Highly-Ordered Perpendicularly Oriented ZnO Nanobelt Array Films: Synthesis, Characterization, and Application

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ZnO nanobelt array films were prepared using an electrodeposition method with liquid crystal template. The as-prepared sample was amorphous and changed to nanocrystalline ZnO after sintered at 500 °C for 1 h. The influences of reaction conditions to the morphology of the samples were checked in detail. When the distance between WE (working electrode) and CE (counter electrode) was 3 mm, the electrodeposition potential was −0.9 V versus SCE (saturated calomel electrode), the electrodeposition temperature was 65 °C and the surfactant concentration was 60 wt%, the ZnO nanobelt arrays were densest, most ordered and perpendicularly oriented. The sintered two-layer film was applied as a photoanode of a dye-sensitized solar cell (DSC), and a relatively high short-circuit photocurrent density of 10 mA/cm² and an overall light-to-energy conversion efficiency of 2.1% were achieved.

Keywords:

1. INTRODUCTION
ZnO has been one of the most promising oxide semiconductor materials because of its good optical, electrical, and piezoelectric properties. It can be used in many fields, such as field-emission displays, gas sensors, and solar cells. Quasi-one-dimensional nanostructure arrays of ZnO, such as nanowire arrays, nanorod arrays, nanobelt arrays, and nanotube arrays are attracting much interest for their properties and potential applications in nanotechnology. Many methods have been used for the synthesis of ZnO nanowire, nanorod and nanotube arrays including chemical and physical vapor depositions, solution process, template. By contrast, very little work has been focused on ZnO nanobelt arrays. Generally, the belt-like semiconductors with a well-defined cross section and perfect crystallinity have proven to be an ideal system for the understanding of dimensional confinement and the applications of technologically related nanoscale devices. Recently, Yang15 and Wen16 have reported the preparation of ZnO nanobelt arrays by a gas–solid reaction process. By contrast, very little work has been focused on ZnO nanobelt arrays. Generally, the belt-like semiconductors with a well-defined cross section and perfect crystallinity have proven to be an ideal system for the understanding of dimensional confinement and the applications of technologically related nanoscale devices. Recently, Yang15 and Wen16 have reported the preparation of ZnO nanobelt arrays by a gas–solid reaction process. However, this method needs complicated process, and it is still a challenge to synthesize highly-ordered ZnO nanobelt arrays with simple process. An alternation strategy for synthesis quasi-one-dimensional nanostructure arrays is using the method of electrodeposition, which is little reported.

This method has the virtue of simplicity, low cost, environmental friendly and easy control. Here, we prepared novel ZnO nanobelt array films using the electrodeposition method. The formation conditions and mechanism of the ZnO nanobelt array films was discussed. A dye-sensitized solar cell (DSC) was assembled by using the sintered array film, and photovoltaic properties of the DSC were investigated.

2. EXPERIMENTAL DETAILS

2.1. Preparation of ZnO Nanobelt Array Films

The preparation of ZnO nanobelt array films was similar to the previously described electrodeposition method, developed by Attard.17 18 g 0.1 M Zn(NO₃)₂ solution was added to 27 g polyoxyethylene (10) cetyl ether (Brij56, a surfactant) and stirred at 65 °C. The electrodeposition was carried out using CHI604A electrochemical working station with saturated calomel electrode (SCE) equipped with a huggin capillary as the reference electrode, 2 × 2 cm² platinized gauze as the counter electrode and 1.5 × 1.2 cm² ITO (Sn doped In₂O₃) conductive glass (Beijing Building Materials Institute, China) or FTO (F doped SnO₂) conductive glass (Asahi Glass, Japan) as the working electrode. The reaction conditions were as follows without further mentioning. The distance between the working
electrode and the counter electrode was 3 mm. The electrodeposition potential was −0.9 V versus SCE. The electrodeposition time was 5 h. After electrodeposition, the films were soaked in deionized water for 24 h which was replaced for several times to remove the surfactant mixture. The as-prepared films were then sintered at 500 °C for 1 h.

The distance between WE and CE, electrodeposition potential, electrodeposition temperature and the concentration of surfactant were critical to the formation of ZnO samples with nanobelt array morphologies. The influences of the aforementioned reaction conditions were discussed in detail.

