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A suitable chemical conversion route to synthesize ZnO/CdS core/shell heterostructures for photovoltaic applications

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Abstract

In order to improve the performance of ZnO-based solar cells, ZnO/CdS core/shell heterostructures were synthesized via a facile chemical conversion route. Large area and quasi-aligned ZnO nanowire arrays were firstly fabricated on conductive glass substrates, and then the synthesis of ZnO/ZnS and ZnO/CdS heterostructures were realized by a chemical conversion method. The morphology and structure of the obtained products has been confirmed by field-emission scanning electron microscopy and X-ray diffraction measurements. The synthesized ZnO/CdS core/shell heterostructures were successfully applied in solar cells. The photovoltaic performance investigation demonstrates that the synthesized ZnO/CdS heterostructure-based solar cell shows a higher short-circuit current density compared with the N719 dye-sensitized ZnO nanowire array counterpart. The enhancement in current density may be due to the fact that the surface coverage of the light absorption layer in the ZnO/CdS core/shell heterostructure is very high. These results indicate that the synthesized ZnO/CdS heterostructures by the present method are very suitable for the application as photoelectrode in solar cells.

Keywords: Nanostructures; Semiconductors; Chemical synthesis

1. Introduction

In recent years, considerable attention has been paid to the study of efficient solar cells due to the ever-increasing demand for clean energy [1–5]. Among the different types of solar cell technologies, quantum dot sensitized solar cells (QDSSCs) have attracted a great deal of interest in the last few years [5–12]. The quantum dots (QDs) have been intensively studied for the development of solar cell devices due to their unique features. These include composition-dependent optical absorption spectra, large extinction coefficients, and extended photostability, which underlie efficient harvesting of light energy [6]. Up to now, QDs such as CdS [7,8], PbS [9], PbSe [10], CdSe [11], and CdTe [12] have been extensively investigated as light harvesters.

Despite numerous advantages associated with QDSSCs, effective loading of QDs on the surface of metal oxide nanostructure electrodes remains a significant challenge. Two techniques have been widely adopted during the deposition of QDs onto the surface of nanostructures: the ex-situ adsorption method [13–16] and the in-situ synthesis technique [17–20]. Direct adsorption (i.e. the ex-situ adsorption method) leads to a high degree of QD aggregation and a low surface coverage of approximately 14% of the real surface area [21]. Therefore, the ex-situ adsorption method generally involves the introduction of bifunctional linker molecules to improve the loading density of QDs [13–16]. Although the usage of linker molecules can improve the surface coverage of QDs on the electrodes, they may introduce additional interface problems that hinder the injection of photogenerated electrons from QDs to electrodes and consequently the charge separation efficiencies decrease [22]. Besides the ex-situ adsorption method, another approach for deposition of QDs on the surface of nanostructures is the in-situ synthesis technique. This method can overcome the

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aforementioned problems. Direct growth is done by repeatedly successive immersing nanostructured electrodes into a solution that contains the cationic and anionic precursors or by atomic layer deposition [17–20]. In order to coat high-aspect ratio surfaces, a number of deposition cycles are required. Consequently, the in-situ synthesis technique is a time-consuming synthesis process. Take a recent report for example[23], in order to realize the synthesis of ZnO/CdS core/shell heterostructures, a substrate with ZnO nanowires on it was immersed in an ethanol solution containing $Cd(NO_3)_2$ (0.05 M) for 30 min, and rinsed with ethanol. It was then immersed in a Na_2S methanol solution (0.05 M) for another 30 min, and rinsed with methanol. The above dipping process was repeated several times. Obviously, this process is a time-consuming one. Therefore, further development of a facile synthetic method to synthesize ZnO/CdS core/shell heterostructures for photovoltaic applications is quite necessary.

