

# (0001)-Preferential Growth of CdSe Nanowires on Conducting Glass: Template-Free Electrodeposition and Application in Photovoltaics

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By contrast with the rich, wurztite-related, one-dimensional nanostructure of ZnO and its wide variety of applications, there only exists a few methods for the controlled and designed synthesis of one-dimensional CdSe nanostructures. Here, we describe a low-temperature and directed preparation of CdSe nanowires in a simple one-step, template-free electrochemical deposition. The preparation takes advantage of both the wurtzite structure characteristics and current-induced preferential orientation. High-resolution transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) patterns clearly verify that the prepared CdSe nanowires have a single-crystal wurtzite structure and grow along the [0001] (c-axis). With the discovery of other one-dimensional CdSe nanostructures and CdS nanowires, it is anticipated that this electrochemical synthesis method can be extended to other nanostructures of CdSe and to other II-VI semiconductors and can also be developed into a systematic synthesis for nanostructured semiconductors. The average diameter of the thus prepared CdSe nanowires is larger than those synthesized by chemical vapor deposition (CVD) and solution—liquid—solid (SLS) methods. This may be an advantage in some applications, for example, as the light-harvesting material in photovoltaic cells. Organic/inorganic hybrid photovoltaic cells fabricated with CdSe nanowires and PEDOT:PSS give a good photovoltaic performance, demonstrating the attractive potential of CdSe nanowire applications in photovoltaics.

### 1. Introduction

Over the past decade, one-dimensional nanostructured CdSe, especially CdSe nanowires, has drawn much scientific research attention and has been extensively investigated because of its unique anisotropic characteristics in optical, electrical, and physical properties. At present, CdSe nanowires have been successfully synthesized by several methods, including the template-assisted solution chemical reaction<sup>1</sup> and electrodeposition,<sup>2,3</sup> laser ablation-assisted chemical vapor deposition (CVD),<sup>4,5</sup> as well as the representative catalyst-assisted syntheses of vapor-liquid-solid (VLS)<sup>6,7</sup>

and solution-liquid-solid (SLS) processes. 8-10 These methods, especially the SLS method advanced by Buhro<sup>11,12</sup> have achieved the controlled and designed synthesis of CdSe nanowires, while requiring either high temperature (up to 800 °C) or foreign metal catalyst or template assistance. Therefore, it is still necessary to develop a low temperature, facile, and directed one-step and template-free route to synthesize oriented CdSe nanowires.

As we know, the hexagonal crystal structured ZnO forms a diverse group of one-dimensional (1D) nanostructures 13-18 due to the wurtzite structural characteristics of the fastest growth<sup>13</sup> directions and polar surfaces. <sup>13–17</sup> It is anticipated that it could be extended to other II-IV semiconductors with the wurtzite structure, 13 for example, ZnS19 and CdSe. 20 Structurally, CdSe is analogous to ZnO: the three fastest growth directions of  $\langle 0001 \rangle$ ,  $\langle 01\overline{1}0 \rangle$ ,  $\langle 2\overline{1}10 \rangle$ , and  $\pm (0001)$ 

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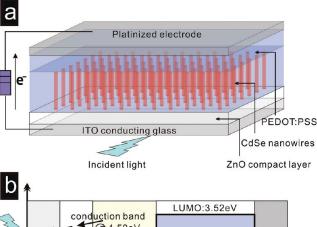
polar surfaces. The three fastest growth directions may induce anisotropic growth and usually form CdSe nanoparticles in template-free electrodeposition. However, in further considering the kinetics of the electrochemical deposition process, not only the structural characteristics but also the electrodeposition conditions, especially the current direction on the surface of the substrate, will affect the architecture of the deposits.<sup>21</sup> The (0001) direction is parallel to the current direction on the surface of the substrate (the direction normal to the substrate) and is also one of the three fastest growth directions. Given appropriate conditions, the (0001) direction may be the sole preferred direction and CdSe may grow into nanowires. Therefore, it is feasible to develop a template-free electrochemical synthesis for CdSe nanowires by considering both the structural characteristics and the kinetics of the electrodeposition process.

