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Template-free synthesis of vertically aligned CdS nanorods and its application in hybrid solar cells

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1. Introduction

Organic photovoltaic (OPV) devices based on nanostructured composites of electron donor and acceptor materials are drawing much attention [1–4]. Bulk heterojunction (BHJ) devices based on polymer-fullerene blends already demonstrated power conversion efficiencies exceeding 5% [5–10]. A key factor in OPV device design and fabrication is the careful control of morphology, which may lead to efficient dissociation of all generated excitons, and subsequently transport of charge carriers out of the device. It is reported that the ideal structure for OPV consists of a direct and ordered path for photogenerated electrons to the collecting electrode [11,12]. This can be done by using template porous nanostructures [13] or vertically oriented nanowires and nanorods structures [14,15].

The photovoltaic (PV) devices based on inorganic semiconductors with vertically oriented nanowires and nanorods structure have been extensively investigated, such as TiO2 [16–19], ZnO [20–27], carbon nanotube [28–32], CdSe [33,34], CdTe [14] etc. These solar cells with ordered or well-aligned nanowires or nanorods, in comparison with the bilayer structure, have the advantages of very large donor–acceptor (D–A) interface area, continuous and minimized carrier conduction pathways [12,13,15], which can significantly increase the power conversion efficiency of cells. For example, Kang et al. [14] have successfully fabricated hybrid solar cells with vertically aligned CdTe nanorods and poly(3-octylthiophene), and obtained a 1.06% power conversion efficiency (PCE) under illumination of 100 mW/cm². Peiró et al. [21] also fabricated hybrid polymer/ZnO nanorods solar cells combining dipping and spin-coating methods, and the devices showed an overall efficiency of 0.15% and 0.2% based on poly[(1,4-phenylene-(4-methyl)phenyl)amino-4,49-diphenylene-(4-methylphenyl)amino-1,4-phenylene-ethenylene-2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene-ethenylene)-co-(2,5-dimethoxy-1,4-phenylene-ethenylene-2-methoxy-5-(2-ethyl-hexyloxy)-1,4-phenylene-ethenylene)] (TPE (4M)-MEH-M3EH-PPV) and poly[3-hexylthiophene] (P3HT), respectively. These demonstrations intrigued the researcher’s interest to explore new hybrid solar cells with these vertically aligned nanorods.

CdS has been proved to be an excellent photoactive and charge transport material in optoelectronic devices [35–38], and its direct band-gap of 2.4 eV is appropriate to be an acceptor in OPV devices. Recently, the synthesis and application of CdS nanowire arrays or nanorod arrays have become an attractive research field. Template-assisted synthesis has been a common approach to prepare aligned nanowires. Liang et al. [39] successfully prepared...
noncollapsed and free-standing CdS nanowire arrays on a conductive Au film with anodic aluminum oxide (AAO) template-assisted electrodeposition by combining the supercritical CO2 drying process. Kang et al. [40] also synthesized the well-aligned CdS nanorods with AAO template-assisted method and the hybrid photovoltaic devices combining with MEH-PPV exhibited 0.60% power conversion efficiency. Further improvement in CdS nanowires or CdS nanorods-based hybrid solar cells was reported by Lee et al.[41], who successfully synthesized the high-density CdS nanowire arrays on fluorine-doped tin oxide-coated glass substrates by a vapor–liquid–solid mechanism and obtained a 1.62% power conversion efficiency device combined with conjugated polymer. Other synthesis methods, such as electrochemical synthesis [42,43] and template-free liquid-phase synthesis [44], have been developed in preparing CdS nanowires or nanorods.

Here, we reported the hybrid solar cells using the vertically aligned CdS nanorod arrays and MEH-PPV. The CdS nanorod arrays were synthesized through facile one-step and template-free hydrothermal approach directly on indium tin oxide (ITO)-coated glass substrates. The photovoltaic devices were fabricated by two deposition methods, dip- and spin-coating. The extent of the infiltration of the soft MEH-PPV phase into the rigid CdS nanorod network is changed with different deposition methods and conditions, which determines the ordered BHJ device performance. The influence of MEH-PPV layer thickness and annealing treatment on the device performance is also investigated.

