ions as well as that of mercaptoethanol. The reaction was carried out under N$_2$ because air would cause oxidation reaction of Na$_2$SeSO$_3$ precursor and give an impure product contaminated with powdered selenium.

During the growth of CdSe particles, the phenomenon of color change was noted. The color of particles transferred from transparent color into yellow, and then turned into orange. Finally, the color of orange-red was observed. This phenomenon resulted from the particle growth and the fluorescent feature of CdSe nanocrystals. The color change was accomplished in an hour, representing the particle growth was restricted after one hour and the reaction could be finished in this period.

To fulfill the ATRP of N-vinylcarbazole on the surface of CdSe nanocrystals, the hydroxyl-group endcapped ligands were then attached with halide groups by the reaction of BrIB with the hydroxyl groups on the CdSe surface to form the surface-modified nanocrystal initiator CdSe-BrIB. During the polymerization period of ATRP, the molecular weight of the polymer arms, as determined using GPC, increased with the polymerization conversion, and the molecular weight distribution
remained narrow after the initial stages of the polymerization. In the present article, a CdSe-PVK composite with shorter chain length of PVK compared to the previous study [25] was synthesized to meet the demand of photovoltaic device. Data of molecular weight and polydispersity index (PDI) of the resultant CdSe-PVK are shown in Table 1. For comparison, a similar chain length polymer PVK was also synthesized by ATRP and its data were also listed in Table 1.

Since X-ray diffractograms analysis and optical properties (UV-Vis and photoluminescence spectra) for the hydroxyl-coated CdSe nanoparticles (CdSe-OH), CdSe-PVK, and PVK have been reported previously [25], their discussions will not be addressed here.

3.2 Thermal properties

The thermal stability for CdSe-OH, CdSe-BrIB initiator, CdSe-PVK nanohybrid and PVK in nitrogen is illustrated in Fig. 1. As seen in the figure, the onset decomposition temperature for CdSe-OH is higher than the boiling point of ME (157°C), indicating robust bonding was formed between CdSe and thiol stabilizer. Compared to CdSe-OH, a lower onset degradation temperature for CdSe-BrIB is observed. It is possible due to the initial degradation of BrIB segments. Subsequently, a multi-step and rapid weight loss may be attributed to the degradation of residual BrIB segments in conjunction with the mercaptoethanol species. In the case of PVK, the TGA curve shows only single degradation step and almost no char residue above 700°C, a characteristic of common organic polymers. However, for the CdSe-PVK nanohybrid, a three-step degradation mechanism is observed, indicating the thermal stability of CdSe-PVK is enhanced via the formation of inorganic/organic hybrid as compared to PVK. In addition, a 19.7% residue is left due to the presence of CdSe particles.
For PVK and CdSe-PVK, the second heating DSC curves are shown in Fig. 2. As illustrated in the figure, both $T_g$ values are lower than typical $T_g$ of PVK (ca. 200°C), which is due to the lower molecular weights of PVK synthesized in this study. In particular, the CdSe-PVK nanohybrid has a lower $T_g$ compared to PVK. As stated in the literature [27], it may be attributed to the fact that the star-shaped polymer hybrid with more branching has more free volume and will reduce $T_g$.

### 3.3 Electrochemical properties

Cyclic voltammogram (CV) is a preliminary characterization technique to determine the redox properties of organic and polymeric materials. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of PVK and CdSe-PVK could be determined from the $E_{1/2}$ (Fig. 3) and the onset absorption wavelength ($E_g$, energy band-gap) (Table 1) [28].

As seen in Fig. 3, the oxidation onset potential for PVK and CdSe-PVK have been determined as 0.80V and 0.61V vs. Ag/Ag+, respectively. The external ferrocene/ferrocenium (Fc/Fc+) redox standard $E_{1/2}$ is 0.04V vs. Ag/Ag+. Assuming that the HOMO energy for the Fc/Fc+ standard is 4.80 eV with respect to the zero vacuum level, the HOMO energy for PVK has been evaluated to be 5.56 eV. Hence the LUMO level determined from its HOMO and band gap ($E_g$) is 2.06 eV. The HOMO and LUMO level for CdSe-PVK have also been evaluated in a similar manner and the results are listed in Table 1.

