SCIENCE CHINA
Technological Sciences

April 2010 Vol.53 No.4: 1146–1149
doi: 10.1007/s11431-010-0066-8

Synthesis of nanostructural ZnO using hydrothermal method for dye-sensitized solar cells

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Received June 18, 2009; accepted September 10, 2009

ZnO nanocrystals with different morphologies were successful synthesized by a simple hydrothermal method combined with and without hexadecyl trimethyl ammonium bromide (CTAB). The phases and morphologies of the products were measured using X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM), respectively. The results indicated that the ZnO nanocrystals with different morphologies were of hexagonal wurtzite structure. ZnO nanorods were obtained without using CTAB, and then the morphology of ZnO changed to ZnO nanoflower and the density of nanoflower became denser with the increase of CTAB concentration. ZnO nanoflower and ZnO nanorod as photoanode were applied to dye-sensitized solar cells (DSSC), respectively. The nanoflower shows a higher dye loading, so DSSC with the use of the ZnO nanoflower possesses a higher conversion efficiency than ZnO nanorod.

Citation: Wang C X, Zhang X D, Wang D F, et al. Synthesis of nanostructural ZnO using hydrothermal method for dye-sensitized solar cells. Sci China Tech Sci, 2010, 53: 1146–1149, doi: 10.1007/s11431-010-0066-8

1 Introduction

Dye-sensitized solar cells (DSSCs) are a new type of photo electrochemical solar cells. They are easy to produce and have a good application prospect. At present, TiO_2 as DSSC photoanode has a better photoelectric conversion efficiency and shown a good prospect for the industry [1]. However, nano-porous TiO_2 thin films have a large number of surface states, which can reduce the conversion efficiency of DSSC. Therefore, other semiconductor optical anode oxide has become a research hot point in DSSC [2]. ZnO is a very important II-VI semiconductor. The direct band-gap is 3.37 eV and the large exciton binding energy is 60 meV [3]. In addition, ZnO with high electronic mobility is expected to increase the electronic mobility of the film, and the synthesis of ZnO nanostructure is much simpler than that TiO_2 [4]. Therefore, it can further reduce the fabrication cost. Keis et al. [5, 6] reported that ZnO nanoparticles as DSSC photoanode had conversion efficiency analogous to TiO_2 DSSC. Great efforts have been attempted to synthesize high-performance ZnO DSSC [7–10]. However, ZnO DSSC photoanodes with different morphologies have different capacities for the dye loading and optical absorption [11], so how to obtain ZnO crystalline suitable for the application for DSSC is an important aspect.

In this paper, ZnO nanocrystals with different surface morphologies were synthesized and they were also used for DSSCs.

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2 Experimental details

All of the reagents (analytical grade purity) were purchased from Tianjin Chemical Reagents Co. and used without further purification. All the aqueous solutions were prepared using deionized water.

2.1 Synthesis of ZnO material

In a typical experiment, Zn $(NO_3)_2 \cdot 2H_2O$ and NaOH were firstly dissolved in deionized water under constant stirring. Secondly, CTAB (0, 1 g, 2 g) was introduced into the above-mentioned solution with 5 mL ethanol. The solution with white flocculent precipitate immediately appeared. The total 80 mL solution balanced with deionized water was transferred into a 100 mL in volume Teflon-lined stainless steel autoclave. Hydrothermal treatment was carried out at 120°C for 24 h. After that, the autoclave was allowed to cool down. White precipitates were collected and then washed with deionized water and ethanol three times to remove impurities. Finally, the precipitates were dried at 60°C for 5 h.

2.2 Fabrication of DSSC

To measure the photo electrochemical properties of the obtained ZnO materials, ZnO colloid was prepared on conducting glass sheets (fluorine-doped SnO_2 glass with a sheet resistance of 15 Ω/sq and 90% transmittance) by using doctor blade method. ZnO colloid was prepared by introducing 0.5 g PEG20000 and 1.8 mL PEG200 into 1 g ZnO powder. Then the film was calcined at 500°C for 30 min. After the film cooled down to 80°C, it was immersed into the dye solution consisting ruthenium N719 for 6 h at room temperature. The area of the DSSC with ZnO photo electrode was about 0.25 cm^2.

