Preparation of Tree-Structured ZnO Films And Application In Quantum Dots Sensitized Solar Cells

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Abstract

This study reported the fabrication of tree-structured ZnO films through hydrothermal method. Long ZnO nanowires (NWs) were firstly deposited on the transparent conductive glass substrates. ZnO branches were then grown on the surface of ZnO NWs. The morphology of the as-prepared tree-structured ZnO films was affected by several factors, such as the concentration of $\text{Zn}(\text{CH}_3\text{COO})_2$ in the seed precursor solution, and the hydrothermal reaction time. ZnO branches were vertically grown on the ZnO NWs when the concentration of $\text{Zn}(\text{CH}_3\text{COO})_2$ was 0.04 M. Quantum dots (QDs)-sensitized solar cells were assembled using the CdS/CdSe QDs co-sensitized ZnO films as the photoanodes. The value of Incident photon-to-current conversion efficiency (IPCE) in the range of 550–650 nm was obviously enhanced with the growth of ZnO branches. The short-circuit current density (J_{SC}) was increased from 9.65 to 12.60 mA cm^{-2} when the growth time of ZnO branches was 6 h. The overall PCE increased from 3.21% to 5.19%.

Introduction

In the past few years, quantum-dot-sensitized solar cells (QDSCs) have attracted immense scientific and technological interest because of their advantages, such as simple preparation process, cost-effectiveness, and high power conversion efficiency (PCE) [1–4]. The PCE of QDSCs has been improved to be 14.4%, which is comparable with those of other solar cells [5, 6]. There are three main parts in QDSCs, photoanode, electrolyte, and the counter electrode parts [7, 8]. The photoanode is the key section of QDSCs which is responsible for the light capture and the generation of electrons [9–11]. The photoanodes have been prepared based on different oxide semiconductors with wide band gap. ZnO is an important environment-friendly, cost-effective n-type semiconductor material which has a high electron mobility ($200\text{--}1000\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) [12, 13]. At the same time, the morphology of ZnO could be easily controlled using various methods. Various nanostructures of ZnO, such as nanorods (NRs), nanosheets (NSs), nanowires, nanoflowers, and nanoballs, have been successfully prepared and applied in solar cells [14–16].

ZnO nanorods were widely studied in QDSCs because the 1D crystalline nanostructured ZnO could provide a direct conduction pathway for the photogenerated electrons. However, the surface area of the ZnO NRs film was much lower than the conventional nanoporous TiO_2 films used in QDSCs. To further enhance the surface area of ZnO NRs film, various nanostructures were prepared on ZnO NRs. Deng et al. prepared TiO_2 nanoparticles and ZnO nanowires hybrid photoanodes which improved the light-trapping of photoanode due to the strong light scattering effect of ZnO NWs [17]. Tian et al. have prepared ZnO NR-NS-structured film by adjusting the growth orientation of the ZnO crystals in the reaction solution. The power conversion efficiency exhibits one-time improvement compared with that of pure ZnO NRs photoanodes [18]. Ko et al prepared high density, long branched “treelike” multigeneration hierarchical ZnO nanowire photoanodes [19]. Generally, hierarchical nanostructured ZnO films exhibit better properties compared to single-structured ZnO films. However, it was challenging to control the morphology of the second ZnO nano-layer on ZnO NWs. In this experiment, ZnO NWs were firstly deposited on FTO

substrates using the hydrothermal method, and ZnO branches were vertically grown on the primary ZnO NWs. The tree-structured ZnO films were co-sensitized with CdS and CdSe QDs to prepare photoanodes for QDSCs. A power conversion efficiency of approximately 5.19% was obtained.

Experimental

2.1. Materials

Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2$), monoethanolamine ($\text{HO}(\text{CH}_2)_2\text{NH}_2$), hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$), cadmium nitrate tetrahydrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$), cadmium sulfate (CdSO_4), trisodium nitrilotriacetate monohydrate ($\text{C}_6\text{H}_6\text{NNa}_3\text{O}_6 \cdot \text{H}_2\text{O}$), and sodium sulfide (Na_2S) were purchased from Sinopharm Chemical Reagent Co. (SCRC, China). Ethanol and methanol (purities > 99.9%) were purchased from Aladdin Reagent Co. (China). All of these materials were used as received without any further purification.

