Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 40 (2014) 3637–3646

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Growth of flower-like ZnO on polyhedron CuO fabricated by a facile hydrothermal method on Cu substrate

Ruixia Shi, Ping Yang*, Sha Zhang, Xiaobin Dong

School of Materials Science and Engineering, University of Jinan, 250022 Jinan, PR China

Received 4 July 2013; received in revised form 24 August 2013; accepted 13 September 2013
Available online 19 September 2013

Abstract

Flower-like ZnO on polyhedron CuO microstructures have been fabricated on Cu substrate via a simple hydrothermal method without any surfactant at low temperature (70 °C). The time-dependent experiments indicated that flower-like ZnO and the polyhedron CuO crystallites were obtained when the reaction time is 30 min and 1 h, respectively. Based on these experiments, possible growth mechanism was proposed to account for the growth of the flower-like ZnO on polyhedron CuO. The different ionic radius and charge density of alkali metal hydroxide used to generate $Zn(OH)_4^{2-}$ ions have significant influences on the growth of ZnO. The different concentrations of alkali metal hydroxide result in different concentrations of $Zn(OH)_4^{2-}$, which leads to the different rates of nucleation and crystal growth. The multinuclei aggregates serve as the sites for the intrinsic growth of one dimension ZnO to form early forms of flower-like ZnO microstructures under hydrothermal conditions. The strong electrolyte neutralizes the surface charges of the CuO, which causes the formation of dispersed CuO.

Keywords: D. ZnO; Hydrothermal synthesis; Growth mechanism; Cu substrate

1. Introduction

Semiconductors have attracted much interest due to their physical properties and potential for diverse electronic and photonic device applications [1]. Zinc oxide (ZnO) is one of the most important and versatile semiconductors due to its wide band gap (~3.37 eV), large exciton binding energy (~60 meV), and a noncentral symmetric wurtzite crystal structure. Because the novel properties of nanomaterials depend on their sizes and shapes, various methods [2–5] have been developed for the synthesis of ZnO with different sizes and shapes during the past several years. Among these methods, the hydrothermal method has also attracted considerable attention because of its simple, lower temperature, higher yield and more controllable process [6–8]. Therefore, well-defined ZnO nanostructures with an abundant variety of shapes [9–13] have been obtained through the facile hydrothermal method.

Among these shapes, the flower-like ZnO, as a special three-dimensional structure of nano-ZnO, has been paid much attention in recent years. Flower-like ZnO microstructures composed of nanorods are usually prepared with hydrothermal or solvent-thermal methods, in which some polymers and surfactants are used as the structure-directing agents. For instance, Raula and coworkers have fabricated mainly flowerlike zinc oxide nanostructures using the ascorbate ion as a shape-directing/capping agent at relatively low temperature (30 and 60 °C) [14]. Zeng et al. have prepared flower-like ZnO nanostructures by a polyethylene glycol-assisted hydrothermal process at 80 °C [15]. With the introduction of mannite, Feng et al. have synthesized hollow flower-like complex superstructures assembled by ZnO nanorods via a simple hydrothermal method [16].

In addition, some of the studies focused on the synthesis of ZnO nanostructures on the substrate via inhomogeneous nucleation. Wang et al. prepared flower-like ZnO particles on various substrates such as amorphous glass, crystalline quartz, and PET without any surfactant [17]. However, when the reaction temperature is lower than 75 °C, ZnO crystals cannot form on the substrates. Jia and coworkers have fabricated large scale flower-like ZnO nanosheets on zinc foil at 150 °C for 12 h by a simple hydrothermal method [18]. Lin and Jiang hydrothermally synthesized flower-like ZnO on

*Corresponding author. Tel.: +86 531 89736225; fax: +86 531 87974453.
E-mail address: mse_yangp@ujn.edu.cn (P. Yang).

0272-8842/$ - see front matter © 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2013.09.061

glass and aluminum substrates, which demonstrated that different substrates have important effects on the morphologies of the ZnO nanostructures [19]. The results demonstrate that the surface morphologies of the resulting ZnO nanostructures are governed by the highly anisotropic surface energies of the substrate. The crystal orientation of the substrate is one of the main factors determining the surface morphologies of the nanostructures. Xu and coworkers fabricated zinc oxide nanorods on copper substrate by a hydrothermal reaction in ammonia and zinc chloride solution without any surfactant at 95 °C in a sealed bottle [20]. Guo et al. prepared ZnO/CuO heterohierarchical nanotrees array via a simple hydrothermal approach combined with the thermal oxidation method on Cu substrates [21].