For assembling a DSC, the photoanode was prepared by electrodepositing the above ZnO film on FTO glass and sintering at 500 °C for 1 h, repeating for two times. Then the ZnO photoanode was immersed in a 0.3 mM ethanolic solution of (Bu4N)2Ru(dcbpyH)2(NCS)2 (N719 dye) for 12 h at room temperature. The cell, whose active area was 0.25 cm², was fabricated by using the dye-adsorbed ZnO photoanode and a platinized counter electrode, filled with acetonitrile solution containing 0.03 M I2, 0.3 M LiI and 0.5 M tertbutylpyrididine.

2.2. Characterization

X-ray diffraction (XRD) and Raman spectra were used to characterize the crystalline phase of the samples. XRD pattern was recorded using an X-ray diffractometer (D/max-rA, Rigaku, Japan) with CuKα radiation (λ = 0.15418 nm). Raman spectra were recorded using a microscopic confocal raman spectrometer (RM2000, Renishaw, England) excited with a 514.5 nm Ar⁺ laser. The morphology and microstructure of the samples were examined by a scanning electron microscopy (SEM, LEO-1530, Germany). The morphology and the size of the nanobelts were examined by a transmission electron microscopy (TEM, JEOL JEM-2010F, Japan). Samples for TEM images were prepared by scraping films from the working electrodes onto carbon-coated copper grids.

Photovoltaic behavior of the fabricated cell was investigated under solar irradiation using a 500 W metal halide lamp (CMH-250, Photoelectric Instrument Factory of Beijing Normal University, China) at an intensity of 100 mW/cm², recorded with a source meter (Keithley-2400, Keithley Co.Ltd., USA).

3. RESULTS AND DISCUSSION

3.1. Structural Characters of the ZnO Nanobelt Array Films

Figure 1(a) shows the XRD patterns of the samples. There are no ZnO peaks observed for the as-prepared film. By contrast, three ZnO main peaks appeared in the film after sintered at 500 °C for 1 h. The peaks denoted as “∗” can be indexed to ITO. Similar to the XRD patterns, there are no peaks in the Raman pattern for the as-prepared film, but there are two peaks corresponding to crystalline ZnO phase after sintered, as shown in Figure 1(b). It is noted that the XRD peaks are wide and weak. This means that the crystallinity of the sintered films is not so high. The weak XRD peaks also results from the small thickness (1.3 μm) and high porosity of the ZnO films, as we can see from Figures 2 and 3. Figure 2 shows TEM and HRTEM images of a piece of as-prepared nanobelt and a piece of sintered nanobelt. The amorphous ring in Figure 2(a) and no clear crystal lattices in Figure 2(c) indicate that the as-prepared ZnO is amorphous. On the other hand, the crystal ring in Figure 2(b) and clear ZnO crystal lattice fringes in Figure 2(d) mean that the sintered ZnO is crystalline.
From Figures 1 and 2, we can conclude that the phase of the as-prepared ZnO was amorphous and changed to nanocrystalline ZnO after sintered.

From Figures 2(a) and (b), it can be observed that the height of the nanobelts is about 1.3 μm which also is the thickness of the ZnO films on the conductive glass. In Figure 3, all the as-prepared films and the sintered films show uniform, highly-ordered, perpendicularly oriented nanobelt arrays. There are only two differences between the two kinds of films. One is that the SEM micrographs can be clearer and higher resolution micrographs can be obtained owing to the better conductivity of the ZnO after sintered (see Fig. 3(d)). The other one is that the width of the sintered nanobelts is a little smaller than that of the as-prepared nanobelts. The reason is clear that ZnO has shrunk during the sintering process. The width of the sintered nanobelts is about 5 nm. From the micrographs of the as-prepared films, we can see some nanobelts are wider than 10 nm. The reason for this is that the wide layers contain several single layers connected together. After sintered, the connected layers separate due to the shrinkage of ZnO, as we can see from the micrographs of the sintered films which show nanobelts with uniform width. The intervals between nanobelts are ranging from several nanometers to several hundred nanometers.

The most striking feature for the films is that the degree of order of the nanobelts is very high. The nanobelts parallel to each other. Some of them form a stripe structure (Figs. 3(c and d)), some form concentric circles (Figs. 3(e and f)). Here it can be considered that the stripe structure is the outer part of large concentric cycles. Another interesting feature is that the height direction of the nanobelt arrays is perpendicular to the substrate and the length direction parallels to the substrate, which is absolutely different from previous of nanobelt arrays in both Refs. [15] and [16]. In addition, the nanobelt arrays can be electrodeposited repeatedly, i.e., conductive glass with sintered ZnO nanobelt array film thereon can be used as new working electrode in the electrodeposition process, and then another ZnO nanobelt array film can be electrodeposited on the new working electrode. Figure 3(g) shows a ZnO electrode with two-layer ZnO nanobelt array film. From this figure, the structural characters of ZnO nanobelt arrays can be further confirmed.