2.2 preparation of tree-structured ZnO films

For the preparation of ZnO NWs, a thin ZnO seed layer were firstly deposited on glass substrates according to the former studies [20]. Long ZnO NWs were grown through hydrothermal reaction at 95 °C in a high pressure reactor. The primary precursors were zinc nitrate ($\text{Zn}(\text{NO}_3)_2$, 4 mM) and hexamethylenetetramine (HMTA: $\text{C}_6\text{H}_{12}\text{N}_4$, 4 mM) with polyethylenimine (PEI, $(\text{C}_2\text{H}_5\text{N})_n$) as additive chemicals in the solution. The hydrothermal reaction time is controlled to be 24 h. The former hydrothermal reaction processes were repeated for the preparation of longer ZnO NWs. The detailed experiments were described in the former studies [20]. The prepared ZnO NWs were immersed in an ethanol solution containing $\text{Zn}(\text{CH}_3\text{COO})_2$. Then, the ZnO NWs samples were hanged in deionized water solution which consisted of 0.05 mol/L $\text{Zn}(\text{NO}_3)_2$ and 0.04 mol/L $\text{C}_6\text{H}_{12}\text{N}_4$ under 90 °C to grow ZnO branches on the former prepared NWs. The growth time was controlled to be 1, 6, 12 and 24 h. The obtained tree-structured ZnO films were dried under room temperature and sintered at 450 °C in muffle furnace.

2.3 Sensitization of tree-structured ZnO films and QDSCs fabrication

CdS QDs were firstly deposited on the tree-structured ZnO films through successive ion layer absorption and reaction technique (SILAR) method. The detailed processes were performed following the former studies [21]. For the deposition of CdSe QDs, the CdS sensitized tree-structured ZnO films were then immersed in a mixed aqueous solution containing Na_2SeSO_3 , CdSO_4 , and $\text{C}_6\text{H}_6\text{NNa}_3\text{O}_6$ for ca. 4 h at room temperature. The CdS and CdSe QDs co-sensitized ZnO films were rinsed with DI water and dry at room temperature in dark.

The CdS and CdSe QDs co-sensitized ZnO films were used as photoanodes. PbS films, which were prepared through the treatment of Pb sheets in a 2.0 M of Na_2S , 0.5 M of S, and a 0.2 M KCl mixed

solution for another 1 h at 70 °C, were used as the counter electrodes. The electrolyte was polysulfide aqueous solution containing 1 M of Na₂S, 1 M of S, and 0.1 M of NaOH. The photoanodes and PbS counter electrodes were sandwiched to be a simple solar cell device.

2.4 Measurement and characterization

The morphology and structure of the tree-structured ZnO films were characterized through field-emission scanning electron microscopy (FE-SEM, JSM-7001F). The crystalline phase of the samples was examined using X-ray diffraction (XRD, DX-2700) with a monochromatic Cu K_α irradiation ($\lambda = 0.154145$ nm).

The photovoltaic performance of QDSCs was measured using a Keithley 2440 source meter under AM 1.5G illumination from a Newport Oriel solar simulator with an intensity of 1 Sun. The incident light intensity was calibrated using a standard Si solar cell obtained from Newport Oriel. The active cell area of the assembled QDSCs was 0.25 cm². Incident photon-to-current conversion efficiency (IPCE) spectra were recorded on an IPCE system especially designed for QDSCs (Crowntech. Inc.). To generate a monochromatic beam, a 150-W tungsten halogen lamp was used as the light source. A silicon solar cell was used as the standard during calibration. IPCE values were measured using a Keithley model 2400 source meter.

Results And Discussion

Regular ZnO NWs were mostly vertically grown on the FTO glass substrate. The length of the NWs could be regulated to be ca. 3.08, 6.27 and 11.3 μ m, respectively (shown in Fig.1), with the extension of the hydrothermal reaction times. The hydrothermal reaction time was 24 h for one growth processes. So the growth time of the ZnO NWs were controlled to be 24 h, 48 h and 72 h. It also can be seen that there were almost no dividing lines in the whole ZnO NWs in Fig. 1(c) although the ZnO NWs were grown through three times of hydrothermal reaction. At the same time, there were large distance between the adjacent ZnO NWs, which provided convenience for the growth of ZnO branches.