CuO is an important p-type semiconductor with a narrow band gap and has wide and potential applications [22–24]. By combining the advantages of both nanostructures in a composite a simple, reliable and cost effective synthesis route might be realized [25]. Consequently, many combinations of CuO and ZnO nanostructures have been investigated, but involve high temperature (> 500 °C) to oxidize a Cu foil to CuO followed by the deposition of ZnO [26]. Jung et al. recently demonstrated the fabrication of flower-like CuO–ZnO nanowire heterostructures by photochemical deposition, which is a slow and rather expensive process [27]. Zainelabdin and coworkers demonstrated hydrothermal synthesis of coral-like CuO nanostructures by selective growth on ZnO nanorods (NRs) on ITO substrate at low temperatures [25]. However, flower-like ZnO grown on polyhedron CuO hydrothermally fabricated on Cu substrate is still not reported. Moreover, copper substrate, as a good conductor, is also rarely employed during other fabrication methods. Consequently, it is necessary to investigate the effects of copper substrate on morphologies of ZnO.

In the present work, flower-like ZnO grown on polyhedron CuO were fabricated on copper substrate by a facile, cost-efficient and environmentally-friendly hydrothermal method. The effects of different alkali and concentration of Zn^{2+} and OH^- on the morphologies of ZnO were discussed in some detail. In addition, time-dependent experiments of morphology evolution process were examined by field-emission scanning electron microscopy (FESEM). On the basis of above experiments and mechanisms

Table 1
Preparation conditions of ZnO products on Cu substrate synthesized in deionized water.

Sample	$ZnAc_2 \cdot 2H_2O$ (M)	Alkali (M)	H_2O (ml)	Temperature (°C)	Time (h)
1	0.035	NaOH 0.65	40	70	24
2	0.035	NaOH 0.55	40	70	24
3	0.035	NaOH 0.45	40	70	24
4	0.035	NaOH 0.35	40	70	24
5	0.035	NaOH 0.25	40	70	24
6	0.0175	NaOH 0.275	40	70	24
7	0.007	NaOH 0.11	40	70	24
8	0.035	KOH 0.65	40	70	24
9	0.035	KOH 0.55	40	70	24
10	0.035	KOH 0.45	40	70	24
11	0.035	LiOH 0.65	40	70	24
12	0.035	LiOH 0.55	40	70	24
13	0.035	LiOH 0.45	40	70	24
14	0.035	LiOH 0.25	40	70	24