In this article, a facile chemical conversion route has been demonstrated to prepare quasi-aligned ZnO/CdS core/shell heterostructures. Compared with the previously reported methods for the synthesis of ZnO/CdS core/shell nanostructures for photovoltaic applications [23–26], the present synthetic procedure has the advantages of simplicity (no need to repeat several times) and high surface coverage (the surface coverage of CdS is nearly 100%). The key point of the present method is to employ the concept of chemical conversion on quasi-aligned ZnO nanowire templates for forming ZnO/ZnS and then ZnO/CdS core/shell nanostructures. The obtained products were successfully used in solar cells. Compared with the ZnO nanowire-based dye sensitized solar cell, the ZnO/CdS core/shell heterostructure solar cell exhibits a significant enhancement of short-circuit current density due to the high CdS coverage degree.

2. Experimental details

Quasi-aligned ZnO nanowire arrays were prepared via the typical synthetic procedure: FTO (fluorine doped tin oxide, SnO_2:F) glass substrates were firstly cleaned by sonication in ethanol and water. A seed layer of ZnO was then formed according to the method described by Greene et al. [27]. Finally, the synthesis of quasi-aligned ZnO nanowire arrays was realized by immersing the seeded FTO glass substrates in an aqueous solution containing 10 mM zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6\,H_2O$) and 10 mM hexamethylenetetramine ($C_6H_{12}N_4$) at 92 °C for 2.5 h. This synthetic process was repeated several times to obtain ZnO nanowire arrays with the desired length.

To prepare ZnO/CdS core/shell heterostructures, the synthesis of ZnO/ZnS core/shell nanostructures was firstly realized by transferring the substrates with quasi-aligned ZnO nanowire arrays on them into a glass bottle containing 0.2 M thioacetamide (TAA) at 90 °C for a desired time period. The obtained products were finally treated in a 40 mM aqueous cadmium chloride solution for a desired time period. During this process, the solution temperature was kept at 90 °C.

The morphologies of the samples were characterized using a field-emission scanning electron microscope (FE-SEM; Philips XL30FEG). The energy-dispersive X-ray (EDX) microanalysis was also performed during the FE-SEM measurements. The microstructure of the samples were characterized using a transmission electron microscope (TEM; JEOL JEM-2010F). X-ray diffraction (XRD) was carried out on a D-max/2550 (Rigaku) X-ray diffractometer system equipped with a Cu K_α source ($\lambda = 1.5406$ Å). Raman spectra were measured at room temperature on a Jobin Yvon LabRAM HR 800UV micro-Raman/PL system.

The FTO substrate with the synthesized ZnO/CdS core/shell heterostructures on it was used as the photoelectrode. An FTO glass coated with a layer of sputtered Pt was used as the counter electrode. A drop of the acetonitrile solution consisting of 0.6 M tetra-butylammonium iodide, 0.1 M lithium iodide, 0.1 M iodine, and 0.5 M 4-tert-butylpyridine was introduced between the two electrodes. The photoelectrode and the counter electrode was separated by a spacer and pressed by clamps. In order to compare the performance of the two types of solar cells, the prepared pure ZnO nanowire arrays sensitized in a 0.5 mM N719 dye solution was also used as photoelectrode. The photocurrent–photovoltage measurements were performed using a CHI-660 electrochemical working station by varying an external load voltage. A Newport-Oriel 69911 (150 W) solar light simulator was used as a light source. The intensity of incident light was calibrated to be 100 mW/cm^2 by a radiometer. During measurements, a mask was adopted to create an exposed area of 0.15 cm^2 for all solar cells.