2. Experimental

MEH-PPV was purchased from Canton OLEDKING Optoelectronic Materials and used as received. Its molecular weight (Mw) is 1,980,000 g mol−1 with a polydispersity index (PDI) of 2.4. All other chemicals were reagent grades and used as received.

CdS nanorod arrays were fabricated on patterned indium tin oxide (ITO)-coated glass substrates with a sheet resistance of 200 nm. Scale bars are 200 nm.
10 Ω/cm² according to our previous report [45]. The ITO glasses were pre-cleaned by ultrasonic agitation in detergent solution, distilled water, acetone and isopropanol for 10 min, and dried under nitrogen flow. The solution used for the preparation of CdS nanorod arrays was composed of 1 mmol of cadmium nitrate Cd(NO₃)₂·4H₂O, 3 mmol of thiourea, and 0.6 mmol of glutathione. The etched ITO glass was placed vertically to the bottom of the Teflon-lined stainless autoclave, which was then sealed and maintained at 200 °C for 3.5 h. After deposition, the film was rinsed with distilled water and dried under nitrogen flow.

Two deposition methods were adopted to fabricate the CdS/MEH-PPV composites as shown in Schemes 1. (1) The CdS nanorod arrays were first immersed in a chlorobenzene solution of MEH-PPV overnight and then spin-coated; (2) the MEH-PPV solution was directly spin-coated onto CdS nanorod arrays. The thickness of MEH-PPV layer was controlled by changing the spin-coating speed and the concentration of the solution. Thermal annealing was carried out on a hotplate in a glove box under N₂ atmosphere. Gold electrode (50 nm) was then deposited by evaporation through a shadow mask to complete the photovoltaic device fabrication. The device structure is presented in Fig. 2a. For this inverted geometry, the back Au electrode is the positive contact due to its high work function, forming an ohmic contact with the polymer. Each sample of CdS nanorod arrays contains six devices with an active area of ~6.0 mm² for each device.

The obtained MEH-PPV/CdS nanorod array composites were imaged with S-4800 (Hitachi) field-emission scanning electron microscope (FESEM). Before observation, a very thin platinum (Pt) layer was sputtered on the sample surface to improve the electron conductivity. The current–voltage characteristics of the photovoltaic devices were measured with the Keithley 236 source measuring unit. The photocurrent was measured under illumination from the Thermo Oriel solar simulator with an AM 1.5 global solar irradiation (100 mW/cm², 1 Sun), the light intensity of which was calibrated with a calibrated silicon diode.

3. Results and discussion

3.1. Morphology and photovoltaic characteristics of MEH-PPV/CdS nanorod array composites fabricated from dip-coating

The CdS nanorod arrays we synthesized are hexagonally-faced (inset in Fig. 1a), which is rare for nanocrystals grown on substrates. The CdS nanorod arrays are composed of uniform rods about 100 nm in diameter and 300–400 nm in length. The spacing between nanorods is about 100–200 nm (inset in Fig. 1b). The morphologies of MEH-PPV/CdS nanorod array composites made by dip-coating from MEH-PPV solutions with different concentrations are shown in Fig. 1. When the CdS nanorods were combined with low concentration MEH-PPV (2 mg/mL), the CdS nanorods hexagonally-faced become unclear compared to pure CdS nanorods. Some CdS nanorods are connected with MEH-PPV fibers and there are lots of voids existed among CdS nanorods. However, the cross-section SEM image in Fig. 1b shows that each CdS nanorod is wrapped with a thin MEH-PPV film, suggesting that the heterojunction interfacial covers the whole CdS nanorods surface. With increase in the MEH-PPV concentration, the voids among CdS nanorod arrays are gradually filled with MEH-PPV. The diameter of CdS nanorod becomes larger, indicating that a thicker MEH-PPV layer is coated on the surface of CdS nanorods. When the MEH-PPV concentration increases up to 10 mg/mL, the top surface of CdS nanorod arrays are covered with MEH-PPV film completely and the shape of CdS nanorods could not be identified as shown in Fig. 1c; the voids of CdS nanorods are fully filled with MEH-PPV. The MEH-PPV interpenetrates inside the CdS nanorod arrays, embraces the nanorods from the root to top, and occupies nearly the entire space surrounding the nanorods.