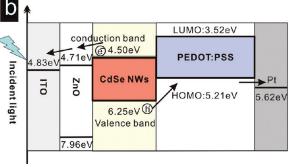
Applications of CdSe nanowires have previously focused on light-emitting diodes (LEDs),<sup>6</sup> optoelectronic devices,<sup>6,7</sup> and field-effect transistors (FETs).<sup>5</sup> Because of their direct band gap (~1.74 eV at room temperature), good visible-light absorption, and excellent photoelectrical characteristics,<sup>6,7</sup> CdSe nanowires are also a kind of promising light-harvesting material to be applied in photovoltaics. However, the studies on the applications in photovoltaic cells of CdSe nanowires are limited, and the conversion efficiencies are still unsatisfying.<sup>22</sup> Therefore, more studies are essential for the application of CdSe nanowires in photovoltaics.

We therefore attempted to set up a one-step, templatefree, electrochemical synthesis route for CdSe nanowires at a relatively low temperature, employing both currentinduced preferential orientation in the kinetics and wurtzite structural characteristics of the fastest growth directions and  $\pm (0001)$  polar surfaces. The application of our CdSe nanowires was focused on photovoltaics. To facilitate the fabrication of photovoltaic cells, the CdSe nanowires were deposited on indium tin oxide (ITO) conducting glass substrates or on conducting substrates having a ZnO compact layer. We constructed hybrid photovoltaic cells using inorganic semiconductors of these CdSe nanowires and a ZnO compact layer (electron transport material), an organic hole transport material of poly-(ethylene dioxythiophene) doped with polystyrene sulfuric acid (PEDOT:PSS, a conducting polymer), and a counter Pt electrode.

## 2. Experimental Section

Electrochemical Growth of CdSe Nanowires. The cathodic electrodeposition of CdSe nanowires was carried out galvano-statically in a two-electrode system, in which a pretreated indium tin oxide (ITO) conducting glass (20  $\Omega$   $q^{-1},\,1\times2$  cm²) substrate (or with a ZnO compact layer) was used as the working electrode, a platinum (Pt) foil parallel to the working electrode served as the counter electrode, the distance of the two electrodes being as close as 1 mm. Deposition was carried out in a constantly stirred bath containing CdCl<sub>2</sub> (Alfa Aesar) and saturated solution of elemental





**Figure 1.** (a) Structure and (b) energy diagram and operating principle of the hybrid photovoltaic cells with the structure of ITO/ZnO/CdSe nanowires/PEDOT:PSS/Pt.

Se (Alfa Aesar) in dry dimethylformamide (DMF). Cyclic voltammograms were measured to study the deposition process (Figure S1 in the Supporting Information). The electrochemical reaction process can be simply expressed as eq 1:

Se 
$$\xrightarrow{+2e}$$
 Se<sup>2-</sup> (1)

Elemental Se was reduced to Se<sup>2-</sup>, and then CdSe was formed as a result of the electrostatic attraction:

$$Cd^{2+} + Se^{2-} \rightarrow CdSe$$
 (2)

The electrodeposition conditions include the bath temperature, the current density, the stirring rate, and the concentrations of the reactants, which were varied to generate the CdSe nanowires (details will be discussed below and in the Supporting Information). Finally, a current density of 0.22 mA cm<sup>-2</sup>, a temperature of 147 °C, a concentration of 10 mM for CdCl<sub>2</sub> and 5 mM for elemental Se, and a stirring rate of 1000 revolutions per minute (rpm) were used as the typical electrodeposition conditions to make the CdSe nanowires. After deposition, CdSe nanowire samples were sequentially cleaned in acetone and ultrapure water and then annealed at 350 °C under inert gas (N<sub>2</sub>) shielding for 60 min to acquire the better photovoltaic performance.<sup>24</sup> A comparison of optical properties, and the structural and photovoltaic performance of the CdSe nanowires before and after annealing were studied (see the Supporting Information).