3. Results and discussion

Fig. 1(a) demonstrates the cross-sectional FE-SEM image of the obtained nanowire arrays. From Fig. 1(a), one can clearly see that the quasi-aligned one-dimensional nanowire arrays were directly grown on the FTO glass substrate. The top-view SEM image of the nanowire arrays shown in Fig. 1(b) indicates the density of the nanowires grown on the FTO substrate is very high, which is similar to the previous reported work [28]. The density of ZnO nanowires is calculated to be about $8.5 \times 10^8 cm^{-2}$. EDX spectroscopy result and XRD analysis demonstrated in Fig. 1(c) and (d) confirms the obtained products are ZnO. The signal of Au peak shown in Fig. 1(c) originates from the thin gold film sputtered on the surface of specimen for the SEM observations. The X-ray diffraction peaks corresponding to ZnO presented in Fig. 1(d) can be respectively indexed to the (100), (002), (101), (102), and (110) planes of wurtzite phase ZnO [Joint Committee for Powder Diffraction Standards (JCPDS) no. 36-1451]. The dominant (002) peak of the ZnO nanowires is due to the vertical alignment of the [0001] growth direction, which is consistent with the SEM results shown in Fig. 1(a). The additional peaks correspond to the tetragonal SnO_2 structure (JCPDS no. 77-0450), which originate from the conductive substrate.

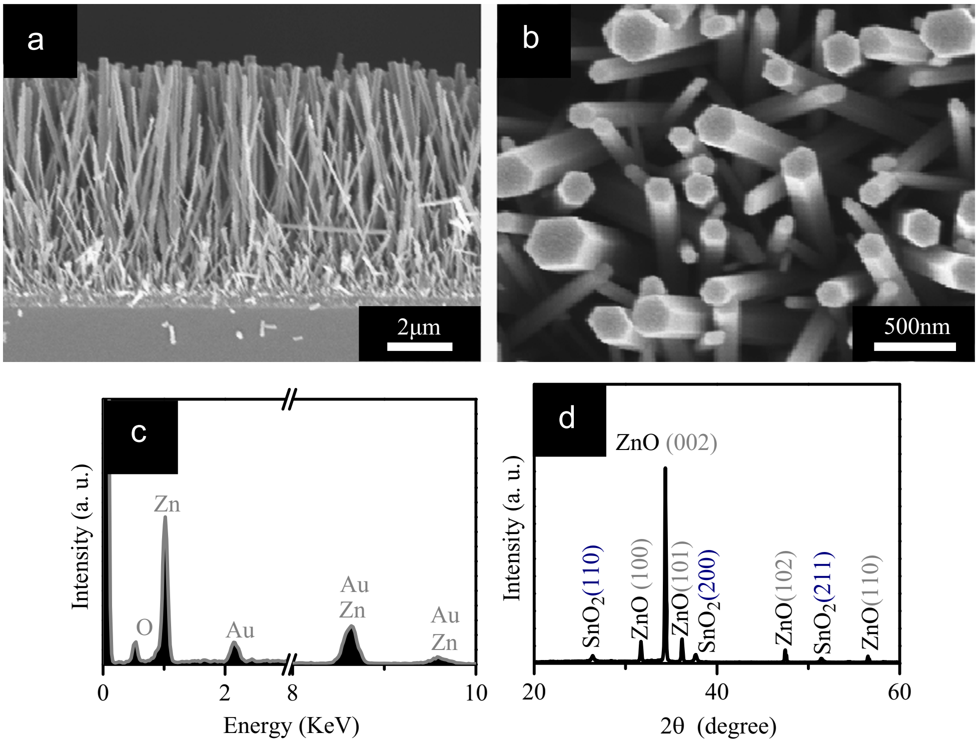

Fig. 1. (a) Cross-sectional and (b) top-view FE-SEM images of the prepared ZnO nanowire arrays; (c) EDX spectrum and (d) XRD pattern of the obtained ZnO nanowire arrays.