The corresponding current density–voltage (J–V) characteristics of devices (ITO/CdS/MEH-PPV(dip-coating))/Au) were measured in the dark and under illumination at an AM 1.5 global solar irradiation (100 mW/cm², 1 Sun); and (c) schematic energy band diagram of ITO/CdS/MEH-PPV/Au devices.
studied under illumination and in the dark as shown in Fig. 2b. The device dip-coated from a low MEH-PPV concentration of 5 mg/mL does not exhibit the diode-rectified characteristic and its dark current is considerably high. However, the current is increased by more than one order of magnitude upon exposure to an AM 1.5 global solar irradiation (100 mW/cm², 1 Sun). The device from a higher MEH-PPV concentration (10 mg/mL), shows morphology presented in Fig. 2f, exhibits classic photovoltaic characteristics under 1 Sun with a short-circuit current ($J_{SC}$) = 0.06 mA/cm², an open-circuit voltage ($V_{OC}$) = 0.36 V, a fill factor ($FF$) = 0.227 and a power conversion efficiency ($\eta$) = 0.0049%. Taking into account the MEH-PPV highest occupied molecular orbital (HOMO) level of about 5.4 eV [46], and the CdS nanorods lowest unoccupied molecular orbital (LUMO) level of about 4.5 eV [42], the vacuum work function of ITO is 4.5 eV [47] and Au is 5.3 eV [42], and the energy band diagram of ITO/CdS/MEH-PPV/Au junction is drawn in Fig. 2c. From the energy band diagram, the contact of ITO/CdS and Au/MEH-PPV should be ohmic, and the photovoltaic characteristics of ITO/CdS/MEH-PPV/Au device should come from the excitons separation at MEH-PPV/CdS nanorods heterojunction interface and charge carrier collection at respective electrodes.

3.2. Morphology and photovoltaic characteristics of MEH-PPV/CdS nanorod array composites fabricated from spin-coating

Fig. 3 shows the morphologies of MEH-PPV/CdS nanorod array composites made by spin-coating from MEH-PPV solutions with different concentrations. The morphology of the composites is different from that by dip-coating. As seen from Fig. 3a, when the MEH-PPV solution with a low concentration is directly spin-coated onto the top of CdS nanorods, the morphology is similar to that by dip-coating, and the shape of CdS nanorod is very clear as the pure CdS nanorod with few CdS nanorods connected by MEH-PPV nanofibers. The increase in the concentration of MEH-PPV shows that the voids of CdS nanorods are gradually filled by MEH-PPV, and the CdS nanorods are almost immersed in MEH-PPV layer, which is obvious from the top view of the SEM image as shown in Fig. 3d. However, the cross-section SEM image corresponding to the

![Fig. 3. Top view SEM images of MEH-PPV/CdS nanorod array composites made by spin-coating MEH-PPV solutions in chlorobenzene with different concentrations of (a) 2 mg/mL, (b) 5 mg/mL, (c) 7.5 mg/mL, and (d) 10 mg/mL. (e) Cross-section SEM image corresponding to (d). Scale bars are 200 nm.](image-url)
high concentration (Fig. 3e) shows clearly that the voids of CdS nanorods are only partly filled by MEH-PPV; the infiltration depth is about 50 nm. Moreover, MEH-PPV also deposits above the CdS nanorods, forming a solid film of approximately 50 nm thickness, which can potentially prevent electron back transfer and thus reduce the dark (leakage) current.