3 Results and discussion

3.1 Crystalline properties and morphologies of ZnO

Figure 1 shows the X-ray diffraction (XRD) patterns of the obtained products by hydrothermal method with different weights of CTAB assisted. All the diffraction peaks can be indexed from the hexagonal wurtzite phase structure ZnO (JCPDS card No. 36-1451, a = 0.325 nm and c = 0.521 nm). The strong and narrow diffraction peaks indicate that the products have good crystallization. The narrow full width at half maximum (FWHM) indicates the high crystal quality and crystalline [12]. No impurity phases such as Zn $(OH)_2$ and NaOH can be observed from the X-ray patterns.

Figure 2 shows the SEM images of ZnO nanostructure with different morphologies. From Figure 2(a), it can be clearly seen that there are a large quantity of nanorods,

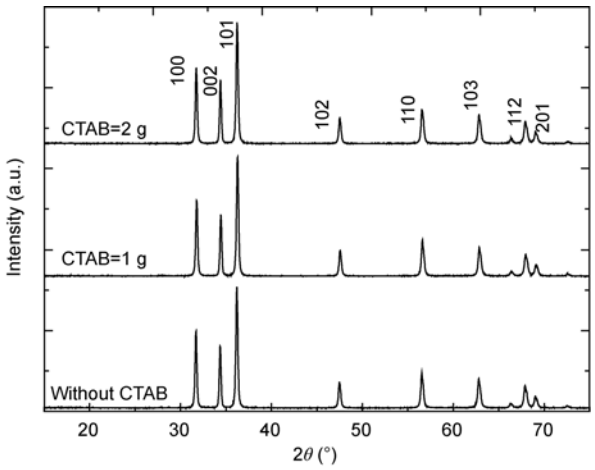

Figure 1 XRD patterns of the obtained ZnO nanocrystals.

which have diameters ~0.5–1 μm and lengths ~5–6 μm. Most of the nanorods' ends are conical. When 1 g CTAB (Figure 2(b)) was introduced into the solution, the morphology of the ZnO nanostructure changed a lot. The ZnO nanorods assembled and became the nanoflowers. The diameters of the nanoflowers are ~4–5 μm. It is interesting to notice that there are two different kinds of ends in a nanoflower, flat in the centers and conical in around. When 2 g CTAB (Figure 2(c)) was introduced into the solution, the morphology of the ZnO was not changed, however, the density of the nanoflowers increased.

Cationic surfactant CTAB was used in the growth solution, it was completely ionized in the solution as CTAB→ $CTA^+ + B^-$. The resulted cation is a positively charged tetrahedron with a long hydrophobic tail, which is electrostatically attached to $[Zn(OH)_4]^{2-}$ [13]. This ion pair formation is helpful for perfect landing of the growth unit $[Zn(OH)_4]^{2-}$ as described by Sun et al. [14]. The surfactant generally reduces the surface tension of material [15]. So, the surfactant CTAB can be adsorbed on the ZnO. The ZnO nanorods are self-assembled into nanoflowers with the CTAB assistant. The surface tension of the ZnO is reduced much more with increasing CTAB concentration, therefore, the ZnO nanoflowers become denser and denser.

Figure 3(a) shows the TEM images of ZnO nanoflower with 2 g CTAB. From the TEM images, it is clearly seen that the diameter of the ZnO nanoflowers is about 4 μm. Figure 3(b) indicates that the ZnO nanoflower is single crystalline in nature. It is consistent with the X-ray pattern result of the hexagonal ZnO phase.

3.2 Photo electrochemical properties of ZnO nanocrystals

In order to check the properties of ZnO with different morphologies, DSSC were fabricated using ZnO nanoflower and nanorod as photoanodes, respectively. The performance