### 3.4 SEM morphology and EDS

Fig. 4 displayed a representative scanning electron micrograph of the CdSe-PVK nanocomposite particles. It can be clearly seen that spherical particles with approximately uniform size has been prepared. The average particle size has been
estimated by TEM and will be shown below. EDS measurements on CdSe nanocrystals indicated the presence of Cd, Se, C, S and O with the atomic ratio of Cd and Se was approximately 1:1 (Table 2). The results confirmed that the orange-red precipitates were hydroxyl-coated CdSe nanocrystals. The presence of S atoms corresponded to the stabilizing thiol molecules coordinated on the particle surface. In the case of CdSe-PVK sample, the EDS measurements displayed the presence of Cd, Se, O, and C, with the calculated atomic ratio of Cd and Se was 0.040:0.049, which confirmed that the sample was PVK coated CdSe nanocrystals.

3.5 TEM analysis

Transmission electron microscopy (TEM) was used to study the morphology and size distribution of selenide particles as well as their composites. Fig. 5(a) shows a typical TEM overview image of CdSe nanoparticles. The average size of the CdSe nanoparticles is ca. 6.1 nm, based on estimates from the TEM image. Fig. 5(b) shows the micrograph of the CdSe-PVK composite film, in which particles with an average size of 258 nm are observed. This image displays CdSe particles were coated with PVK. Compared to the particle size of CdSe, it seems that the inorganic cores are composed of the aggregates of CdSe nanoparticles. The grain sizes estimated by TEM are also listed in Table 1. Fig. 5(c) shows bright field, SAED and dark field images of the as-prepared CdSe-PVK sample, taken from a CdSe-PVK particle of Fig. 5(b). The bright field image shows that the CdSe nanocrystals are well coated with PVK. As seen in the upper right inset of Fig. 5(c), the SAED pattern of the CdSe-PVK nanocomposite indicates that the central region of CdSe-PVK nanohybrid comprises crystallites of differing orientations, corresponding to different crystal planes of CdSe nanocrystals. The lower right inset of Fig. 5(c) is the dark field TEM image of CdSe-PVK nanohybrid. The CdSe nanocrystals are
more clearly visible as bright spots indicative of scattering of the electrons according to Bragg’s law.

3.6 Photovoltaic behavior and film topography

At present, bulk heterojunction structures are the main candidates for high-efficiency polymeric solar cells. The bulk heterojunction solar cells based on P3HT in combination of the CdSe-PVK nanohybrid or CdSe nanocrystal (CdSe-OH) have been prepared and investigated. The employed device structure was ITO/PEDOT:PSS/P3HT:CdSe-OH or P3HT:CdSe-PVK/Al. Two blend solutions (P3HT:CdSe and P3HT:CdSe-PVK) were prepared with 1:1 weight ratio as the active layer. The current-voltage (J-V) curves under illumination from solar simulator at 100 mW/cm² light intensity are shown in Fig. 6, and the corresponding open-circuit voltage (V_{oc}), short-circuit current (J_{sc}), fill factor (FF), and power conversion efficiency (PCE, \eta ) are listed in Table 3. The CdSe nanocrystal or CdSe-PVK composite was used as the electron acceptor in the active layer. The PSC based on P3HT:CdSe-OH shows a J_{sc} of 0.052 mA/cm² and a V_{oc} of 0.074, combined with a filling factor (FF) of 24.95 %, which leads to a PCE of only 0.001%. However, when the CdSe-PVK nanohybrid was substituted for CdSe nanocrystal, the J-V curve reveals an increase of J_{sc} to 0.385 mA/cm² and an increase of V_{oc} to 0.166 V which is more than twice of that of P3HT:CdSe system. These data together with a better FF of 31.30% lead to a PCE of 0.02% for the device based on P3HT:CdSe-PVK which is almost 20 times of that of device based on P3HT:CdSe-OH. In the meantime, different PSC devices based on P3HT:CdSe-PVK were fabricated to investigate the effect of molecular weight of PVK arms on CdSe nanoparticles and weight ratio of P3HT:CdSe-PVK on the PSC performance. It was found that all investigated photovoltaic properties were influenced by both molecular weight of PVK arms and
weight ratio of the blend films. The optimal conditions for $M_n$ of PVK arms and weight ratio of P3HT:CdSe-PVK are 806 and 1:1, respectively, as shown in Table 4.