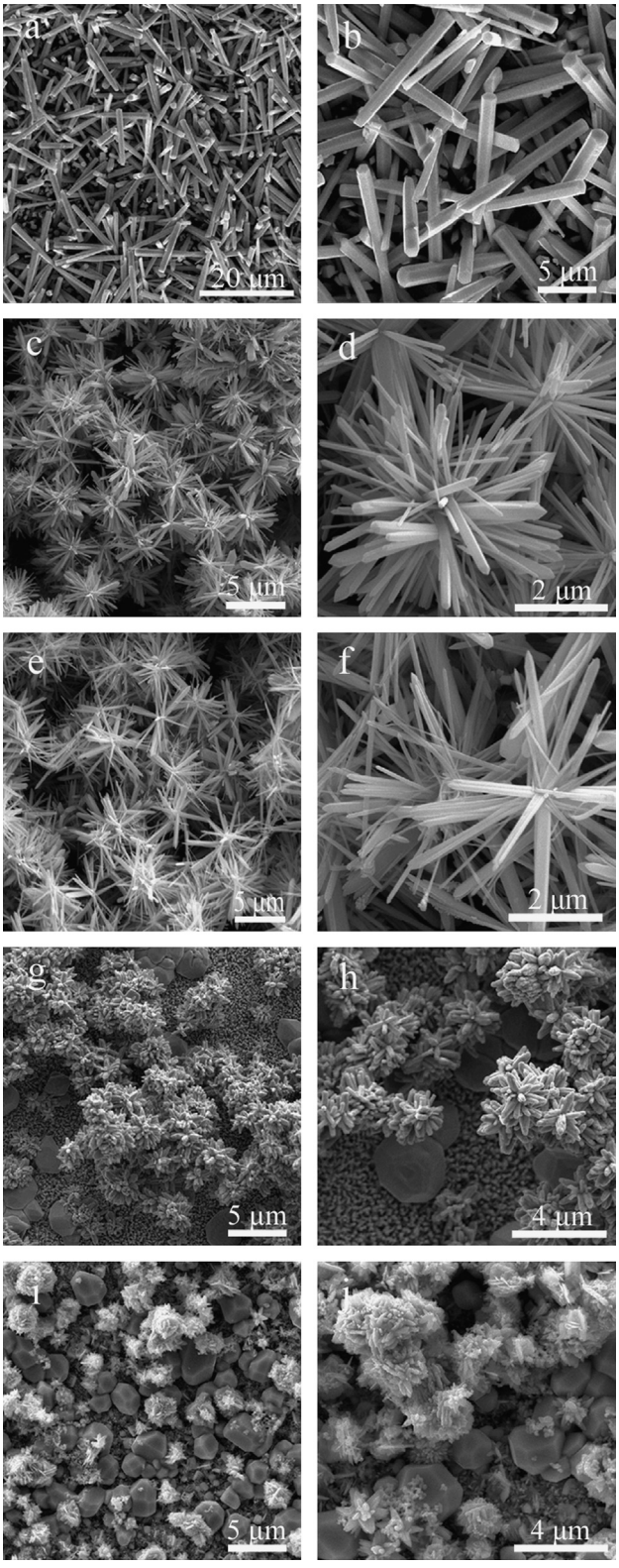

Fig. 1. Typical SEM micrographs of ZnO prepared using NaOH on Cu substrate (a, b)sample 1; (c, d) sample 2; (e, f) sample 3; (g, h) sample 4; and (I, j) sample 5.

proposed previously, the possible growth mechanism of flower-like ZnO on copper substrate was proposed.

2. Experimental section

2.1. Experimental procedures

All the reagents and solvents, which were purchased from the Chinese National Medicine Group, were of analytical grade and used as received without further purification. ZnO grown on polyhedron CuO on Cu substrate were fabricated according to following typical procedures. Briefly, the Cu foils (1 cm × 1 cm) were ultrasonicated in alcohol and distilled water for about 10 min to refresh the surface, respectively. The 40 ml solution of 0.035 M $Zn(AC)_2 \cdot 2H_2O$ and 0.55 M sodium hydroxide is magnetically stirred for 15 min in autoclave. Then the Cu substrate cleaned is put into the bottom of reaction solution. Subsequently, the autoclave is heated at 70 °C for 24 h. Finally, the sample with a white deposition layer is rinsed with distilled water and alcohol and dried in air for further characterization. Other parallel experiments were carried out just by changing the alkaline or the concentration of alkaline. Detailed preparation conditions were summarized in Table 1. Additionally, the time-dependent experiments were conducted to study the growth mechanism of the ZnO and CuO microstructures.

2.2. Characterization

The morphologies and microstructures of as-synthesized ZnO were investigated with a Quanta 200 FEG environmental scanning electronic microscopy (ESEM) equipped with an attached EDS system for elemental analysis (X-MAX50, Oxford). XRD patterns of the samples were recorded on a multipurpose X-ray diffraction system (D8 ADVANCE, Bruker) with a Cu K_α radiation source.

3. Results and discussion

3.1. Role of sodium hydroxide

SEM analysis of samples 1–5 with various amounts of sodium hydroxide is shown in Fig. 1. Fig. 1a and b shows the hexagonal rod structured ZnO prepared with 0.65 M sodium hydroxide (sample 1). The diameters of rods ranged from 400 nm to 1.7 μm. Further reducing the concentration of sodium hydroxide to 0.55 M, flower-like ZnO with nonuniform petals were obtained (sample 2, Fig. 1c and d). The diameters of petals ranged from 100 to 500 nm. When the concentration of sodium hydroxide was lowered to 0.45 M, the flower-like ZnO with few and nonuniform petals were formed (sample 3, Fig. 1e and f). Then, many flower-like ZnO consisted of rough short rods in diameters of 500 nm were observed when decreasing the concentration of sodium hydroxide to 0.35 M (sample 4, Fig. 1g and h). When the concentration of sodium hydroxide is further decreased to 0.25 M, flower-like ZnO and some irregular aggregates were emerged (sample 5, Fig. 1i and j). It is worth to mention that the polyhedrons were both observed when the concentration of sodium hydroxide is 0.35 M and 0.25 M. The EDS results demonstrated that the irregular aggregates comprised Zn and O elements and the polyhedron only contained the Cu and O elements. Furthermore, the atomic ratios of Zn to O and Cu to O are both equal to 1:1, respectively (Fig. 2).