In order to realize the synthesis of ZnO/CdS core/shell heterostructures, the chemical conversion method was adopted. Previous studies on the transformation of ZnO nanospindles to ZnO/ZnS core/shell nanospindles have indicated that the chemical conversion is a feasible method to convert ZnO nanostructures to ZnO/ZnS core/shell nanostructures [29]. Fig. 2 schematically displays the formation process of the core/shell nanostructures. By transferring the substrates with quasi-aligned ZnO nanowire arrays on them [Fig. 2(a)] into a glass bottle containing 0.2 M TAA at 90 °C for 1 h, the synthesis of ZnO/ZnS core/shell nanostructures can be realized [Fig. 2(b)]. Similar to the previous reported work, the following reactions are involved in this step for the formation of ZnO/ZnS core/shell nanostructures [29].

$$CH_3CSNH_2 + H_2O \leftrightarrow CH_3CONH_2 + H_2S \quad (1)$$

$$ZnO(s) + H_2S \leftrightarrow ZnS(s) + H_2O \quad (2)$$

The main attempt in the present work is to realize the synthesis of ZnO/CdS core/shell heterostructures and investigate the photovoltaic performance of the synthesized nanostructures. An ion-exchange method was used to convert the ZnS shells into CdS shells for preparing ZnO/CdS core/shell heterostructures by transferring substrate with ZnO/ZnS core/shell nanostructures [Fig. 2(b)] on it into a 40 mM aqueous cadmium chloride solution for a desired time period. The driving force for the ion exchange is provided by the large difference in solubility between ZnS and CdS [solubility product constant (Ksp) of ZnS is 2.93×10^{-25}, while Ksp of CdS is 1.40×10^{-29}] [30]. The ion-exchange method used here only replaces the Zn ion in ZnS with Cd ion in solution; therefore, the obtained nanostructure arrays should be ZnO/CdS core/shell heterostructures [Fig. 2(c)].

Fig. 3(a) shows the SEM image of the final products. Compared with pure ZnO nanowire arrays demonstrated in Fig. 1(b), the surfaces of the obtained nanowires become rough, which could be attributed to the agglomeration of CdS shell layers. Fig. 3(b) displays the cross-sectional SEM image of the ZnO/CdS core/shell heterostructures. The cross-sectional SEM result of the obtained product is similar to that shown in Fig. 1(a). The EDX result demonstrated in Fig. 3(c) clearly shows that besides Zn, O, and Au, new elements Cd and S appear in the synthesized products. TEM measurements have also been carried out to investigate the microstructure of the obtained nanostructures. The TEM images with different magnification of the obtained product are shown in Fig. 3(d–f). From Fig. 3(d), one can see that the edge of the nanowire is paler than the center, indicating the formation of core/shell structure. The high resolution TEM image shown in Fig. 3(f) indicates that the CdS shell is polycrystalline.

Raman spectra can be used to provide valuable structural information on semiconductor nanostructures. The curves (a) and (b) in Fig. 4 represent the Raman spectra of ZnO and ZnO/CdS core/shell nanostructure arrays, respectively. From this Figure, one can also see the transformation process from ZnO to ZnO/CdS core/shell nanostructures. In curve (a), the sharp Raman peak located at 437 cm^{-1} is the nonpolar optical phonon E_2(high) mode of wurtzite ZnO. The other two weak peaks centered at 332 cm^{-1} and 581 cm^{-1} can be assigned to the ZnO multiple-phonon (MP) scattering process and

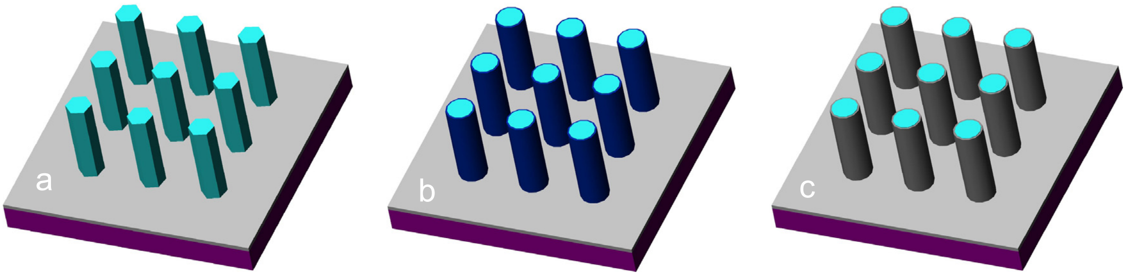

Fig. 2. Schematic diagram for the formation of three types of nanostructures: (a) ZnO nanowire arrays, (b) ZnO/ZnS core/shell heterostructures, and (c) ZnO/CdS core/shell heterostructures.