Since the morphology of the heterojunction plays an important role on the performance of polymer solar cells, we studied the topography of blend films of P3HT:CdSe-OH (1:1, w/w) and P3HT:CdSe-PVK by AFM. The images of film surfaces are shown in Fig. 7. As seen from Fig. 7(a)(b), the root-mean-square roughness for P3HT:CdSe-OH blend is 1.76 nm, and P3HT:CdSe-PVK blend is only 0.85 nm. The more rough surface observed in P3HT:CdSe-OH blend may be due to the incompatibility between organic polymer (P3HT) and inorganic nanocrystal (CdSe-OH), which decrease the miscibility of CdSe nanoparticles into conjugated polymer domain. In addition, it is evident from Fig. 7(c)(d), the phase image of P3HT:CdSe-OH blend shows some particles deposited on the film surface, whereas the phase image of P3HT:CdSe-PVK blend looks relatively homogeneous. Hence, the grafting of PVK polymer on CdSe nanocrystal has increased the compatibility of organic component (P3HT) with inorganic nanoparticle (CdSe) and reduced large-scale phase segregation between P3HT and CdSe nanocrystals. In other words, the P3HT:CdSe-PVK system has a smaller degree of phase separation than that of device based on P3HT:CdSe-OH. Since for charge generation, the interface between donor and acceptor should be maximized and located near the place where the excitons are formed, the donor/acceptor interface area might increase due to the smaller degree of phase separation in the P3HT:CdSe-PVK system [29].

4. Conclusions

In this article, both hydroxyl-coated CdSe nanocrystal (CdSe-OH) and CdSe-PVK nanocomposite were prepared and used as the electron acceptors in polymer solar cells. The CdSe-PVK nanocomposite was synthesized by grafting PVK on surfaces
of CdSe nanocrystals through ATRP technique and its physical properties together with electrochemical properties were investigated. Thermal properties displayed that the incorporation of CdSe nanoparticles enhanced the thermal stability of PVK but reduced its T_g. Combined with the band gap data obtained from UV-Vis absorption spectra (shown in the previous report [25]), HOMO and LUMO levels of PVK and CdSe-PVK could be determined from the data of CV and UV-Vis spectra. SEM and TEM micrographs displayed the CdSe-PVK hybrid particles were well separated and coated with PVK polymer. Both P3HT:CdSe-OH and P3HT:CdSe-PVK blend films were used as the active layer in bulk heterojunction solar cells. The performance of the device was found to significantly improve when P3HT:CdSe-PVK blend was used as the active layer in comparison with P3HT:CdSe-OH blend. This result was further confirmed by the surface morphology study using tapping mode AFM, which showed a better photovoltaic performance for the P3HT:CdSe-PVK system, with a more smooth and more homogeneous film morphology in the active layer.

ACKNOWLEDGMENT

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References

2009;30:1679.


