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Aqueous solution fabrication of large-scale arrayed obelisk-like zinc oxide nanorods with high efficiency

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Abstract

Two-dimensional (2D) arrays of obelisk-like zinc oxide nanorods were successfully synthesized with high efficiency on quartz and glass substrate on a large scale through a simple aqueous solution deposition method with zinc nitrate, ammonia, and ammonium chloride as the precursors. Characterized by XRD, EDS, TEM and SEM, the as-grown zinc oxide rods had a single crystalline obelisk-like hexagonal wurtzite structure with diameters of about 300–400 nm and length up to 5 μm. Both XRD and SEM studies revealed the orientation of ZnO rods, and the orientation of ZnO rods can be controlled easily by temperature, pH of the reaction system and the concentration of reactants.

Keywords: Zinc oxide; Two-dimensional arrays; Aqueous solution deposition; Nanorods

1. Introduction

The control of architecture and morphology and the patterning of inorganic materials with nanoscale dimensions have rapidly developed into a promising field in materials chemistry [1]. Especially, the two-dimensional (2D) oriented arrays comprised of one-dimensional metal and metal oxide nanorods or nanowires are currently under investigation for their potential applications in functional nano-devices. Up to now, a few arrays of one-dimensional materials have been successful synthesized by using various methods [2–7]. Among these materials, zinc oxide represents an important basic material due to its low-cost, large-band [8], and luminescent properties and has wide applications in photocatalyst [9], gas sensor [10], varistor [11], transparent conductive coating [12], and electrodes in solar cell [13]. Recently, the room temperature ultra-violet property of ZnO highlighted the prospect of 2D arrays of ZnO crystals, which have become the focus of the next-generation functional devices [2,14,15].

A variety of chemical and physical deposition techniques can be used to synthesize ZnO films with oriented structure. For example, chemical vapor deposition (CVD) [14,16], radio frequency (RF) magnetron sputtering [17], pulsed laser deposition [18], templating against anodic alumina membrane [19], and molecular beam epitaxy (MBE) [20] have been partially successful in creating 2D oriented arrays of ZnO rods. However, these methods are usually complex and expensive due to rigorous synthetic conditions such as high vacuum and temperature. Recently, a simple method, aqueous solution deposition, which is based on wet chemical and bottom-up process, has become the subject of interest in the fabrication of 2D oriented arrays of ZnO film because of its simple, low-temperature and low cost features. For example, Vayssieres et al. [21,22] synthesized 2D arrays of ZnO micro-/nanorods by decomposing hexamethylenetetramine (HMT) with zinc nitrate ($ZnNO_3$) in aqueous solution. O'Brien et al. [23] synthesized oriented ZnO rods with a prepared ZnO film as undercoat, which was obtained by $ZnNO_3$ and triethanolamine on glass or tin oxide (TO) base substrate, by using zinc acetate (ZnAc) and HMT as reactants. In addition, ZnO film undercoat derived from ZnAc and monoethanolamine was utilized by Imai et al. [24] to fabricate ZnO arrays using ammonium salts in NaOH aqueous solutions.

In this paper, we report a new nanostructure of ZnO that has an obelisk-like shape with layered hexagonal edges, which is different from the rod-like

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nanostructures previously reported. Moreover, very large 2D arrays of obelisk-like ZnO nanorods were fabricated on crystalline quartz and amorphous glass substrates through aqueous chemical growth method without any surfactant, template or undercoat. Furthermore, this process has a high efficiency (30 min) and only simple precursors such as $ZnNO_3$, ammonia and ammonium chloride were used as the reactants. Especially, the morphology of ZnO arrays can be simply controlled with the reaction temperature, pH of the reaction solution and the concentration of reactants.

2. Experimental

Hexahydrate zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$), ammonia (25%), ammonium chloride (NH_4Cl), purchased from Shanghai Chemical Reagent Company, were analytical grade reagents, and used as received. Clean crystalline quartz and amorphous glass wafers ($2 \times 2\,cm^2$) were used as substrates, first soaked in boiling sulfuric acid (98%) for 10 h, then rinsed ultrasonically in acetone and deionized water, finally dried in vacuum oven.