3.2. Formation Mechanism of the ZnO Nanobelt Array Films

The mechanism of deposition of ZnO film from Zn(NO$_3$)$_2$ aqueous solution has been suggested that nitrate ions were first reduced with an increase of OH$^-$ concentration ($\text{NO}_3^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{NO}_2^- + 2\text{OH}^-$), and then Zn(OH)$_2$ was formed and converted to ZnO when the deposition was carried out at a temperature of about 65 °C (Zn$^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2 \rightarrow \text{ZnO} + \text{H}_2\text{O}$). Crystalline ZnO will
Fig. 3. Surface SEM micrographs of the as-prepared films (a, c, e), the films sintered at 500 °C for 1 h (b, d, f) and the two-layer film (g). The two-layer film was prepared by using conductive glass with sintered ZnO nanobelt array film thereon as new working electrode in the electrodeposition process, then electrodepositing another ZnO nanobelt array film on the new working electrode, and finally sintering the two-layer film at 500 °C for 1 h.

be achieved at temperature of about 65 °C according to Ref. [18]. However, the phase of the ZnO prepared at −0.9 V versus SCE is amorphous in our experiment. We found that the presence of the template largely reduced the deposition velocity comparing to the deposition without the template. As a result, it can be reasonably supposed the template may hinder the crystal growth of ZnO, resulting in an amorphous phase. In fact, crystalline ZnO has been achieved when the deposition potential was adjusted up to −1.1 V versus SCE at only 65 °C (figure not shown), since the deposition velocity was much larger at this condition.

The formation mechanism of the nanobelt arrays can be ascribed to the template effect. It has been reported previously that different surfactants or even the same surfactant at different concentrations may have provided different microemulsion soft templates that resulted in the formation of nanomaterials with different morphologies and structures, such as spheres, rods, layers, etc. The surfactant of polyoxyethylene (10) cetylene is a relatively simple and symmetric molecule. The hydrophilic oxy-ethylene chain tended to arrange along the surface and formed the colloids of layer shape, and thereby the whole solution formed layer-structured liquid crystal phase. This has subsequently provided the template leading to the formation of the nanobelt arrays.

We noted that the nanobelts arranged in regular order. It is also found that the distance between the working electrode and the counter electrode is very important for the morphology of films. When the two electrodes were only 3 mm apart, high-density nanobelt arrays formed with a large steady-state deposition current density of 0.2 mA/cm². On the other hand, when the two electrodes became widely placed, e.g., moved 5 mm apart, the deposition current density was significantly reduced to 0.07 mA/cm² and poor quality nanobelt arrays were produced. This suggests that the narrowly separated electrodes

Fig. 4. Schematic diagram of the ZnO nanobelt array film.
may create an electric-field high enough to align the layer-structured liquid crystal parallel to the electric-filed direction through electro-osmotic flows within the aqueous domains.\textsuperscript{21} To increase the alignment effect, applying high electrodeposition potentials may be another effective method. However, this is not preferred because a rather high deposition potential may cause undesirable side reactions that disturb the preformed liquid crystal phase. In fact, we found that only ZnO nanoparticles formed when the electrodeposition potentials were increased to −1.2 V versus SCE (see Fig. 8(c)) or higher. Thus, the decrease of the distance between the two electrodes is the most effective way to increase the alignment effect by increasing the electric-filed strength. Figure 5 is the schematic diagram of the possible improved alignment of the liquid crystal phase during electrodeposition.

Another question is how the concentric circles form. In the present stage, we believe it has some relation with the un-uniform distribution of the deposition potential on the conductive glass. Further efforts are undergoing to clarify the phenomenon.

