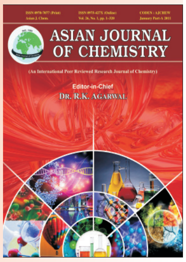
Asian Journal of Chemistry; Vol. 26, No. 24 (2014), 8277-8280

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.16691



Preparation and Photoelectric Properties of ZnO Arrays with Top Hollow Pits

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Received: 14 November 2013; *Accepted*: 14 March 2014; *Published online*: 1 December 2014; AJC-16345

In this paper, ZnO array with hollow pits on the surface was prepared by hydrothermal reaction and its photoelectric properties was also reported. The morphologies of the prepared products were measured using scanning electron microscopy and the results demonstrated that dissolution of ZnO crystal could happen by regulating the reaction time under high concentration of precursor solution, which brought about the variation of ZnO arrays' surface topography and form the top hollow pits. The photoelectric properties of the ZnO array, which was used as photoelectrode for dye-sensitized solar cells (DSSCs), were investigated by current-voltage (J-V) characteristic test and the parameters indicated that hollow shape on the surface of ZnO arrays leaded to the short circuit current density (Jsc) increase and buffer layers provided by thick ZnO arrays resulted in the increase of open circuit voltage (Voc). The present research may be helpful to improve the conversion efficiency of ZnO array-based dye-sensitized solar cells.

Keywords: ZnO array, Top hollow pit, Hydrothermal reaction, Dissolution of ZnO crystal, Photoelectric property.

INTRODUCTION

One-dimensional (1-D) nanomaterials have drawn a lot of attention because of their novel and unique properties and a wide range of applications. Among various nanomaterials, ZnO nanostructures have been very popular in the nano-research field due to their semiconductive, optical, electrical and chemical properties.

It is known that, the solar cells using arrays as photoelectrode show higher conversion efficiency compared to those using disorder structures[1], because array semiconductor materials can offer direct electrical pathways for the rapid collection of photogenerated electrons, thus enhancing the electron transport speed in the photoelectrode and diminishing the possibility of charge recombination. Recently, considerable efforts have been devoted to the synthesis of ZnO arrays (nanowires[2], nanotubes[3], nanobelts[4], nanosheets[5,6] and nanotips[7]) that used as photoelectrodes of dye-sensitized solar cells and some achievement in improving the conversion efficiency have been got attributed to the specific microstructures of ZnO arrays. However, most of the syntheses of these nanostructures are complex.

In this paper, ZnO array with hollow pits on the surface was prepared using a typical hydrothermal process under high concentration of precursor solution. The relationship between reaction condition and morphology of the products involved in the experiment was discussed and the effects of ZnO arrays' morphology on the performance of ZnO array-based dye-sensitized solar cells were also studied.

EXPERIMENTAL

Cis-bis(isothiocyanato)*bis*(2,2'-bipyridy1-4,4'-dicarboxylato)ruthenium(II)*bis*-tetrabutylammonium (also called N719) was from Heptachroma, China. Other chemicals (Kelong Chemical Reagents Co.) used in our experiments were of analytical reagent grade without further purification. All the aqueous solutions were prepared using deionized water. Fluorine-doped tin oxide substrates (FTO TEC-7, Heptachroma, China) were first cleaned through sonication in acetone/ethanol for 0.5 h and then dried using a stream of nitrogen gas.

Preparation of ZnO arrays

Preparation of ZnO seeds on fluorine-doped tin oxide substrates: Zinc acetate dihydrate and ethanolamine were dissolved in 2-methoxyethanol successively. The concentration of both $Zn(CH_3COO)_2{\cdot}2H_2O$ and ethanolamine in the resulting solution was 0.50 M. The solution was then spin-coated onto fluorine-doped tin oxide substrates at 1,500 rpm for 3 times. Subsequently, the substrates were annealed at 500 °C in air for 1 h in order to convert zinc acetate to ZnO.

Hydrothermal deposition: In a typical reaction process, ZnO arrays were grown by placing vertically the ZnO-seeded fluorine-doped tin oxide substrates into precursor solution at

95 °C for a certain time, the precursor solution was aqueous solution containing zinc nitrate hydrate and hexamethylenetetramine ($C_6H_{12}N_4$, HMT). The molar ratio of $Zn(NO_3)_2 \cdot 6H_2O$ and hexamethylenetetramine was kept to be 1:1. In this paper, the concentration of precursor solution was 200 mM and the reaction time was set to 8, 12 and 24 h. When the reaction completed, the grown ZnO arrays were washed with deionized water and dried in air to remove the residual organics.