For the growth of ZnO branches on the NWs, the obtained ZnO NWs films were immersed in the ZnO seed solution containing 1.2 M Zn(CH₃COO)₂ and sintered at 450 °C for 30 min. Then, the ZnO NWs was hanged in the solution containing 0.05 mol/L Zn(NO₃)₂ and 0.04 mol/L C₆H₁₂N₄ under 90 °C. The time of the hydrothermal treatment was controlled to be 1, 6 and 12 h, respectively. Figure 2 shows the surface and cross section of the tree-structured ZnO films after different hydrothermal treatment time. There were some short branches grown on the surface of the ZnO NWs when the hydrothermal treatment time was 1 h. The short branches were ca. 100 nm. The length of the branches was improved to be ca. 500 nm when the hydrothermal treatment time was 6 h. The length of the branches was further increased to be ca. 1.0 μ m after 12 h hydrothermal treatment. The length of ZnO branches depended on the hydrothermal treatment time. It can also be seen from the cross section of these samples that the ZnO branches were

almost grown surrounding the ZnO NWs. However, there were few ZnO branches at the end of ZnO NWs. This phenomenon might be related with the capillary effect during the immersion process of Zn seeds.

Though ZnO branches could grow at the surface of ZnO NWs, the ZnO branches were much messy. In this experiment, it was investigated about the effects of the concentration of $\text{Zn}(\text{CH}_3\text{COO})_2$ in the ZnO seed solution on the morphologies of the ZnO films. The concentration of $\text{Zn}(\text{CH}_3\text{COO})_2$ was increased from 1.2 M to 2.4 M. The branches became more dense and chaotic (shown in Fig. 3 (a-d)). The branches were ca. 500 nm in length. The concentration of $\text{Zn}(\text{CH}_3\text{COO})_2$ was also decreased to 0.24 M and 0.04 M. It can be seen from the SEM images (Fig. S1 and Fig. 3 (e) and (f)) that the length of branches increased with the decreasing of the concentration of $\text{Zn}(\text{CH}_3\text{COO})_2$. Meanwhile, the branches were mostly vertical to the ZnO NWs when the concentration of $\text{Zn}(\text{CH}_3\text{COO})_2$ was 0.04 M. The length of the branches was over 1 μm .

The obtained ZnO NWs films and tree-structured ZnO films were co-sensitized with CdS and CdSe quantum dots. The sensitized ZnO films were assembled with PbS counter electrode as Sandwich-structured solar cells. Figure 4 (a) and (b) show the photovoltaic characteristics of these quantum dots sensitized solar cells. The characteristic parameters were summarized in Table1. It can be seen from Fig.4 (a) that the short-circuit current density (J_{SC}) increased with the lengthening of the growth time of ZnO NWs. The improvement of J_{SC} should be due to the increase of quantum dots deposited on the ZnO NWs. Meanwhile, the fill factor (FF) and open-circuit voltage (V_{OC}) also was enhanced with the lengthening of the growth time. The specific surface area of the ZnO films should be further improved with the growth of ZnO branches. On the other hand, the growth of branches might increase the diffuse reflection properties of these ZnO films. The former two effects were both benefit to the increase of J_{SC} of the quantum dots sensitized solar cells. Figure4 (b) shows the photocurrent density–voltage of the CdS and CdSe quantum dots co-sensitized tree-structured ZnO films. It can be seen that the main parameters of QDSCs, such as J_{SC} , V_{OC} and FF , were all obviously enhanced with the growth of ZnO branches. The J_{SC} was increased from 9.65 to 12.60 mA cm^{-2} when the growth time of ZnO branches was 6 h. Meanwhile, the fill factor and open-circuit voltage were increased to be 676 mV and 0.61, respectively. The overall PCE increased from 3.21–5.19%. The fill factor and open-circuit voltage showed almost no changes when the growth time of ZnO branches was further increased. However, the value of J_{SC} began to decrease when the growth time of ZnO branches was further increased. So the optimum growth time of ZnO branches should be ca. 6 h.