In a typical preparation process of ZnO arrays, 0.1 M zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and 0.02 M ammonium chloride aqueous solution were transferred into a Teflon vessel with a lid. The pH value of reaction system was strictly controlled at 10.5 by adjusting with ammonia. After the solution became clear, the quartz substrates were vertically immersed in the solution by the support of a Teflon base with grooves. Then the reaction temperature was quickly increased to 95°C and kept for 30 min without any stir. After the reaction, the Teflon vessel was cooled to room temperature by flowing water. Finally, the quartz wafers were rinsed ultrasonically in deionized water for 2 min and dried in the air.

The as-prepared film was characterized by X-ray powder diffraction (XRD, Bruker-AXS D8 ADVANCE X-ray diffractometer) by employing a scanning rate of 0.01°/s in a 2θ range from 20° to 80° with a Cu$K\alpha$ radiation ($\lambda = 0.154178$ nm). The morphologies and dimensions of the films were observed by scanning electron microscopy (SEM, LEO 1550 VP) and transmission electron microscopy (TEM, JEM-100 CX) operating at 100 keV accelerating voltage. An energy dispersive spectroscopy (EDS) analysis of the film was performed at 30 keV coupled to the SEM.

3. Results and discussion

Fig. 1 shows the SEM images of the product film prepared on a quartz substrate by aqueous solution deposition method, in which (a) is the vertical image of product film, and (b) is the amplified image of (a). The same results were obtained on crystalline and amorphous glass substrates, which showed that substrates had little effects on the nanocrystals arrays. Fig. 1a shows that the product film is composed of well-defined crystals with rod-like structures on the substrate on a large scale (the whole substrate is evenly covered by the product film). All the rods are highly oriented along the *c*-axis of the crystals, and the morphology of the rods is obelisk-like and hexagonal which can be seen clearly from the amplified image in Fig. 1b. From Fig. 1b, we also found that the obelisk-like crystals had a layered (step) structure and the steps became gradually thinner up to the crystals. Each step kept the hexagonal structure with a unique *c*-axis of the crystal and the whole crystal was single crystalline, which will be proved in the following discussion. Fig. 1c is the cross-section image of product film, which is obtained by scratching with a quartz knife. The cross-section also shows that the rods grow vertically on the substrate. The average top, middle and bottom width of the obelisk-like rods is about 200, 400, 800 nm accordingly, and the length is about 5 μm. All images in Fig. 1 show uniform orientation of the obtained crystals. The same results were obtained on crystalline quartz and amorphous glass substrates, which showed that substrates had little effect on the nanocrystal arrays. The synthesis method in this report has a wide application.

Fig. 2a shows the XRD patterns of the as-prepared film on quartz substrate. All peaks can be indexed to the hexagonal phase of zinc oxide (wurtzite structure, space group *P*63*mc*). The cell constants are calculated to be $a = 3.25$, $c = 5.2$, which agree with the reported value (JCPDS card NO36-1451). No characteristic peaks of impurities, such as zinc nitrate, $Zn(OH)_2$, and other precursor compounds are observed. In addition, it can be seen clearly from the XRD pattern that the [002] reflection is greatly enhanced relative to the usual [101] maximum reflection for zinc oxide. This unusual phenomenon can be explained by the orientation of zinc oxide crystals. An energy dispersive spectroscopic (EDS) analysis of the film (Fig. 2b) shows that zinc and oxygen are the only detected elements. Fig. 3 shows the TEM image of individual ZnO nanorod (Fig. 3a) and its related SAED pattern (Fig. 3b). The diffraction pattern shows a single crystalline structure of the obtained crystal, and the ED pattern suggests that ZnO rods grow along the [002] direction [25]. In conclusion, all results show that the as-prepared product is single crystal of obelisk-like hexagonal ZnO with layered structures. Fig. 4 is the model of obelisk-like hexagonal ZnO single crystal, which shows that ZnO is a polar crystal and its polar axis is *c*-axis. The orientation in the [002] direction is consistent with the growth of *c*-axis oriented ZnO rods. The results from XRD pattern, TEM and SEM studies combined well to explain the orientation of 2D