**Hybrid Photovoltaic Cell Assembly.** Figure 1 shows the structure (part a) and the energy diagram and the operating principle (part b). The band values were obtained using ultraviolet photoelectron spectroscopy and optical and electrochemical measurements. (Details are as shown in the Supporting Information) of the hybrid photovoltaic cells with the structure of ITO/ZnO/CdSe

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nanowires/PEDOT:PSS/Pt. Here, the as-prepared CdSe nanowires were used as light-harvesting materials. The corresponding CdSe nanowire arrays can provide a large interface where the photogenerated electron—hole pairs are separated.

To fabricate hybrid photovoltaic cells, a thermally sprayed ZnO compact layer, about 100 nm thick, was first deposited on the ITO conducting glass substrate. A ZnO compact layer was used as the electron transporting material, and it reduced short-circuiting of the cells. Second, the CdSe nanowires were electrodeposited on the substrate of ITO/ZnO and then annealed at 350 °C under an atmosphere of  $N_2$  for 60 min. After that, the PEDOT:PSS used as the hole transporting material was spin-coated, about 2  $\mu$ m thick. Platinum, about 300 nm thick, was finally sputtered as the ohmic contact (SEM images of CdSe nanowires/PEDOT:PSS films and a photograph of the completed photovoltaic cells are provided in Figures S2 and S3 in the Supporting Information).

As shown in Figure 1b, an energy barrier of 1.71 eV was generated at the interface of ZnO/CdSe as a result of the difference in the valence bands between ZnO and CdSe, and this energy barrier blocked the holes flow to ZnO. Likewise, an energy barrier exists at the interface of CdSe/PEDOT:PSS because of the difference between the conduction band of CdSe and the lowest unoccupied molecular orbital (LUMO) of PEDOT:PSS, blocking the electron flow to the counter electrode. Both energy barriers will reduce the recombination of electrons and holes. A maximum open circuit voltage ( $V_{\rm oc}$ ) of 0.79 V may be obtained for this kind of photovoltaic cell considering the difference in the work functions of ITO and Pt. <sup>23,30</sup>

Photovoltaic Characterization. The photovoltaic performance of the cells was evaluated with a photoelectrochemical system, which consisted of a potentiostat (model 273a, EG&G, PAR.) and a two phase lock-in amplifier (model 5301, EG&G, PAR.) with a chopper (model 194a, EG&G, PAR.). A solar simulator (class B, model 91160, Newport) with a 300 W xenon lamp and an Air Mass 1.5 filter (AM1.5) provided standard white light illumination of 100 mW cm<sup>-2</sup>. Monochromatic light in the range of 300–800 nm was obtained from a 300 W xenon lamp using a SpectraPro 275 monochromator (Acton Research Corporation). The incident light power of the white light and monochromatic light were calibrated by an RK-5710 power radiometer (Laser Probe Inc.) with an RkP-575 pyroelectric power probe and an RkP-576a silicon power probe, respectively. The devices are masked to have an illuminated active area of 1 cm<sup>-2</sup>. More instrumental details are in the Supporting Information.

# 3. Results and Discussion

Growth Mechanism of CdSe Nanowires. Bath temperature, current density, stirring rate, and the concentrations of reactants were varied (listed below) to investigate and optimize the electrodeposition conditions for the growth of CdSe nanowires.

bath temperature	90 − 152 °C
current density	$0.05-5 \mathrm{mA  cm}^{-2}$
stirring rate	150-1500 rpm
concentration of CdCl <sub>2</sub>	1-50  mM
concentration of elemental Se	0.5-7.5 mM

We found temperature is the key parameter in the synthesis of CdSe nanowires. CdSe nanowires can only form above 145 °C. Below this temperature, it is only possible to form CdSe nanoparticle layers (Figure S4 in the Supporting Information). Limited by the boiling

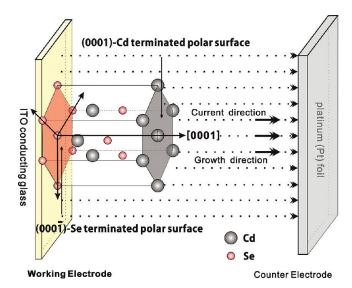


Figure 2. Schematic diagram of the wurtzite structure and the proposed electrodeposition process of the CdSe nanowires, showing one of the three fastest growth directions of [0001] and the  $\pm$ (0001) polar surfaces in structure. The [0001] direction is parallel to the current direction, and the active Cd terminated (0001) polar surface induces the fastest growth along [0001] of the CdSe nanowires.