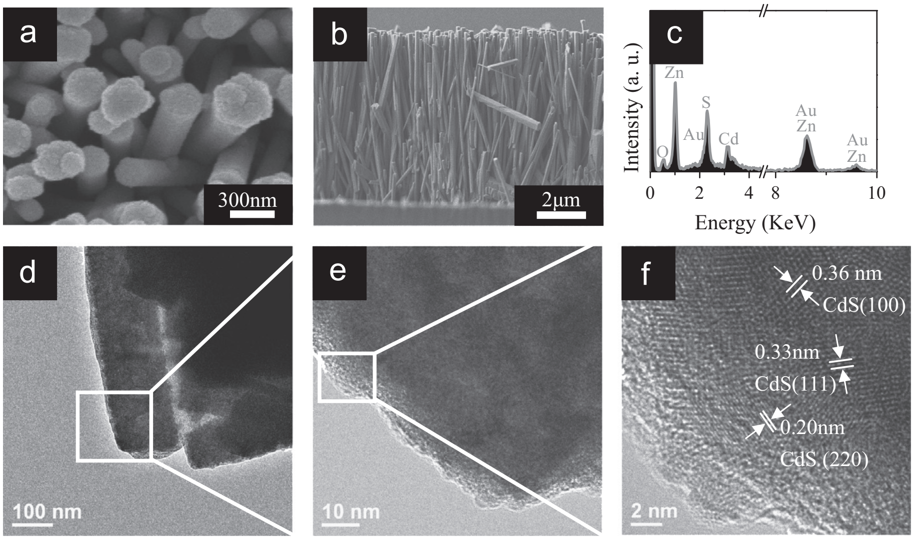

Fig. 3. (a) Top-view and (b) cross-sectional FE-SEM images of the ZnO/CdS core/shell heterostructures. (c) EDX spectrum of the obtained ZnO/CdS core/shell heterostructures. (d–f) TEM images of the obtained ZnO/CdS core/shell heterostructures with different magnification.

E_1[longitudinal-optical (LO)] mode, respectively [31,32]. It is generally believed that the E_1(LO) mode shown in Fig. 4 curve (a) is associated with the oxygen vacancies in the synthesized ZnO nanowires [33]. Previous work has shown that the oxygen vacancies can increase the electrical conductivity remarkably by inducing defect states in the band gap [34,35]. Therefore, the synthesized ZnO nanowire arrays are suitable for fabricating solar cells, in which the direct conduction pathways are needed for transporting the photogenerated electrons. After chemical conversion coating treatments, besides the typical Raman active branch of ZnO located at 437 cm^{-1}, two new peaks located at 301 and 602 cm^{-1} are observed, which can be ascribed to the E_1 and $2E_1$ vibrational modes (first- and second-order longitudinal optical (LO) phonon modes) of CdS, respectively [36]. The observed LO Raman peak positions agree very well with the previously reported work for cubic CdS [37].