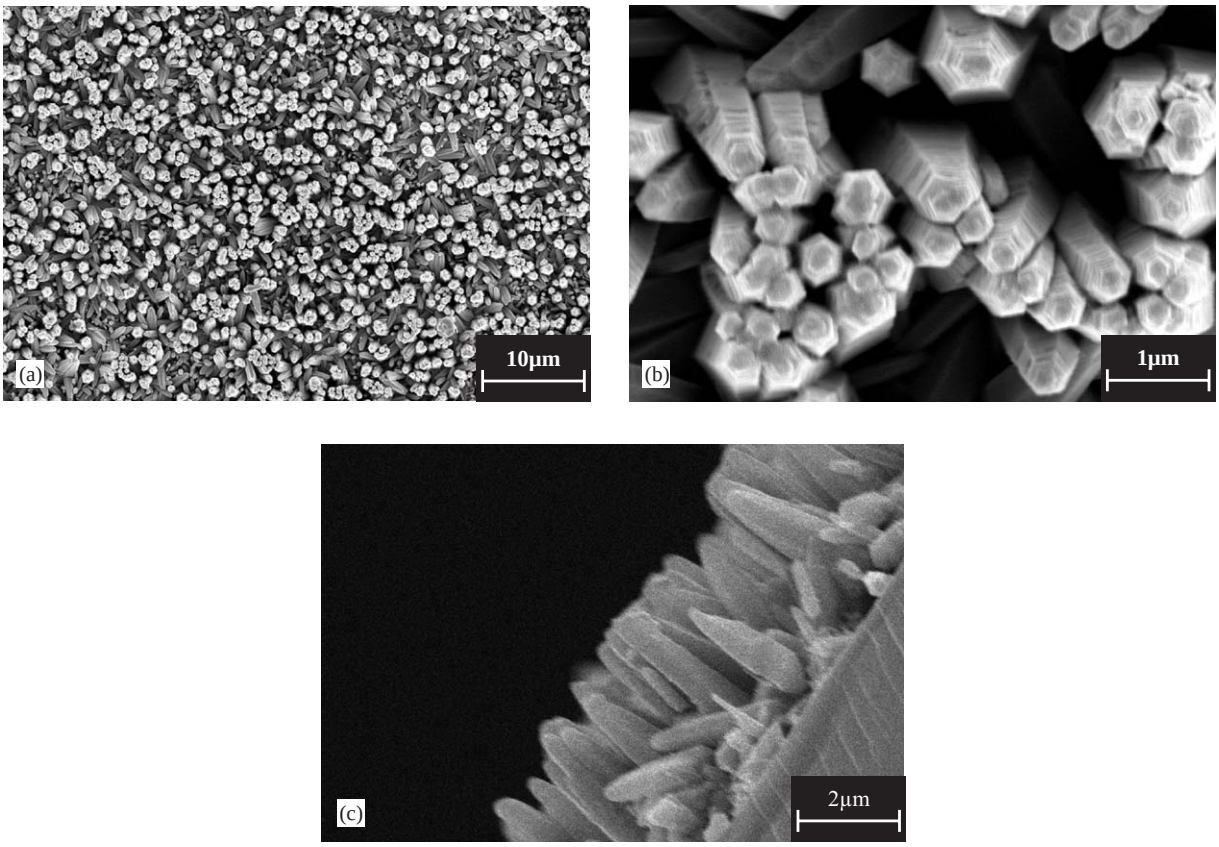

Fig. 1. SEM images of the as-prepared 3D arrays of obelisk-like ZnO rods grown on quartz substrate. (a) Vertical image, (b) amplified image of (a), (c) cross-section image.

oriented arrays of ZnO nanorods, and this combined characterization method (XRD and SEM) to prove the orientation of materials has been reported recently [14,21–24].