Assembling of dye-sensitized solar cells: The resulting substrates grown with ZnO arrays were immersed in absolute ethyl alcohol containing 0.3 mM N719 dye for 24 h. To assemble the solar cell, a Pt-coated conducting glass was placed on the ZnO array films separated by a 50 µm thin membrane spacer. Then the assembled cell was clipped together as an open cell. The area of the dye-sensitized solar cell with ZnO photoelectrode was about 0.64 cm^2. An electrolyte, which was made with 0.1 M LiI, 0.1 M I_2, 0.6 M dimethylpropylimidazolium iodide and 0.5 M tert-butylpyridine in acetonitrile, was introduced *via* capillary action into the gap formed between the two electrodes.

Characterization: The morphology of the products was characterized using scanning electron microscopy (SEM, Hitachi S-4800). Photocurrent-voltage measurements were performed under AM 1.5G of simulated sunlight (CEL-S500, Beijing of China) with an output power of 100 mW cm^{-2}.

RESULTS AND DISCUSSION

The ZnO seed film on fluorine-doped tin oxide substrate was obtained by spin-coating method. The scanning electron microscopy image of ZnO seed film is shown in Fig. 1, which was compact and composed of ZnO particles with the size of 50 nm.

The morphologies of ZnO arrays grown on ZnO-seeded fluorine-doped tin oxide substrates under high concentration of precursor solution (200 mM) for different time (8, 12 and 24 h) at 95 °C exhibited regular change (Fig. 2). Fig. 2(a, a_1, a_2) show the tilted, cross-sectional and top view of ZnO arrays grown for 8 h (sample A), which indicating that the arrays were approximative hexagonal prisms and had shallow pits on the top, the average length of the ZnO arrays was 3.2 µm with a 400 nm diameter. Fig. 2(b, b_1, b_2) are the scanning electron microscopy images of ZnO arrays grown for 12 h (sample B). It can be seen from the cross-sectional view that the ZnO arrays were vertically aligned on the fluorine-doped tin oxide substrate, about 3 µm long and the top view of the arrays was also similar to hexagonal prism with an average diameter of 400 nm, but the hollow pit on the top was deeper and more regularly arranged than that of sample A, like honeycomb. Differently, ZnO nanorod arrays grown for 24 h (sample C) had no pits on the top, seen from Fig. 2(c, c_1, c_2), averagely 400 nm wide and 2.5 µm long. We can see from Fig. 2 that the ZnO arrays would dissolve and form regular hollow pits on the top when the reaction time increased from 8 to 12 h and then shorter ZnO nanorod arrays would be obtain when the reaction time increased to 24 h. This phenomenon may be explained by the principle of chemical equilibrium involved in the formation of ZnO crystal[8] and character of ZnO crystal structure. The equilibrium equation of chemical reaction was as follows:

$$Zn^{2+} + 2OH^- + 2H_2O \rightleftharpoons [Zn(OH)_4]^{2-} + 2H^+ \rightleftharpoons ZnO + 3H_2O \quad (1)$$

High concentration of $Zn(NO_3)_2$ solution provides a large number of growth units ($[Zn(OH)_4]^{2-}$), which unceasingly get into the crystal lattice of ZnO to grow and form nanorod with large diameter and long length. As the growth progresses, the early rapid reaction causes the amount of $[Zn(OH)_4]^{2-}$ in precursor solution quickly reduced, then the chemical reaction shift to the left, causing the dissolution of ZnO nanorod from the top and the length of the nanorod shortened, after a certain time of new chemical equilibrium formation, the length keeps unchanged. Furthermore, ZnO would preferentially dissolve on the top and form the top pit, that because ZnO is a polar crystal for the distribution of zinc atoms and oxygen atoms are dissymmetrical along the C axis (Fig. 3), bring about the metastable and polar (0001) crystal faces in ZnO crystal structure dissolve faster than the nonpolar crystal faces[9], the dissolution process is shown in Fig. 4. As the reaction progressed, the dissolution of (0001) crystal faces would reach an equilibrium while the crystal faces continue to dissolve until they reach an equilibrium too, so the top pits would disappear. Therefore, the dissolution phenomenon could happen by regulating the reaction time under high concentration of $Zn(NO_3)_2$ solution.