To confirm the phase composition the XRD experiment was carried out. Fig. 3 revealed the crystal structure and phase purity of the ZnO/CuO structures. It could be found that the ZnO diffraction peaks are very weak, which is likely due to the small amount of ZnO formed on the Cu substrate. However, all

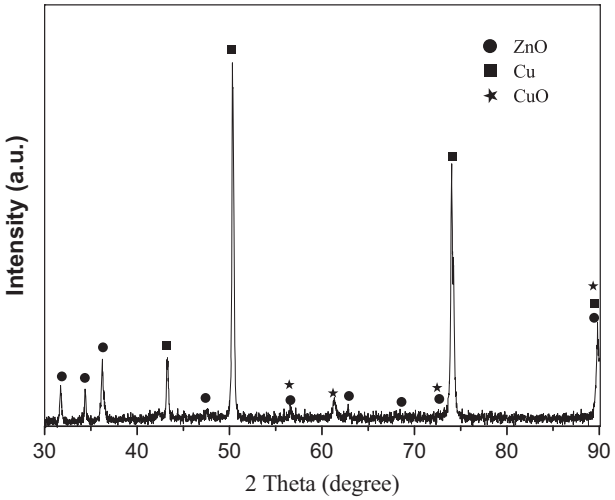

Fig. 3. XRD patterns of sample 2 prepared from precursor with 0.55 M NaOH.

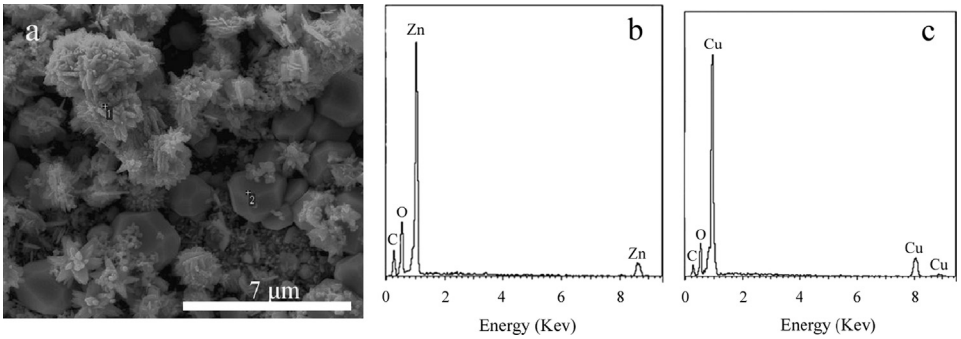

Fig. 2. SEM images of sample 5 with 0.25 M NaOH (a) and EDS analysis of point 1 (b) and point 2 (c). The sample coated with carbon.