The mechanism of the formation of zinc oxide crystals is usually accepted as follows [26,27].

$$NH_3 + H_2O \rightleftarrows NH_3 \cdot H_2O \rightleftarrows NH_4^+ + HO^-$$

$$Zn^{2+} + NH_3 \rightarrow Zn(NH_3)_4^{2+}$$

$$Zn(NH_3)_4^{2+} + OH^- \rightarrow ZnO$$

or

$$Zn^{2+} + OH^- \rightarrow Zn(OH)_4^{2+}$$

$$Zn(OH)_4^{2-} \rightarrow ZnO$$

In the process of the formation of ZnO, complexion $Zn(NH_3)_4^{2+}$ or Zn $(OH)_4^{2-}$ forms first by mixing $Zn(NO_3)_2$, ammonia and NH_4Cl. Then, with the increase in temperature, zinc oxide crystal form heterogeneous nucleus at the interface between substrate and solution by the dehydration of $Zn(OH)_4^{2-}$ or $Zn(NH_3)_4^{2+}$. After that, crystals begin to grow along the *c*-axis of ZnO crystals. Finally, after 30 min the formation of ZnO rod arrays completes. The chemical properties and amount of ZnO nuclei formed on the substrates play a key role in the formation of oriented ZnO nanocrystals and plays an important part in the growth process. In many previous papers [23,24], undercoat is used to promote the formation of oriented ZnO nanocrystals arrays. The crystalline nature of the undercoat can control the orientation of the obtained ZnO crystals. For example, more regular oriented ZnO crystals can be obtained under crystalline ZnO undercoats than amorphous undercoat. So the nuclei nature (crystalline or amorphous) formed first on the substrates play an important role in the orientation of ZnO crystals. In this paper, although no undercoat was used, good orientation of ZnO crystals was obtained. This may be caused by good crystalline nature of ZnO nuclei formed on the substrates. In recent reports by Vayssiers [21,22], good orientation of ZnO crystals arrays can also be obtained by decomposing the zinc amino complex without the undercoats. In this paper, the zinc amino complex ($Zn(NH_3)_4^{2+}$) formed and controlled by the content of Zn^{2+}, $NH_3 \cdot H_2O$ and NH_4^+ can promote the formation of crystalline ZnO nuclei which can ultimately grow into well-oriented ZnO nanocrystals arrays on the substrates. During the evolution, from

$Zn(NH_3)_4^{2+}$ to crystalline ZnO nuclei, NH_4^+ has great effects on the orientation of the crystals. Low-density nanocrystals arrays formed on the substrates without NH_4^+. In some reports [28,29], organic amine and ammonium salt can play a template role in the formation inorganic compound. Here, ammonium salt not only adjusts the pH of the reaction solution and the proportion between $Zn(NH_3)_4^{2+}$ and $Zn(OH)_4^{2-}$, but also have great guiding effects on the formation of ZnO nuclei on the substrate. As a result, large amounts of crystalline ZnO nuclei are formed on the substrates and consequently large-scale oriented ZnO nanostructures

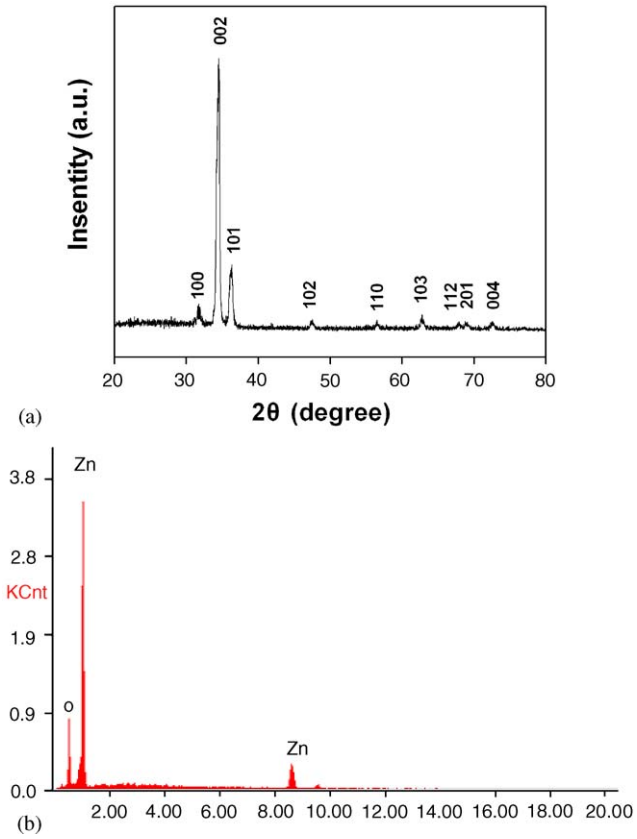

Fig. 2. (a) XRD patterns of the as-prepared ZnO films and (b) energy dispersive spectroscopy (EDS) analysis of the film.