The obtained ZnO/CdS core/shell heterostructures were successfully used as photoelectrodes and applied in solar cells. The effect of CdS shell thickness on the solar cell efficiency was investigated. Since the sulfidation time determines the thickness of the formed ZnS shell on the surface of ZnO nanowire, ZnO nanowire arrays treated in TAA for different time periods were used to fabricate ZnO/CdS core/shell heterostructures with different CdS shell thickness. In order to convert ZnS shells on the surfaces of ZnO nanowires to CdS ones completely, ultralong ion exchange time was used (The ion exchange time is thrice as long as the sulfidation time). The sulfidation time and the ion exchange time of the obtained ZnO/CdS core/shell nanowire arrays are displayed in Table 1 (Photoelectrode nos. 1–4 in Table 1). The corresponding photocurrent density (J)–voltage (V) characteristics of the solar cells based on ZnO/CdS core/shell nanowire arrays was demonstrated in Fig. 5(a). From Fig. 5(a), the corresponding physical values of the solar cells, such as short circuit current (J_{SC}), open circuit voltage (V_{OC}), fill factor (FF), and light to electricity conversion efficiency (η) can be obtained. The results are summarized in Table 1. From Table 1, one can see that the efficiencies of solar cells increase with increasing the shell thickness (Photoelectrode nos. 1–3 in Table 1). The efficiencies of the solar cells do not change too much when the sulfidation time increases from 40 min to 60 min and the ion exchange time increases from 120 min to 180 min (Photoelectrodes no. 3 and no.4 in Table 1), which may be due to the fact that the efficiency reaches maximum value of the present photoelectrode.

During the experimental process, a commercial available N719 dye was also used to adsorb on the surfaces of ZnO nanowire arrays to prepare the photoelectrode (Photoelectrode no. 5 in Table 1). Curves (a) and (b) in Fig. 5(b) show the J–V

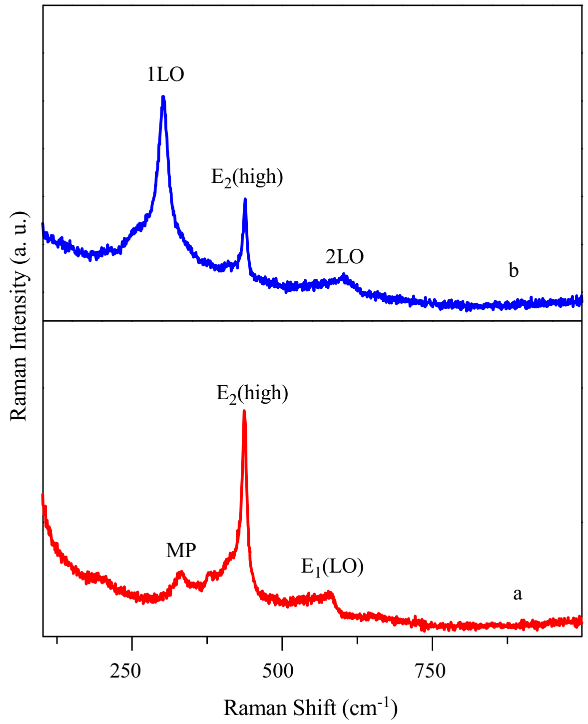

Fig. 4. Room-temperature Raman spectra of (a) ZnO nanowire arrays, (b) ZnO/CdS core/shell heterostructures.

characteristics of the solar cells based on ZnO/CdS core/shell heterostructures (Photoelectrode no. 4 in Table 1) and N719 dye sensitized ZnO nanowire arrays (Photoelectrode no. 5 in Table 1), respectively. The corresponding physical values of the solar cells was also displayed in Table 1. From Fig. 5(b) and Table 1, it can be clearly seen that the short-circuit current density and the overall efficiency of the solar cell based on ZnO/CdS core/shell heterostructures represents a significant improvement over the cell based on N719 dye-sensitized ZnO nanowire arrays. The overall efficiency of the solar cell in the present research is relatively low (0.455% for the ZnO/CdS core/shell nanostructure based solar cell). However, the present work clearly demonstrates that the efficiency of the solar cell can be improved using the ZnO/CdS core/shell nanostructures as photoelectrode. The low efficiency of the solar cell is mainly due to the fact that the length of the nanowires used in the present work is very short. A recent report reveals that the efficiency of solar cells can be improved by using ultra-long nanowires [38]. In their report, the solar cell fabricated with the longest nanowires shows the best performance. The highest efficiency of the solar cell reaches 1.7% as the length of the nanowire increases to 30μm (only several micrometers in our present work, as shown in Fig. 3(b)).