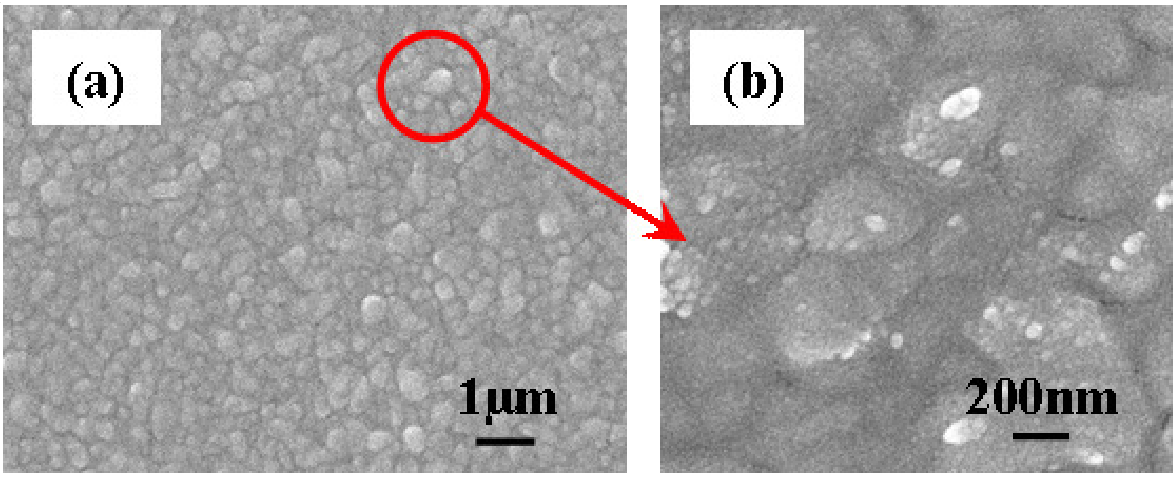

Fig. 1. (a), (b) Scanning electron microscopy images of ZnO seed film

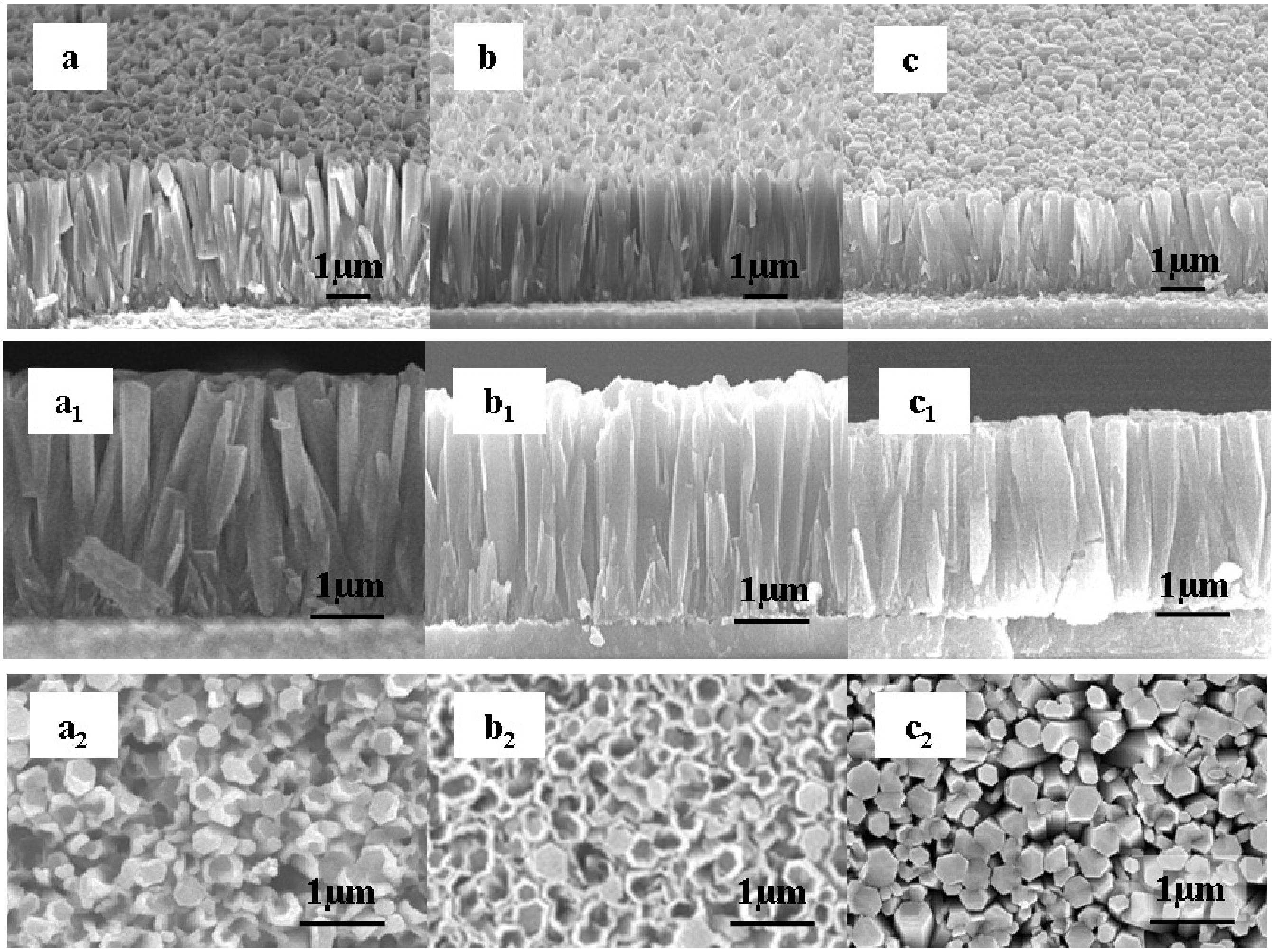

Fig. 2. Scanning electron microscopy images of ZnO arrays grown on ZnO-seeded FTO substrates in 200 mM $Zn(NO_3)_2$ solution for (a, a_1, a_2) 8 h, (b, b_1, b_2) 12 h and (c, c_1, c_2) 24 h. (a, b, c) Tilted view. (a_1, b_1, c_1) Cross-sectional view. (a_2, b_2, c_2) Top view