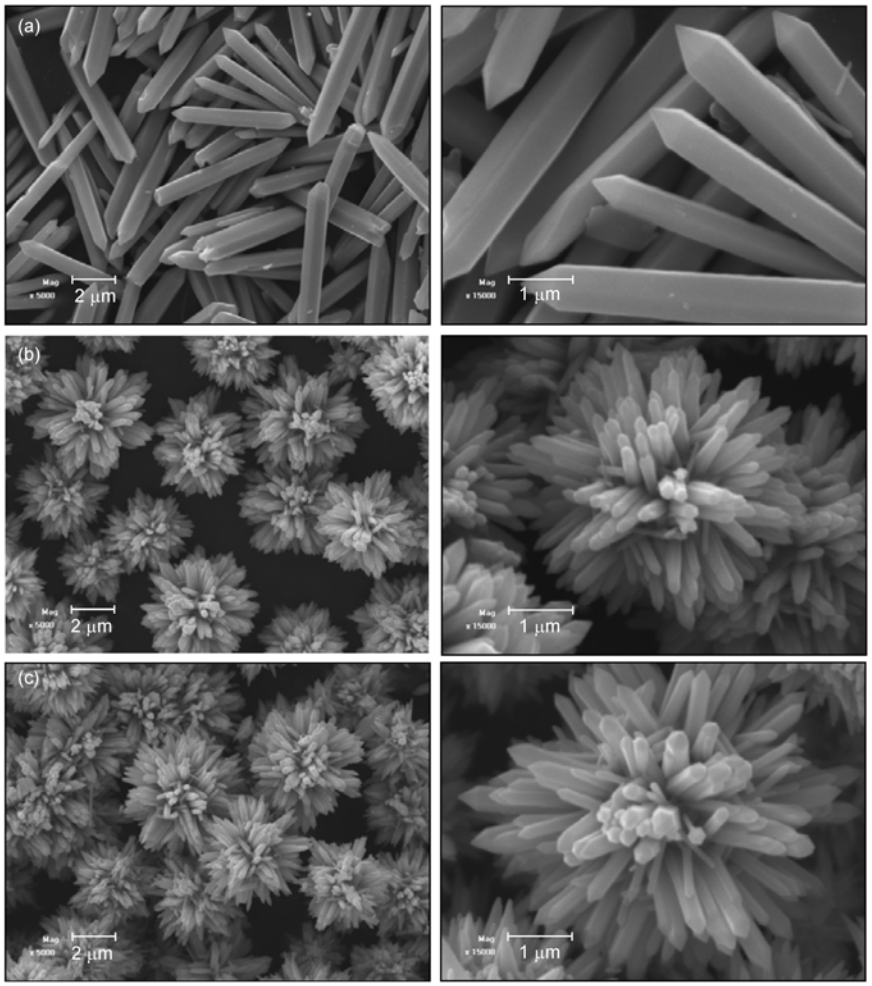

Figure 2 SEM images of the ZnO structures synthesized (a) without CTAB; (b) with 1 g CTAB; (c) with 2 g CTAB (left for ×5000, right for ×15000).

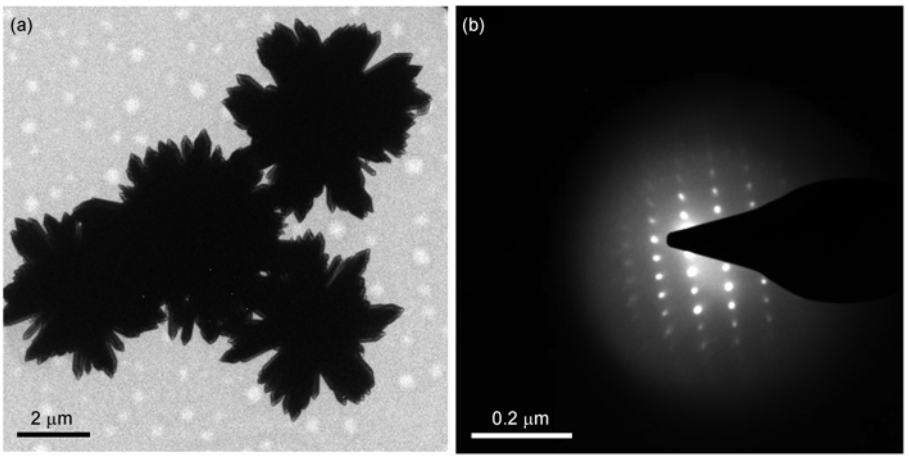

Figure 3 (a) TEM image of a nanoflower with 2 g CTAB; (b) the corresponding SAED pattern.

of solar cells was measured under a simulated illumination of a light intensity of 100 mW/cm^2 (AM1.5). Figure 4 shows the current density-voltage (J-V) characteristic for ZnO-DSSC. It can be seen that the short circuit current density (Jsc), open circuit voltage (Voc), and fill factor (FF) for the nanoflower-DSSC (Jsc=5.23 mA/cm^2, Voc=0.55 V, FF=0.48) are clearly higher than those of nanorod-DSSC (Jsc=2.44 mA/cm^2, Voc=0.27 V, and FF=0.29). Therefore, the nanoflower-DSSC has a conversion efficiency 1.37% higher than that of the nanorod- DSSC.