point of DMF (152 °C), we could only obtain CdSe nanowires in the temperature range of 145-150 °C. In this range, the deposition rate and diameter of the CdSe nanowires slightly increased with temperature. However, the composition, crystal structure, and diameter of the CdSe nanowires were controlled by a combination of the other electrodeposition conditions including current density, stirring rate, and the concentrations of reactants. As the current density increased, the deposition potential of the working electrode grew, followed by increases in both the diameters and Se-Cd ratios in the composition of the CdSe nanowires. The stirring rate directly changes the mass transfer rate and subsequently the deposition rate. The deposition rate also increased with increases in the concentrations of the reactants, and the composition of CdSe nanowires correlated with the concentration ratio of the electrolyte solution. As a result, an optimized current density of 0.22 mA cm<sup>-2</sup>, a temperature of 147 °C, concentrations of 10 mM for CdCl<sub>2</sub> and 5 mM for Se, and a stirring rate of 1000 rpm were selected as standard conditions to synthesize CdSe nanowires with high purity and a perfect single-crystal structure (more details in the Supporting Information).

The morphology and crystal structure of the CdSe nanowires synthesized under the standard deposition conditions are shown (Figure 3). The top view and side view scanning electron microscopy (SEM) images for large-scale CdSe nanowires are shown in Figure 3a and Figure 3b, respectively. It seems that the CdSe nanowires are not all oriented with respect to the substrate in the macroview (Figure 3a). This is mainly attributed to the roughness of the ITO glass surface (Figure S6 in the Supporting Information). The CdSe nanowires are straight and grow perpendicular to the substrate in their first several micrometers (Figure 3b), then bend due to the overlength of the nanowires, having a total length over

Figure 3. Top (a) view and side (b) views of scanning electron microscopy (SEM) images of large-scale CdSe nanowires, (c) low-magnification transmission electron microscopy (TEM) image, (d) X-ray diffraction (XRD) pattern, (e) electron diffraction (ED) pattern, and (f) high-resolution transmission electron microscopy (HRTEM) image, respectively, recorded from area A in Figure 3c. The crystal face in Figure 3f was assigned to (0001) as the interplanar distance of 0.350 nm. As a result, the orientation index of the perpendicular to the crystal face is [0001], which is consistent with the result of its electron diffraction pattern. The incident electron beam is along  $\langle 2110 \rangle$  and implies that the nanowires also grow along  $\langle 2110 \rangle$ . The growth along  $\langle 2\overline{110} \rangle$  is much slower than that along the preferred orientation of [0001], while it leads to larger diameters of nanowires than those synthesized by the SLS and CVD methods. (g) Electron diffraction (ED) pattern and (h) high-resolution transmission electron microscopy (HRTEM) image, respectively, recorded for the protuberances (area B in Figure 3c). The crystal face in Figure 3h was assigned to  $(10\overline{1}0)$  as the interplanar distance of 0.373 nm, which is consistent with its electron diffraction pattern. The incident electron beam along (0001) implies that the growth direction of the protuberances is [0001]. The ED patterns and HRTEM images are analyzed with the data from the PDF card (no. 01-077-2307).

15  $\mu$ m (the length of the CdSe nanowires grows with electrodeposition time, being about 15 µm for 45 min). Low-magnification transmission electron microscopy (TEM) images in Figure 3c and Figure S7 in the Supporting Information clearly show that there are numerous protuberances on the surface of the CdSe nanowires and the average diameter of the nanowires is less than 150 nm. Therefore, the length/diameter ratio (LD ratio) of the CdSe nanowires exceeds 100. The X-ray diffraction (XRD) pattern (Figure 3d) of the CdSe nanowires before annealing highly matches the data of the PDF card (no. 01-077-2307), clearly identifying a hexagonal wurtzite structure consistent with the result of the selected area electron diffraction (SAED) pattern. The much higher relative intensity of the (002) diffraction peak compared with that