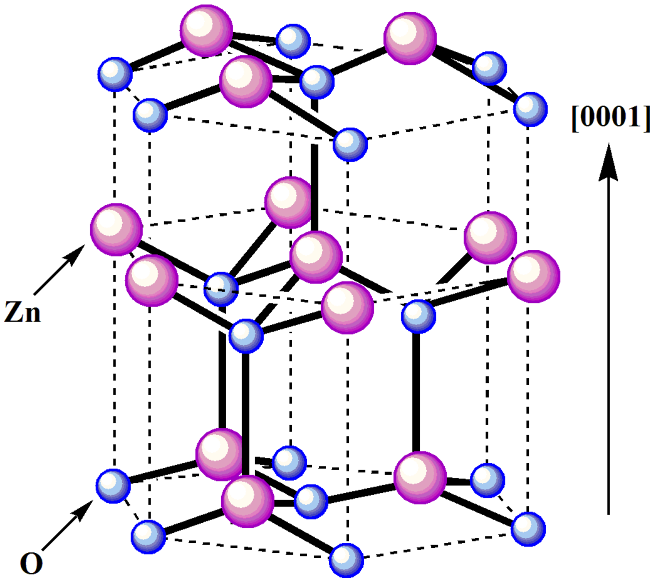

Fig. 3. ZnO crystal structure

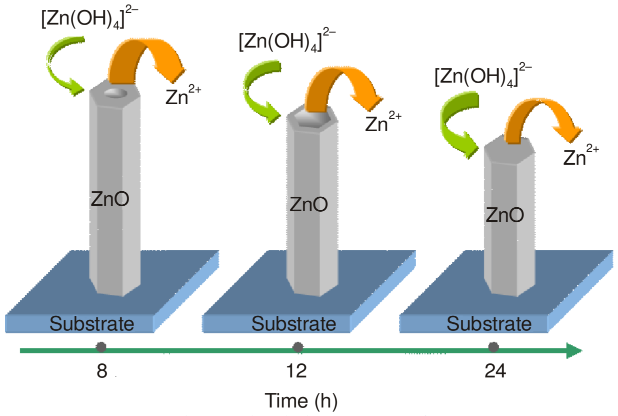

Fig. 4. Dissolution process of ZnO

Zinc oxide arrays with different morphologies were used as photoelectrode for dye-sensitized solar cells and the photoelectric properties were studied by current-voltage (J-V) characteristic test, as shown in Fig. 5, while the parameters are listed in Table-1. Table-1 showed that dye-sensitized solar cells based on ZnO arrays with hollow shape on the top (sample A and B) exhibited better energy conversion efficiency than the one based on ZnO arrays without top pits (sample C). The short circuit current density (Jsc) and open circuit voltage (Voc) for sample A and B were higher than those of sample C that led to the superior dye-sensitized solar cells performance. The increase in short circuit current density indicating that honeycomb structure on the surface of ZnO arrays may cause increase of dye loading on ZnO array photoelectrode. The increase of open circuit voltage may be attributed to that the ZnO layers of sample A and B were both thicker than that of sample C, which can act as blocking layers to suppress carrier recombination occurs across both the film-electrolyte interface and the substrate-electrolyte interface[10], so larger open circuit voltage values could be achieved. In addition, the short circuit current density value of sample B was higher than that of sample A while the open circuit voltage values were nearly the same, demonstrating that deeper hollow shape on the top of ZnO nanorod can absorb more dye for ZnO array photoelectrode.

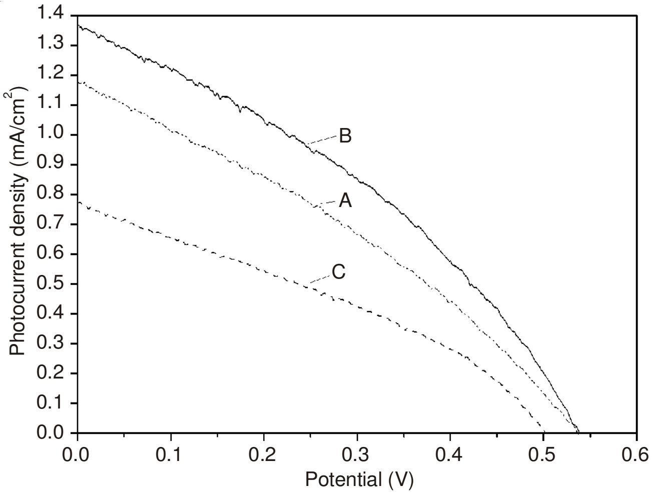

Fig. 5. Current-voltage curves for dye-sensitized solar cells based on ZnO arrays with different morphologies

TABLE-1
PARAMETERS OF DYE-SENSITIZED SOLAR CELLS BASED ON ZnO ARRAYS WITH DIFFERENT MORPHOLOGIES

Sample	Jsc (mA/cm^2)	Voc (V)	FF	η (%)
A	1.170	0.537	0.323	0.203
B	1.371	0.540	0.353	0.261
C	0.771	0.502	0.331	0.128

Conclusion

Zinc oxide array with top hollow pits was assembled by hydrothermal reaction and this structure do advantage to the improvement of dye-sensitized solar cell performance. In a typical reaction process, the concentration of $Zn(NO_3)_2$ solution was set to 200 mM and reacted for 8, 12 and 24 h at 95 °C and obtained ZnO arrays with top honeycomb. The mechanism for the formation of this structure was discussed by referring to chemical equilibrium and structure of ZnO crystal. The morphology of ZnO arrays greatly influenced dye-sensitized solar cell performances according to current-voltage (J-V) characteristic test and hollow shape on the surface of ZnO arrays caused the increase of dye loading on ZnO arrays and leaded to the short circuit current density increase, thick ZnO arrays which acted as buffer layer could suppress charge recombination occurs on both the film-electrolyte interface and the substrate-electrolyte interface and resulted in the increase of open circuit voltage. Further studies on the relationship between the structure and electrical properties of ZnO and modifying the surface of ZnO nanostructure films may help to further improve ZnO array-based dye-sensitized solar cells performance.

ACKNOWLEDGEMENTS

The authors acknowledged the grant from Innovative Research Team of Southwest Petroleum University (2012XJZT002).

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