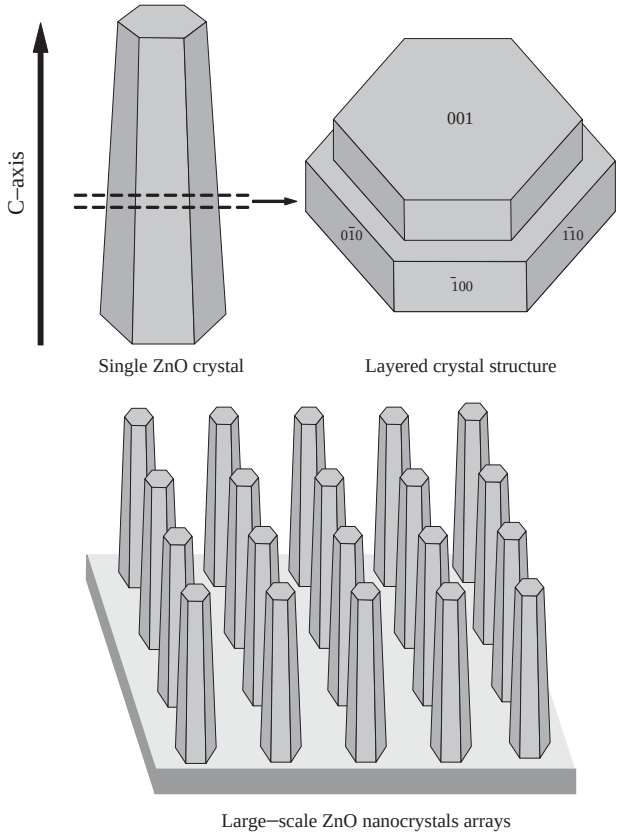

Fig. 4. Crystal structure illustration of obelisk-like hexagonal ZnO rods.

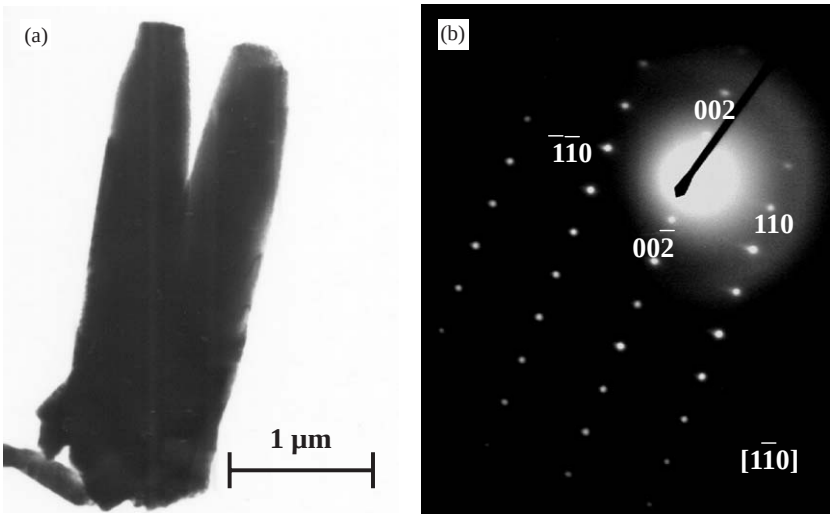

Fig. 3. (a) TEM image of individual ZnO nanorod and (b) its related SAED pattern.