Fig. 4 shows the J–V characteristics of devices (ITO/CdS/MEH-PPV (spin-coating)/Au) with the morphology shown in Fig. 3e. We found that the device performance is regularly increased with the decrease in MEH-PPV layer thickness. When the MEH-PPV thickness is decreased from 300 to 80 nm, the device performance improves systematically, $J_{SC}$ is increased by about thirty folds from 0.0058 to 0.16 mA/cm$^2$, $FF$ is enlarged from 0.287 to 0.363, $V_{OC}$ is decreased from 0.66 to 0.28 V, and $\eta$ is significantly improved from 0.0011% to 0.017%. For organic solar cells, the photoactive layer thickness is a very important factor affecting the device performance. The insufficient thickness of the photoactive layer cannot make full use of the incident light to generate enough excitons. However, if this photoactive layer is too thick, part of the incident light will be absorbed by the photoactive molecules before reaching the D/A interface, which is the source of the device photocurrent. Therefore, to guarantee the adequate utilization of light energy, the thickness of the photoactive layer must be appropriate to efficiently absorb incident photons as well as to favor the migration of the excitons. The ideal J–V property can be achieved when the thickness of the MEH-PPV film is at an appropriate value, which is about 100 nm in our case.

Both the series resistance ($R_{SA}$) and shunt resistance ($R_{SH}$) are important factors in determining the device performance. Table 1 summarizes the parameters of the above devices including $R_{SA}$ and $R_{SH}$. With decrease in the thickness from 300 to 80 nm, $R_{SA}$ is dropped more than four orders of magnitude, and $R_{SH}$ is decreased about two orders of magnitude. $R_{SA}$ can be estimated from the inverse slope at a positive voltage larger than $V_{OC}$, where the J–V curve becomes linear, which is related to the conductivity, i.e. mobility of the specific charge carrier in the respective transport medium. The mobility can be affected by space charges and traps or other barriers (hopping). $R_{SH}$ is also increased with a longer traveling distance of the charges in thicker transport layers. This is because at high positive external voltages, the diode becomes more conducting so that $R_{SH}$ can dominate the shape of the J–V curve. The $R_{SH}$ can be derived from the inverse slope around 0 V.

### Table 1

<table>
<thead>
<tr>
<th>No.</th>
<th>Thickness (nm)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$ (V)</th>
<th>$FF$</th>
<th>$\eta$ (%)</th>
<th>$R_{SA}$ ($\times 10^3$ Ω cm$^2$)</th>
<th>$R_{SH}$ ($\times 10^3$ Ω cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>300</td>
<td>0.0058</td>
<td>0.66</td>
<td>0.287</td>
<td>0.0011</td>
<td>980</td>
<td>146</td>
</tr>
<tr>
<td>2</td>
<td>200</td>
<td>0.0092</td>
<td>0.48</td>
<td>0.317</td>
<td>0.0014</td>
<td>70.3</td>
<td>70.8</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>0.101</td>
<td>0.56</td>
<td>0.301</td>
<td>0.017</td>
<td>2.6</td>
<td>1.2</td>
</tr>
<tr>
<td>4</td>
<td>80</td>
<td>0.154</td>
<td>0.30</td>
<td>0.363</td>
<td>0.017</td>
<td>0.092</td>
<td>4.6</td>
</tr>
</tbody>
</table>

The MEH-PPV solution concentration is fixed to 10 mg/mL. The illuminated intensity is 100 mW/cm$^2$. $J_{SC}$: short-circuit current density; $V_{OC}$: open-circuit voltage; $FF$: fill factor; $\eta$: power conversion efficiency; $R_{SA}$: series resistance; and $R_{SH}$: shunt resistance.
heterojunction interface may be another reason for the better device performance [50]. Annealing treatment may enhance the interaction between MEH-PPV and CdS nanorods, and the reduced interface trap states may increase the \( V_{OC} \). Therefore, the improvement in device performance after annealing treatment could be ascribed to the enhancement of aggregation of MEH-PPV and the improvement of the heterojunction interface.