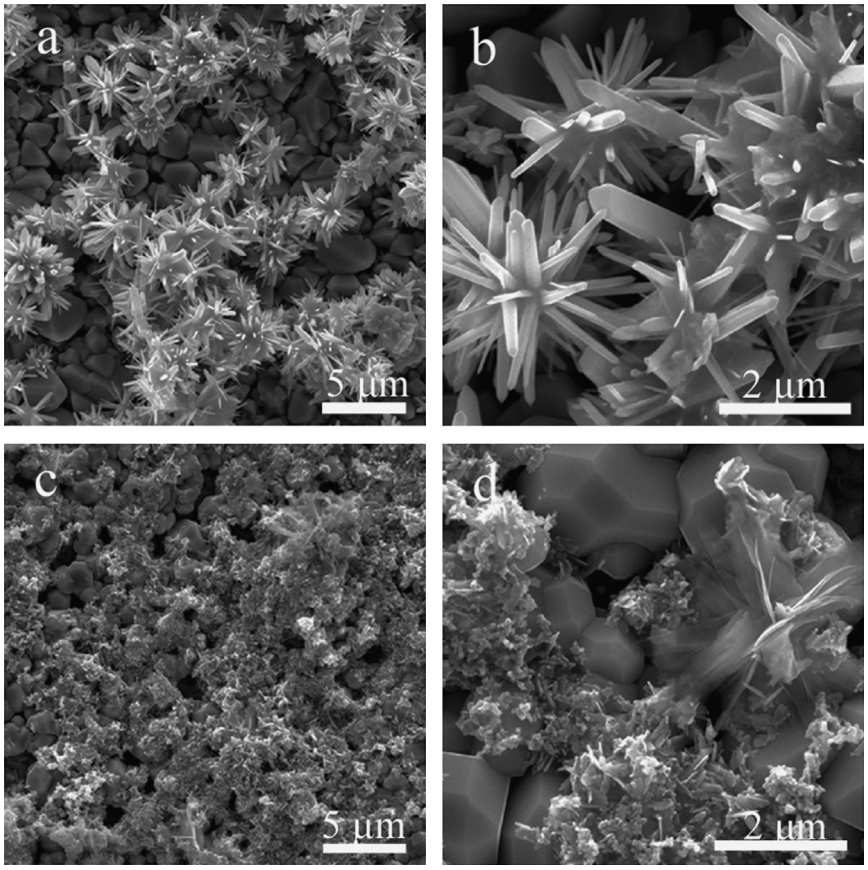

Fig. 4. SEM images of lowering the concentration of Zn^{2+} and OH^- (a, b) sample 6; (c, d) sample 7.

ZnO diffraction peaks are clearly seen and match very well with those of wurtzite ZnO ($a=3.253$ Å, $c=5.209$ Å, JCPDS file No. 04-0831). The Cu diffraction peaks are very strong, which match well with those of face-centered cubic Cu ($a=3.6150$ Å, JCPDS file No. 04-0836). In addition, the crystallographic phase is in good agreement with the JCPDS card (No. 05-0661, $a_0=4.688$ Å, $b_0=3.423$ Å, $c_0=5.132$ Å) for the monoclinic CuO crystals. The above results indicated that the irregular aggregates are ZnO and the polyhedron products are CuO crystals.

3.2. Role of concentration

According to the above results it can be known that the amount of NaOH solution has important effects on the ZnO growth. In order to know the influence of the concentration of Zn^{2+} and OH^- on morphology the experiments of lowering concentration of Zn^{2+} and OH^- were performed. The sample 2 was investigated. The concentrations of sample 6 and sample 7 were reduced to one half and one fifth, respectively, while keeping the ratio of Zn^{2+} and OH^- the same as the sample 2. Fig. 4 shows the morphologies of samples 6 and 7. Fig. 4a and b indicated that some flower-like ZnO with nonuniform petals and many polyhedron CuO were formed when lowering the concentration of Zn^{2+} and OH^- to one half (sample 6). The diameters of petals varied greatly from 40 to 500 nm. Further decreasing the concentration of sample to one fifth, it can be seen that ZnO with irregular shapes on the polyhedron CuO were fabricated (sample7, Fig. 4c and d).

3.3. Role of potassium hydroxide and lithium hydroxide

To investigate the effect of the used alkali metal hydroxide molecules on the morphology of the ZnO, ZnO are fabricated by using KOH and LiOH. Fig. 5 shows the morphologies of samples 8–10 with different amounts of potassium hydroxide. The flower-like ZnO was obtained when potassium hydroxide is 0.65 M, 0.55 M and 0.45 M. However, the symmetry of flower-like ZnO decreased with lowering the concentration of potassium hydroxide and the diameters of petals also became more and more nonuniform.

The SEM images of samples 11–13 with 0.65 M, 0.55 M and 0.45 M lithium hydroxide are shown in Fig. 6. The morphologies of ZnO prepared using lithium hydroxide were totally different from ones using sodium hydroxide and potassium hydroxide. Flower-like ZnO was not observed in this case when lithium hydroxide is 0.65 M. Instead, irregular ZnO crystallites with various sizes were obtained (sample 11, Fig. 6a and b). And it is found that some small ZnO crystallites grew on large ones. By decreasing the concentration of lithium hydroxide to 0.55 M flower-like ZnO grown on irregular ZnO was obtained (sample 12, Fig. 6c and d). Further reducing lithium hydroxide to 0.45 M some spherical assemblies comprised many nanoleaves were formed on the irregular ZnO