of polycrystalline CdSe powder indicates that [0001] is the preferred direction in the growth. As shown in part e and f of Figure 3, the SAED pattern and the highresolution transmission electron microscopy (HRTEM) image (recorded from area A in Figure 3c) confirm that the CdSe nanowires are of a single-crystal wurtzite structure and grow along the [0001] axis (c-axis). Furthermore, the SAED pattern (Figure 3g) and HRTEM image (Figure 3h) of the protuberance on the CdSe nanowire surface (area B in Figure 3c) reveal that these protuberances grow along [0001] (the raise-up direction is [0001]) and further confirm that [0001] is the preferred direction. The chemical composition of the CdSe nanowires was determined using energy dispersive X-ray (EDX) spectroscopy, with a result of almost 1:1 for the Se-Cd ratio (Figure S8 in the Supporting Information), showing the high purity of the nanowires.

The growth mechanism of CdSe nanowires can be explained as follows. Structurally, CdSe has three fastest growth directions of  $\langle 0001 \rangle$ ,  $\langle 01\overline{1}0 \rangle$ , and  $\langle 2\overline{11}0 \rangle$ , which is common in other hexagonal wurtzite structures. CdSe comprises polar surfaces resulting from the positively charged Cd-(0001) and negatively charged Se- $(000\overline{1})$ .<sup>13</sup> The three fastest growth directions usually lead to equal growth in the three directions for CdSe electrodeposition without the assistance for a template and most probably result in the disordered CdSe nanoparticle layer. As the positively charged Cd-(0001) polar surface is chemically active and the negatively charged Se- $(000\overline{1})$  is relatively inert, <sup>13,20,25</sup> this provides a strong tendency to grow the CdSe nanowires along [0001].

In electrodeposition, the preferred growth not only depends on the crystallography but also on the electrochemical nucleation and growth kinetics,<sup>26</sup> mainly the nucleation kinetics. According to the two-dimensional (2D) nucleation and growth mechanism of electrodeposition advanced by Kossel<sup>27</sup> and Strandki,<sup>28</sup> the relationship between the nucleation rate (I) and the nucleation energy  $(W_{hkil})$  is defined by the equation

$$I = A \exp(-W_{hkil}/kT) \tag{3}$$

where  $W_{hkil}$  is the nucleation energy of the nucleus with the (hkil) crystal plane, k is the Boltzmann constant, T is the absolute temperature, and A is a function of the overpotential in the electrodeposition. Under electrodeposition conditions of low current density and low overpotential, A is a constant and the nucleation rate is proportional to  $\exp(-W_{hkil}/kT)$ , CdSe growth takes the "parallel growth" mode (i.e., the [0001] in which the preferred direction is parallel to the current direction).<sup>29</sup> Taking the temperature into account, below 145 °C the nucleation energies  $(W_{hkil})$  of the nuclei with different

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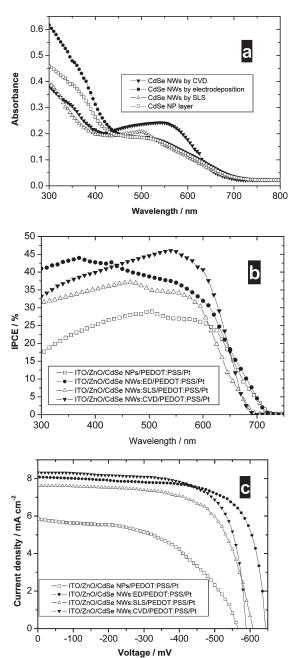
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crystal planes may be close, inducing the disordered growth of CdSe and forming a nanoparticle layer. In the range of 145–150 °C, the lowest nucleation energy of the nucleus is the (0001) crystal plane, and so the fastest nucleation rate results in the [0001] preferred growth in electrochemical growth kinetics. In the control of structural characteristics, nucleation, and growth kinetics, the [0001] direction that is parallel to the current direction will be the dominant growth direction in the CdSe nucleus growth process (Figure 2) and subsequently the nuclei grow into CdSe nanowires along [0001].