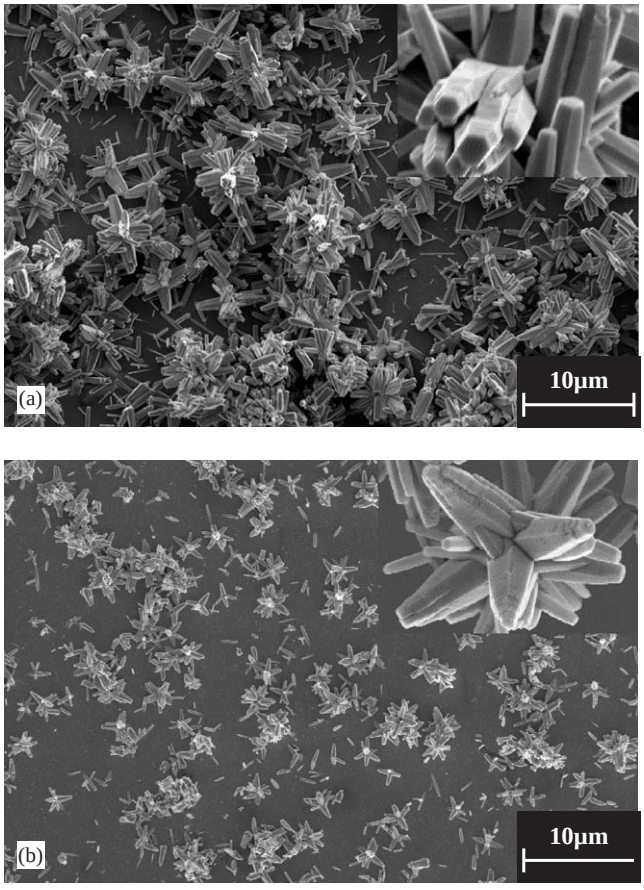

Fig. 5. SEM images of ZnO films with flower-like shape when pH of the aqueous solution is (a) 11 and (b) 10.

are formed. Furthermore, the size, shape and uniformity of the prepared 2D arrays of ZnO nanorods can be controlled by the interfacial thermal dynamics and kinetics of nucleation and growth of the system which are remarkably affected by the interface tension [6]. In the reaction process, concentration of the reactants, temperature and the pH value of the reaction solution play important roles in the formation of ZnO nanorods. These reaction factors provide different amounts of ZnO nucleus which are formed at the interface between the substrate and reaction solution, and as a result remarkably affect the shape of ZnO arrays. When the concentration of $Zn(NO_3)_2$ decreases to 0.02 M, or the reaction temperature decreases to 80–90°C, or the pH value of the solution is away from 10.5 (9.5–10.2 or 10.8–11.2), the amount of ZnO nucleus on the substrate decreases to some extent and flower-like cluster of ZnO arrays were obtained. Fig. 5 is the SEM image of obtained flower-like ZnO sample when the pH value is 11 (Fig. 5a, the inset image is the amplified image) and 10 (Fig. 5b). When the reaction condition are away further from the optimal formation condition of ZnO arrays, that is, the concentration of $ZnNO_3$ decreases below 0.01 M, or the temperature decreases below 80°C, or the pH of the solution decreases below 9 or increases above 11.5, ZnO arrays cannot be obtained onto the substrate. In our experiments, the high concentration of reactants is very important for the formation of ZnO arrays because the high ionic strength can increase the surface charge density and as a result lower the interfacial tension [6].

4. Conclusions

In this paper, highly oriented 2D arrays of obelisk-like ZnO nanorods with a single crystalline structure have been efficiently synthesized by a novel simple aqueous solution deposition method. The orientation of ZnO rods has been proved by both SEM images and the highest intensity of [002] peak in XRD patterns. Simple agents, ammonia and ammonium chloride are found to be effective to the creation of arrays of ZnO nanorods on the quartz substrate. Furthermore, with the change in reaction conditions, different morphologies of ZnO arrays can be obtained. This method can be considered as a promising method for producing novel functional micro/nanosized devices with high efficiency.