Table 1

Photovoltaic characteristics of the QDSCs using CdS–CdSe quantum-dot-sensitized ZnO NWs and tree-structured ZnO films as photoanodes

Growth time of ZnO NWs	Growth time of ZnO branches	$J_{SC}/\text{mA cm}^{-2}$	V_{OC}/mV	FF	$PCE/\%$
24h	0	7.79	567	0.45	2.06
48h	0	8.69	586	0.49	2.46
72h	0	9.65	595	0.56	3.21
72h	1h	10.20	648	0.59	3.89
72h	6h	12.60	676	0.61	5.19
72h	12h	11.75	683	0.60	4.81
72h	24h	10.81	682	0.62	4.57

Fig. 4 (c) and (d) show the IPCE spectrum of the solar cells, assembled with the CdS and CdSe quantum dots co-sensitized ZnO NWs films and tree-structured ZnO films. It can be seen from Fig. 4 (c) that the IPCE in the range of 350–550 nm was increased with the lengthening of the growth time of ZnO NWs. However, the growth of ZnO branches showed effects on the value of IPCE in the range of 350–650 nm (the whole entire extinction range of the assembled solar cells). The most important effect should be the IPCE in the range of 550–650 nm which was fine supplement to the CdS and CdSe quantum dots co-sensitized ZnO NWs films. The results of IPCE gave a good explanation for the improvement of photoelectric conversion performance of the solar cells based on tree-structured ZnO films.

Conclusions

ZnO NWs were deposited on transparent conductive glass substrates. The length of ZnO NWs was ca. 11.3 μm after three times of hydrothermal processes. ZnO NWs films were treated in the ZnO seed solution containing $\text{Zn}(\text{CH}_3\text{COO})_2$ and ethanolamine for the growth of ZnO braches. The concentration of $\text{Zn}(\text{CH}_3\text{COO})_2$ and treating time were the key parameters which affect the morphology of ZnO braches. The branches were mostly vertical to the ZnO NWs when the concentration of $\text{Zn}(\text{CH}_3\text{COO})_2$ was 0.04 M. The length of the branches was over 1 μm . However, the ZnO braches became more and more disorderly with the increasing of the concentration of $\text{Zn}(\text{CH}_3\text{COO})_2$ in the ZnO seed solution. The obtained ZnO NWs films and tree-structured ZnO films were co-sensitized with CdS and CdSe quantum dots and assembled with PbS counter electrode as Sandwich-structured solar cells. The value of IPCE in the range of 550–650 nm was obviously enhanced with the growth of ZnO braches. As a result, the J_{SC} was increased from 9.65 to 12.60 mA cm^{-2} when the growth time of ZnO branches was 6 h. The overall PCE increased from 3.21–5.19%.

Declarations

Author's contributions

Shaokang Dong carried out the experiment. Zeng Chen analyzed the data and finished figures in the manuscript. Shengjun Li, Junhao Cai, and Pin Lv provided useful suggestions to the experiment. All authors read and approved the final manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Figures

Figure 1

SEM images of ZnO nanowires grown from the solution of 4 mM $\text{Zn}(\text{NO}_3)_2$, 4 mM HMT and 3 mM PEI: (a) growth growth for 1 cycle, (b) growth for 2 cycles, (c) growth for 3 cycles and (d) surface images of ZnO nanowires

Figure 2

SEM micrographs of tree-structured ZnO films prepared at different hydrothermal treatment times, (a) and (b) 1 h; (c) and (d) 6 h; (e) and (f) 12 h, 0.12 M $\text{Zn}(\text{CH}_3\text{COO})_2$ seed precursor solution

Figure 3

SEM micrographs of tree-structured ZnO films prepared with different concentrations of $\text{Zn}(\text{CH}_3\text{COO})_2$ in the seed solution, (a) and (b) 2.4 M; (c) and (d) 1.2 M; (e) and (f) 0.04 M.

Figure 4

Photocurrent density–voltage and IPCE curves of QDSCs using CdS–CdSe quantum-dot-sensitized ZnO NWs (a and c) and tree-structured ZnO films (b and d) as photoanodes.

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