The average diameter synthesized by our method is larger than those synthesized by catalyst-assisted CVD or SLS methods, mainly due to the other growth direction of  $[2\overline{110}]$  in the electrodeposition process. However, the modestly larger diameter provides the better light absorption and photoelectric conversion efficiency as illustrated below. Protuberances on the surface of the CdSe nanowires are attributed to secondary growth<sup>30</sup> along [0001], which is likely to grow into so-called "nanopropellers" analogous to ZnO.<sup>13</sup> In addition, the electrochemical conditions of the reactant concentrations and stirring rate were further studied, and the "vertical growth" CdSe nanowires (grown under conditions of high current density and high overpotential) with smaller diameters as well as some other 1D nanostructures of CdSe were observed (Figure S9 in the Supporting Information). CdS nanowires synthesized by a similar method have been found (Figure S10 in the Supporting Information), so it is anticipated that this electrochemical route may be extended to other II-VI semiconductors with wurtzite structures.

Characterization of Photovoltaic Cells. We tried to develop an application of CdSe nanowires to photovoltaic cells as a light-harvesting material. For comparison, we also used a CdSe nanoparticle (NP) layer synthesized at lower temperature (130 °C) and CdSe nanowires synthesized by catalyst-assisted SLS and CVD methods (details in the Supporting Information) to fabricate four kinds of photovoltaic cells with similar structures. The four kinds of photovoltaic cells were fabricated using a similar technique. The cell structures were marked as ITO/ZnO/CdSe NPs/PEDOT:PSS/Pt, ITO/ZnO/CdSe NWs-electrodeposition (ED)/PEDOT:PSS/Pt, ITO/ ZnO/CdSe NWs-SLS/PEDOT:PSS/Pt, and ITO/ZnO/ CdSe NWs-CVD/PEDOT:PSS/Pt, respectively. We evaluated their photovoltaic performances by photocurrent action spectra and current density-voltage (J-V) characteristics. The four kinds of light-harvesting material were normalized by mass, i.e., the same mass of CdSe nanowire on the same substrate area.

UV—vis absorption measurements were performed to estimate the light absorption properties of the four samples on the ITO conducting glass substrate. As the UV—Vis absorption spectra show in Figure 4a, the calculated band gaps (*Eg*) of 1.74 eV, 1.75 eV, 1.77 eV and 1.82 eV in sequence for the CdSe nanoparticle layer, the CdSe nanowires synthesized by electrodeposition, SLS and CVD, are calculated with absorption onsets of 712 nm, 708 nm, 701 nm and 681 nm, respectively. The band gaps of the



**Figure 4.** The UV-vis absorption spectra: (a) incident photon-to-electron conversion efficiency (IPCE) spectra (b) for the four kinds of photovoltaic cells. The current density-voltage (J-V) characteristics (c). The active area is 1 cm<sup>2</sup>.

electrodeposited CdSe nanowires with diameters larger than 100 nm and CdSe nanoparticle layer were close to the bulk band gap (1.74 eV). Blue shifts of 11 and 31 nm were found for the slender nanowires with diameters about 30 and 10 nm, respectively, representing a quantum confinement effect. These values including the Eg values are all in good correlation with those reported. Absorption enhancement in the near-ultraviolet range (300–430 nm) is noteworthy. The absorption enhancement may be due to the strong scattering in the corresponding spectral range (Figure S11 in the Supporting Information). The scattering will increase the optical path, which is conducive to the light absorption and results in a higher incident photon-to-electron conversion efficiency (IPCE) for the cells.

Table 1. Characteristic Parameters of Photovoltaic Cells with Different Light-Harvesting Material<sup>a</sup>

light-harvesting material	$V_{\rm oc}$ [mV]	$J_{\rm sc}$ [mA cm <sup>-2</sup> ]	FF	η [%]
CdSe nanoparticles	566	5.85	0.51	1.7
CdSe NWs by electrodeposition	642	8.08	0.69	3.6
CdSe NWs by SLS	607	7.62	0.66	3.1
CdSe NWs by CVD	587	8.31	0.71	3.4

 $^aJ_{\rm sc}$ , short-circuit current density;  $V_{\rm oc}$ , open-circuit voltage; FF, fill factor, FF =  $[(V_{\rm max}J_{\rm max})/(V_{\rm oc}J_{\rm sc})]$ ;  $\eta$ , energy conversion efficiency,  $\eta = [(V_{\rm oc}J_{\rm sc}FF)/(P_{\rm in})\}$ ;  $P_{\rm in}$ , power of the incident light.