**Table 1**

GPC results and physical properties of CdSe nanocrystals and CdSe-PVK nanohybrid

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<tr>
<th>Specimens</th>
<th>$\bar{M}_n$ (g/mol)</th>
<th>$\bar{M}_w$ (g/mol)</th>
<th>PDI ($\bar{M}_w/\bar{M}_n$)</th>
<th>Particle size (nm)</th>
<th>$E_g$ (eV)$^a$</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
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<td>CdSe-OH</td>
<td>N/A</td>
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<td>d$_{UV}$$^a$=3.4</td>
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<td>d$_{TEM}$=6.1</td>
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<td>CdSe-PVK</td>
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$^a$Data cited from reference [18].
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<th>CdSe-PVK Wt %</th>
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Table 3  
Photovoltaic characteristics of devices fabricated using different active layers

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<th>Active layer</th>
<th>P3HT:CdSe-OH</th>
<th>P3HT:CdSe-PVK</th>
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<tr>
<td>$V_{oc}$ (V)</td>
<td>0.074</td>
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<td>$J_{sc}$ (mA/cm$^2$)</td>
<td>0.052</td>
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<td>FF (%)</td>
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<td>η (%)</td>
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Table 4
Overview of photovoltaic parameters measured on P3HT:CdSe-PVK based photovoltaic devices

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<th>Weight ratio of P3HT:CdSe-PVK</th>
<th>$M_n$ (CdSe-PVK)</th>
<th>PDI (CdSe-PVK)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm²)</th>
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FIGURE/SCHEME CAPTIONS

**Scheme 1.** Synthetic route for the preparation of CdSe-PVK nanohybrid.

**Fig. 1** TGA curves of CdSe-OH, CdSe-BrIB, CdSe-PVK and PVK under nitrogen atmosphere.

**Fig. 2** DSC curves of PVK and CdSe-PVK nanohybrid.

**Fig. 3** Cyclic voltammograms of (a) PVK and (b) CdSe-PVK films on an ITO substrate in CH$_3$CN/AcOH (V/V=7/1) containing 0.1M tetrabutylammonium perchlorate at a scan rate of 50 mVs$^{-1}$.

**Fig. 4** Scanning electron micrograph of the CdSe-PVK nanocomposite.

**Fig. 5** (a) TEM images of CdSe-OH. (b) TEM images of CdSe-PVK nanocomposite. (c) Bright field TEM image of a CdSe-PVK grain with the SAED pattern and dark field image shown in the upper right and lower right inset, respectively.

**Fig. 6** I-V characteristics of devices under AM 1.5 simulated solar illumination at an intensity of 100 mW/cm$^2$.

**Fig. 7** AFM topography images (1 $\mu$m x 1 $\mu$m) of P3HT:CdSe-OH (a,c) and P3HT:CdSe-PVK (b,d) blend films (1:1, w/w) cast from 1,2-dichlorobenzene solutions. (a) 2D height image of P3HT:CdSe-OH. (b) 2D height image of P3HT:CdSe-PVK. (c) Phase image of P3HT:CdSe-OH. (d) Phase image of P3HT:CdSe-PVK.
Scheme 1

\[ \text{Na}_2\text{SeSO}_4 + \text{CdCl}_2 + \text{HSCH}_2\text{CH}_2\text{OH} \xrightarrow{\text{H}_2\text{O}} \xrightarrow{35^\circ\text{C}, 5hr} \text{CdSe} \]

\[ \text{CdSe} + \text{BrC-C-CH}_3 \xrightarrow{\text{TEA, DMAP in dry THF}} \text{CdSe} \]

\[ \text{CdSe} \xrightarrow{N\text{-Vinylicarbazole in CuCl/ bpy, toluene}} \text{CdSe} \]
Fig. 1

![Graph showing the weight loss of different materials as a function of temperature. The x-axis represents temperature in °C, ranging from 100 to 800. The y-axis represents weight loss in percentage. The graph includes lines for CdSe-OH, CdSe-BrIB, CdSe-PVK, and PVK. Each line shows a different pattern of weight loss with temperature.]
Fig. 3

(a) 

(b)
Fig. 5