3.3. Influences of Reaction Conditions

3.3.1. Influence of the Distance Between WE and CE

The morphology of ZnO samples strongly depended on the distance between WE and CE. Figure 6 shows the SEM images of the samples that synthesized using a procedure similar to the standard synthesis (shown in Figs. 2 and 3), except that the distance between WE and CE increased from 4 to 7 mm. When the distance increased, the ZnO nanobelt arrays became more porous and disordered. There were not ordered nanobelt arrays when the distance is larger than 5 mm. On the other hand, the quantity of electric charge changed with the distance. Figure 7 shows how the reaction conditions affected the electric charge of deposition. The larger the distance was, the smaller the quantity was. The reason is that there are more electrolytes between WE and CE when increasing the distance, leading to larger resistance in the electrodeposition process and then smaller
quantity of electric charge (see Fig. 5). From Figures 6 and 7(a), we can conclude that dense ordered ZnO nanobelt arrays can be achieved when the distance was smaller than 5 mm. In addition, when the distance was only 3 mm, the ZnO nanobelt arrays were densest and the most ordered.

3.3.2. Influence of Electrodeposition Potential

Electrodeposition potential was also found to play an important role in the formation of ZnO nanobelt arrays. Figure 8 shows the SEM images of the samples that were synthesized under different potentials. All these four kinds of samples were dense. When the potential was $-0.9$ and $-1.0$ V, the ZnO nanobelt arrays were ordered. When the potential increased to $-1.1$ V, the arrays became disordered. Moreover, some nanobelts didn’t keep...
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perpendicularly oriented. The sample was only nanoparticles when the potential increased to $-1.2$ V. Serious side reactions at this potential destroyed the order of nanobelt arrays and led to the formation of nanoparticles instead. On the other hand, the quantity of electric charge increased with the potential (see Fig. 7(b)). Figure 9 shows the cyclic voltammogram of film deposition on FTO conducting glass from ZnO electrolyte at a scan rate of 10 mV/s over the potential range $+0.2$ to $-1.6$ V. When the potential was lower than $-0.8$ V, the cathode current was almost zero. The current started to increase when the potential was higher than $-0.8$ V, indicating the growth of ZnO. The higher the potential was, the larger the current was and then the larger the quantity was. From Figures 8 and 7(b), we can conclude that dense ordered ZnO nanobelt arrays can be achieved when the potential was $-0.9 \sim -1.0$ V.

### 3.3.3. Influence of Electrodeposition Temperature

Electrodeposition temperature also played an important role in the formation of ZnO nanobelt arrays. Figure 10 shows the SEM images of the samples that were synthesized using a procedure similar to that used in the standard synthesis (Figs. 2 and 3). In this case, however, the electrodeposition temperature was changed to 50 °C and 80 °C. When the temperature was lower (50 °C) than the standard synthesis, the sample was ordered nanobelt arrays and more porous since quantity of electric charge was smaller. On the other hand, when the temperature was higher (80 °C), the sample was disordered nanobelt arrays, some of which didn’t keep perpendicularly oriented. The electrodeposition temperature can strongly affect the ZnO electrolyte. Lower temperature made the molecules move slowly and then the liquid crystal phase ordered, leading to the formation of highly-ordered nanobelt arrays. At the same time, lower temperature increased the viscosity of the electrolyte and then increased the resistance in the electrodeposition process. Oppositely, higher temperature made the liquid crystal phase disordered and then the arrays disordered. As a result, 65 °C was the suitable temperature, which made the nanobelt arrays dense and ordered.

### 3.3.4. Influence of the Concentration of Surfactant

Because our synthesis was template-assist synthesis, the concentration of surfactant is expected to influence the liquid crystal phase and then the morphology of the sample. Figure 11 shows the SEM images of the samples that were synthesized under different concentrations. The nanobelt arrays were dense and ordered when the concentration was 60–70 wt%. When the concentration increased to 80 wt%, the sample was also dense but disordered. In addition, some nanobelts didn’t keep perpendicularly oriented. On the other hand, when the concentration decreased to 50 wt%, the sample changed to ordered nanosheets. The nanosheets became disordered when the concentration further decreased to 40 wt%. From Figure 7(d), we can see that the quantity of electric charge was the largest when the concentration was 60 wt%. It was supposed that when the concentration was 60–70 wt%, the liquid crystal phase arranged orderly, leading to the formation of ordered arrays. 60 wt% concentration of surfactant, comparing to the 70 wt% concentration, the Zn(NO$_3$)$_2$ concentration was larger, leading to larger quantity of electric charge. Larger
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Fig. 11. SEM images of four samples, showing the variation of morphology when the concentration of surfactant was changed. The concentrations were 40 wt% (a), 50 wt% (b), 70 wt% (c) and 80 wt% (d), respectively.

surfactant concentration may make the liquid crystal phase disordered and then the arrays disordered. When the surfactant concentration was lower than 60 wt%, the liquid crystal phase may also become disordered, leading to the breakage of nanobelt arrays. From Figures 11 and 7(d), we can conclude that dense ordered ZnO nanobelt arrays can be achieved when the surfactant concentration was 60–70 wt%. In addition, 60 wt% was better as the quantity of electric charge was larger.