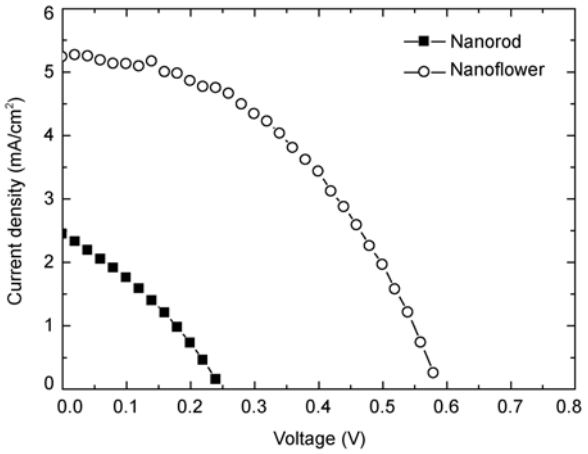

Figure 4 Current density-voltage (J-V) characteristics of ZnO nanorods DSSC and ZnO nanoflowers DSSC.

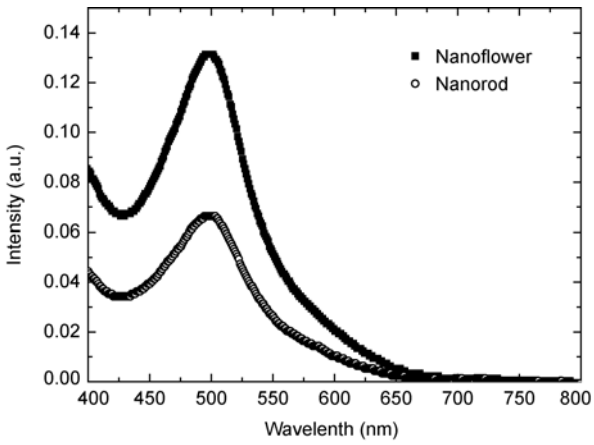

Figure 5 Absorption patterns of dyes detached from the ZnO-nanoflower and ZnO-nanorod.

The low current density of nanorod-DSSC arises from small surface area of the nanorod with low dye loading and light harvesting [16, 17]. The better conversion efficiency of nanoflower-DSSC is attributed to the high dye loading which has been proven by desorption experiment. Figure 5 shows the absorption of the dye detached from the DSSC in a 0.5 mM KOH solution [5]. The amount of absorbed dye is calculated by the integration of spectra area. It can be seen that ZnO nanoflower's dye loading (2.15×10^{-7} mol/cm^2) is higher than ZnO nanorod' dye loading (1.08×10^{-7} mol/cm^2). Therefore, the nanoflower-DSSC has a significant improvement on the dye loading than, as compared to nanorod-DSSC.

4 Conclusions

In hydrothermal method, ZnO surface morphology can be controlled by using surfactant CTAB. ZnO nanorods can be synthesized without using CTAB and then the morphology changes to nanoflowers with the using of CTAB. ZnO nanoflower became denser with increasing CTAB concentration. All of the synthesized nanostructure ZnO materials are of high crystalline wurtzite structures. ZnO nanoflower films have better dye loading than ZnO nanorod films, so nanoflower-DSSC shows an overall conversion efficiency of 1.37% higher than nanorod-DSSC.

This work was supported by the National Hi-Tech Research and Development Program of China ("863" Project) (Grant Nos. 2007AA05Z436, 2009AA050602), the Science and Technology Supporting Program of Tianjin (Grant No. 08ZCKFGX03500), the National Basic Research Program of China ("973" Project) (Grant Nos. 2006CB202602, 2006CB202603), the National Natural Science Foundation of China (Grant No. 60976051), the International Cooperation Project between China-Greece Government (Grant Nos. 2006DFA62390, 2009DFA62580), and the Program for New Century Excellent Talents in University of China (Grant No. NCET-08-0295).

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