The IPCE spectra (calculated without taking into account the reflective loss of the complete cells) (Figure 4b) verified the blue shift of the absorption onsets and confirmed that the electrodeposited CdSe nanowires had a broader spectral range and better photovoltaic performance. The CdSe nanoparticle layer had a similar light absorptivity to the CdSe nanowires but a poorer photovoltaic performance; this was attributed to the recombination of the photon-generated carriers. This recombination<sup>31,32</sup> leads to both a decrease of the fill factor (FF) and the short-circuit current density  $(J_{sc})$  in the current-voltage characteristics (Figure 4c). As shown in the J-V characteristics of Figure 4c and the summarized characteristic parameters in Table 1, photovoltaic cells with CdSe nanowires synthesized by the CVD method had the highest fill factor (0.71) and short-circuit current density (8.31 mA cm<sup>-2</sup>), owing to the perfect single-crystal structure and the induced low recombination.<sup>33</sup> Photovoltaic cells using electrodeposited CdSe nanowires as the light-harvesting material gave the best photovoltaic performance, with the  $J_{\rm sc}$ ,  $V_{\rm oc}$  (open-circuit voltage), and FF of 8.08 mA cm<sup>-2</sup>, 642 mV, and 0.69, respectively; yielding an overall energy conversion efficiency  $(\eta)$  of 3.6%. The results show that the IPCE of electrodeposited CdSe nanowires is lower than that of CVD nanowires in the range of 450-640 nm, which is the main spectral region (Figure S12 in the Supporting Information), and the  $J_{\rm sc}$  of the former device is also lower than that of the latter. Photovoltaic cells with CdSe nanowires synthesized by SLS and CVD methods also showed good photovoltaic performance, and their overall energy conversion efficiencies are 3.1% and 3.4%, respectively. The results primarily achieved were better than

those of photovoltaic cells using CdSe nanorods<sup>22</sup> as the light-harvesting materials. Moreover, it is desired that the power conversion efficiency of the photovoltaic cell with CdSe nanowires will be higher than that of quantum dot solar cells,<sup>22</sup> which are being extensively investigated currently. The electrodeposited CdSe nanowires represented the best photovoltaic performance in the four kinds of photovoltaic cells. There still exists some room for improvement in the short-circuit current density and especially in the open-circuit voltage to upgrade cell performance.

#### 4. Conclusions

A novel one-step, template-free, electrochemical synthesis route for the hexagonal wurtzite structural CdSe nanowires has been established. As a result of the effects of the wurtzite structural characteristics and electrochemical preferential orientation, the CdSe nanowires were found to grow along a uniform direction of [0001]. In further studies, we anticipated that this electrodeposition method would be extended to the construction of other one-dimensional nanostructures of CdSe and other wurtzite structural materials and be developed into a systematic synthetic method. The thus prepared CdSe nanowires, as well as the CdSe nanowires synthesized by the SLS and CVD methods, have been used as lightharvesting materials to fabricate hybrid photovoltaic cells, which were found to exhibit good photoelectric conversion efficiencies and are considered to have huge potential for application in the photovoltaics.

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Supporting Information Available: Details of ultraviolet photoelectron spectroscopy (UPS) and cyclic voltammetry (CV) for the work functions and energy band value measurements, details of the cell assembly, more instruments, details of the CdSe nanowire growth, low-magnification TEM image clearly showing the protuberances, EDS spectrum of the as-prepared CdSe nanowires, SEM image of the CdSe nanoparticle layer electrodeposited in lower temperature, additional SEM images that show the other nanostructured CdSe, and discussion of the optical, structural, and the photovoltaic properties of the CdSe nanowires before and after annealing (PDF). This material is available free of charge via the Internet at http:// pubs.acs.org.

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