From what has been discussed above, we can conclude that the ZnO nanobelt arrays were densest, most ordered and perpendicularly oriented when the distance between WE and CE was 3 mm, the electrodeposition potential was ~0.9 V, the electrodeposition temperature was 65 °C and the surfactant concentration was 60 wt%, which was just the standard synthesis condition (Figs. 2 and 3).

3.4. Application to DSC

ZnO nanobelt arrays may be a desirable material for the photoanode of DSC because the nanobelt arrays can provide direct transport paths for the electrons from their surfaces to the collection electrode while maintaining high surface area for dye adsorption. Here, the sintered two-layer film (see Fig. 3(g)) was tried to be used to the photoanode of DSCs. To our knowledge, we firstly applied highly-ordered perpendicularly oriented ZnO nanobelt arrays to DSCs. The photovoltaic curve of the DSC is shown in Figure 12. The nanobelt-array DSC exhibits a short-circuit photocurrent density ($J_{SC}$) of 10 mA/cm², an open-circuit voltage ($V_{OC}$) of 0.66 V and a fill factor (FF) of 0.32, producing an overall conversion efficiency ($\eta$) of 2.1%. The feature of the photovoltaic properties is the relatively high $J_{SC}$ and the low FF.

As shown in the above section, the nanobelt array films are very porous and about only 2.6 μm thick (2 times electrodeposition). However, the $J_{SC}$ of the nanobelt-array DSC is as high as 10 mA/cm². This may be contributed to the specific morphology, in this case, the perpendicularly oriented ZnO nanobelt arrays. As we know, $J_{SC}$ is mainly

![Fig. 12. Photocurrent-voltage curve of the DSC with the sintered two-layer ZnO nanobelt array film as the photoanode under 100 mW/cm² light irradiation. The active area of the photoanode is 0.25 cm².](image)

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decided by the mount of the adsorbed dye. It can be calculated that the specific surface area of the ZnO can reach up to about 70 m$^2$/g (the area of the two side of the nanobelt divided by the weight of the nanobelt, that is (height × length × width × $\rho$) = (1.3 μm × 1 × 5 nm × 5.6 g/cm$^3$) = 70 m$^2$/g, where the length, height and width of the nanobelt has been defined in Fig. 4). This is even larger than that of the commonly used nanoparticles in DSC. Furthermore, the surface area of the ZnO can be fully utilized owing to the perpendicularly oriented structure and the wide nanobelt interval. As a result, the ZnO film can absorb much more dye than nanoparticle film with the same thickness. On the other hand, nanobelt arrays can provide direct transport paths as described above. All these lead to a relatively high $J_{SC}$.

The much low FF can also be ascribed to the special morphology of the nanobelt array. The intervals between nanobelts are from several nanometers to several hundred nanometers, and span from the substrate to the top of the nanobelts since the nanobelts are perpendicularly oriented. As a result, a large part of the conductive glass can contact with the electrolyte which brings a large dark current, leading to a low FF.

4. CONCLUSIONS

ZnO nanobelts array films were facely prepared by electrodeposition using liquid crystal as a template. Crystalline ZnO can be obtained by sintering the as-prepared film at 500°C for 1 h. The ZnO nanobelts with a width of 5 nm and a height of 1.3 μm are uniform, highly ordered and perpendicularly oriented. The distance between WE and CE was 3 mm, the electrodeposition potential was −0.9 V versus SCE, the electrodeposition temperature was 65°C and the surfactant concentration was 60 wt% were the best reaction condition for synthesis highly-ordered perpendicularly oriented ZnO nanobelt arrays. This kind of ZnO nanobelt array film may provide large surface area and direct transport paths for electron, which is appropriate for the photoanode of DSC. Using the film as the photoanode of a DSC results in a relatively high short-circuit photocurrent density of 10 mA/cm² and a conversion efficiency of 2.1%.

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References and Notes


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