Acknowledgments

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References

[1] S.H. Yu, M. Antonietti, H. Colfen, Hartmann, Nano. Lett. 3 (2003) 379.
[2] M.H. Huang, S. Mao, H. Feick, H.Q. Yan, Y.Y. Wu, H. Kind, E. Weber, R. Russo, P.D. Yang, Science 292 (2001) 1897.
[3] M.J. Zheng, L.D. Zhang, G.H. Li, W.Z. Shen, Chem. Phys. Lett. 363 (2002) 123.
[4] W.Q. Han, S.S. Fan, Q.Q. Li, Y.D. Hu, Science 277 (1997).
[5] J.C. Wang, C.Z. Zhan, F.G. Li, Appl. Phys. A 76 (2003) 609.
[6] L. Vayssieres, N. Beermann, S. Lindquist, A. Hagfeldt, Chem. Mater. 13 (2001) 233–235.
[7] L. Vayssieres, L. Rabenberg, A. Manthiram, Nano. Lett. 2 (2002) 1393.
[8] V. Srikant, D.R. Clarke, J. Appl. Phys. 83 (1998) 5447.
[9] J.T. Hu, T.W. Odom, C.M. Lieber, Acc. Chem. Res. 32 (1999) 435.
[10] K.S. Weißenrieder, J. Müller, Thin Solid Films 300 (1997) 30–41.
[11] V. Tohver, S.L. Morissette, J.A. Lewis, B.A. Tuttle, J.A. Voigt, D.B. Dimos, J. Am. Ceram. Soc. 85 (2002) 123.
[12] T. Minami, J. Vac. Sci. Technol. A 17 (1999) 1765.
[13] H. Rensmo, K. Keis, H. Lindstrom, S. Sodergren, A. Solbrand, A. Hagfeldt, S.E. Lindquist, L.N. Wang, M. Muhammed, J. Phys. Chem. B 101 (1997) 2598.
[14] J.J. Wu, S.C. Liu, Adv. Mater. 14 (2002) 215.
[15] K. Govender, D.S. Boyle, P. O'Brien, D. Binks, D. West, D. Coleman, Adv. Mater. 14 (2002) 1221.
[16] H. Funakubo, N. Mizutani, M. Yonetsu, A. Saiki, K. Shinozaki, J. Electroceram. 4 (1999) 25.
[17] K.H. Yoon, J.W. Choi, D.H. Lee, Thin Solid Films 302 (1997) 116.
[18] J.H. Choi, H. Tabata, T. Kawai, J. Cryst. Growth 226 (2001) 493.
[19] Y. Li, G.W. Meng, L.D. Zhang, F. Phillipp, Appl. Phys. Lett. 76 (2000) 2011.
[20] Y.F. Chen, D.M. Bagnall, Z.Q. Zhu, T. Sekiuchi, K.T. Park, K. Hiraga, T. Yao, S. Koyama, M.Y. Shen, T. Goto, J. Cryst. Growth 181 (1997) 165.
[21] L. Vayssieres, Adv. Mater. 15 (2003) 464.
[22] L. Vayssieres, K. Keis, S.E. Lindquist, A. Hagfeldt, J. Phys. Chem. B 105 (2001) 3350.
[23] D.S. Boyle, K. Govender, P. O'Brien, Chem. Commun. (2002) 80.
[24] S. Yamabi, H. Imai, J. Mater. Chem. 12 (2002) 3773.
[25] J.Q. Hu, Q. Li, N.B. Wong, C.S. Lee, S.T. Lee, Chem. Mater. 14 (2002) 1216.
[26] W.J. Li, E.W. Shi, W.Z. Zhong, Z.W. Yin, J. Cryst. Growth 203 (1999) 186.
[27] J. Zhang, L.D. Sun, J.L. Yin, H.L. Su, C.S. Liao, C.H. Yan, Chem. Mater. 14 (2002) 4172.
[28] G.J.D.A.A. Soler-Illia, C. Sanchez, B. Lebeau, J. Patarin, Chem. Rev. 102 (2002) 4093.
[29] K.H. Lii, Y.F. Huang, V. Zima, C.Y. Huang, H.M. Lin, Y.C. Jiang, F.L. Liao, S.L. Wang, Chem. Mater. 10 (1998) 2599.