In our present work, the increase in the short-circuit current density of the solar cells based on ZnO/CdS core/shell nanostructures is mainly due to the fact that the surface coverage of the light absorption layer in the ZnO/CdS core/shell heterostructure is very high (nearly 100%), i.e., the surfaces of the ZnO nanowires are nearly completely covered by CdS, as demonstrated in the Fig. 3(d). Therefore, the prepared ZnO/CdS core/shell heterostructures by the present method are more suitable for application as photoelectrode in solar cells.

Table 1
Photovoltaic parameters of solar cells using ZnO/CdS core/shell nanowire arrays (nos. 1–4) and dye sensitized ZnO nanowire arrays (no. 5) as photoelectrodes.

Photoelectrodes	Sulfidation time (min)	Ion exchange time (min)	J_{SC}(mA/cm^{-2})	V_{OC} (mV)	Fill factor	η (%)
No. 1	10	30	0.200	0.520	0.432	0.045
No. 2	20	60	0.750	0.565	0.512	0.217
No. 3	40	120	1.640	0.540	0.512	0.454
No. 4	60	180	1.674	0.576	0.472	0.455
No. 5	–	–	0.540	0.610	0.413	0.136

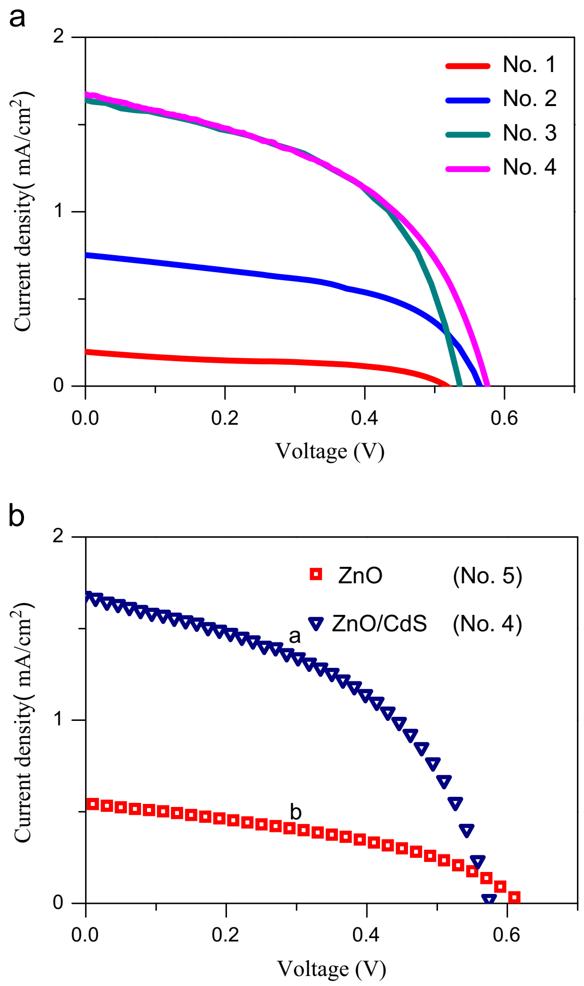

Fig. 5. Photocurrent-photovoltage characteristics of solar cells based on ZnO/CdS core/shell heterostructures (Photoelectrode nos. 1–4) and N719 dye sensitized ZnO nanowire arrays (Photoelectrode No. 5).

4. Conclusions

In summary, a facile and low temperature method has been demonstrated to prepare ZnO/CdS core/shell nanowire arrays.

As the ZnO cores can provide direct conduction pathways for electron transport and CdS shells can act as the light-harvesting layers. Therefore, the synthesized ZnO/CdS core/shell heterostructures can be used in solar cells. Due to the high surface coverage of the light absorption layer in the prepared products, the short-circuit current density of the solar cell based on the ZnO/CdS core/shell heterostructures represents a significant improvement over the cell based on N719 dye-sensitized ZnO nanowire arrays.

Acknowledgments

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