### 3.4. Comparison of the performance of MEH-PPV/CdS nanorod array composite solar cells with different device structures

Table 2 summarizes the photovoltaic performance of the bulk heterojunction devices (ITO/CdS/MEH-PPV/Au) made from dip- or spin-coating as well as the devices in double-layer structure. For the device made from spin-coating, the performance is significantly improved compared to that of double-layer device. The increased \( J_{SC} \) in hybrid devices is thought to originate from the larger interface areas between CdS and MEH-PPV, resulting in more excitons dissociation at the heterojunction interface. The decrease in \( R_{SH} \) is another reason for the performance improvement. In the double-layer device, \( R_{SH} \) is significantly decreased due to the shorter traveling distance of charges to the heterojunction interface in MEH-PPV phase, which comprises an interpenetrating network with CdS nanorods. However, \( V_{OC} \) in the hybrid device is much smaller than that in the double-layer device. This may be due to the lack of backing layer (or buffer layer) between the ITO electrode and CdS nanorods in this work. This buffer layer could avoid the direct contact of the polymer with the ITO electrode, which will result in less leakage currents, increase in \( V_{OC} \) and increase in current density and efficiency. That is why the double-layer device presents higher \( V_{OC} \) [21]. In addition, the devices with partly filled voids of CdS nanorod array exhibit a little better performance than those fully filled devices. This result can be attributed to the shorter charge carrier transport distance for devices by spin-coating. The infiltration depth of MEH-PPV is about 50 nm for the device by spin-coating, which is much smaller than that by dip-coating (~300 nm). Therefore, to this MEH-PPV/CdS nanorod arrays composite-based solar cells it is the charge transportation that limits the device performance because of the low mobility of the MEH-PPV [51]. For polymers with a higher mobility, the situation may be different, and the device with polymer fully filled CdS nanorods may exhibit better performance.

### 4. Conclusions

In summary, we have successfully fabricated the ordered hybrid solar cells composed of vertically aligned CdS nanorods and MEH-PPV. It is found that the infiltration extent of MEH-PPV into the CdS nanorod arrays is different by using different deposition methods. For MEH-PPV/CdS nanorod array composites, the photovoltaic devices with MEH-PPV partly filled CdS nanorod arrays exhibit better performance than those with fully filled ones, which was due to the shorter charge carrier transport path in

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**Table 2** The performance of MEH-PPV/CdS nanorod composites solar cells fabricated with different device structure and deposition methods.

<table>
<thead>
<tr>
<th>Deposition methods</th>
<th>( J_{SC} ) (mA/cm(^2))</th>
<th>( V_{OC} ) (V)</th>
<th>( FF )</th>
<th>( \eta ) (%)</th>
<th>( R_{SH} ) (( \times 10^3 ) ( \Omega ) cm(^2))</th>
<th>( R_{S} ) (( \times 10^3 ) ( \Omega ) cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Double-layer(^a)</td>
<td>0.026</td>
<td>0.84</td>
<td>0.183</td>
<td>0.0040</td>
<td>3.3 ( \times 10^3 )</td>
<td>1.2 ( \times 10^5 )</td>
</tr>
<tr>
<td>Hybrid (^b)</td>
<td>0.060</td>
<td>0.36</td>
<td>0.227</td>
<td>0.0049</td>
<td>9.7</td>
<td>5.4</td>
</tr>
<tr>
<td>Hybrid (^c)</td>
<td>0.213</td>
<td>0.38</td>
<td>0.276</td>
<td>0.022</td>
<td>1.2</td>
<td>2.2</td>
</tr>
<tr>
<td>Hybrid (^d)</td>
<td>0.154</td>
<td>0.36</td>
<td>0.363</td>
<td>0.017</td>
<td>0.092</td>
<td>4.6</td>
</tr>
<tr>
<td>Hybrid (^e)</td>
<td>0.235</td>
<td>0.38</td>
<td>0.387</td>
<td>0.035</td>
<td>0.052</td>
<td>4.5</td>
</tr>
</tbody>
</table>

The illuminated intensity is 100 mW/cm\(^2\).

\(^a\) Device structure: ITO/CdS (50 nm)/MEH-PPV (50 nm)/Au.

\(^b\) The device was measured as prepared.

\(^c\) The device was annealed at 150 °C for 10 min.
MEH-PPV phase and the lack of the buffer layer between the ITO electrode and CdS nanorod arrays. It is believed that the device performance of polymer/CdS nanorod composites can be improved further by improving the CdS nanorod arrays structure and introducing the higher mobility polymers.

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