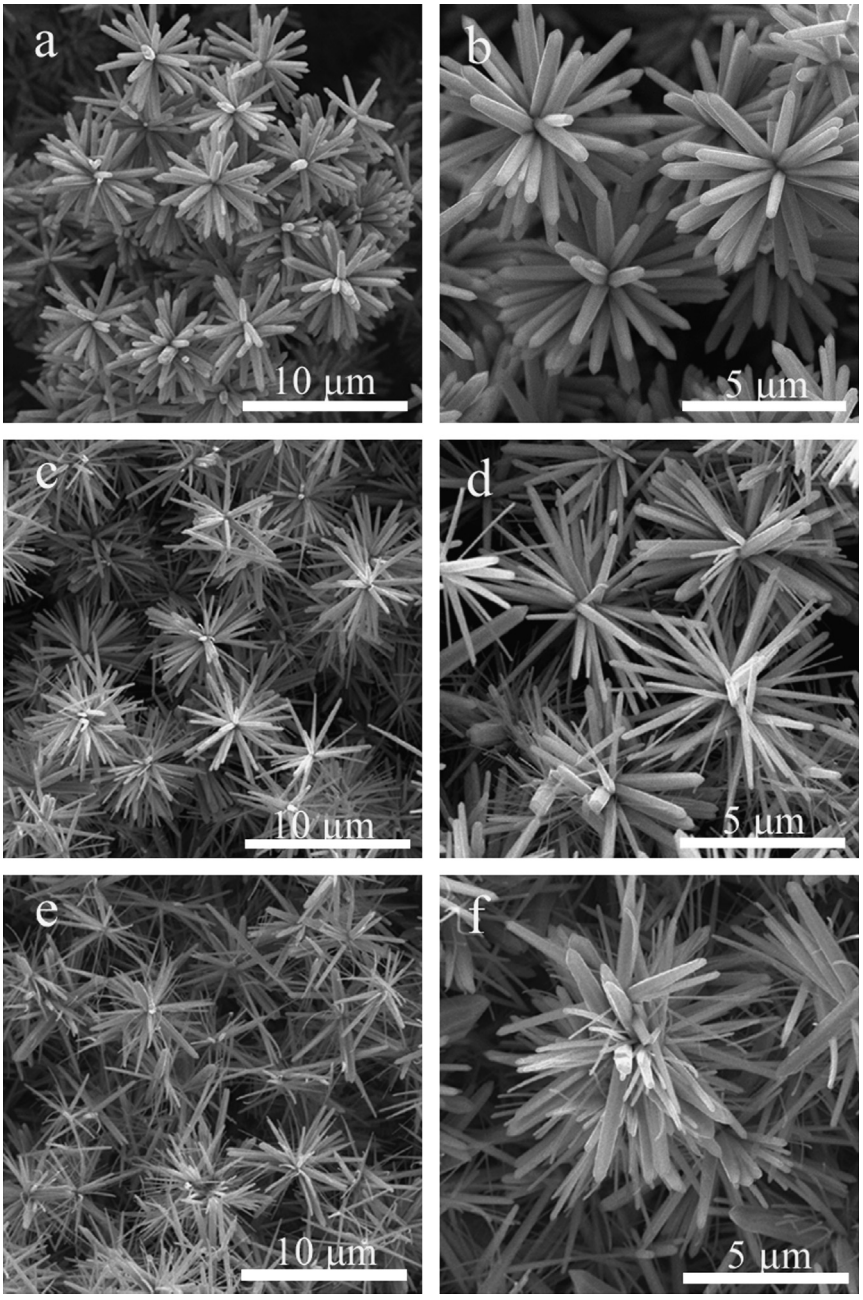

Fig. 5. Typical SEM images of ZnO prepared using KOH on Cu substrate (a, b) sample 8; (c, d) sample 9; and (e, f) sample 10.

(sample 13, Fig. 6e and f). When the concentration of lithium hydroxide is further lowered to 0.25 M while keeping other reaction parameters constant the similar spherical assemblies also were observed (sample 14, Fig. 7a and b). The EDS spectrums correspond to Cu and O, showing that the spherical flowers are composed of Cu and O (Fig. 7c, d and e). And the ratio of Cu and O is 1:1, which indicates the product was CuO.

On the basis of the above experimental results and analysis it is easily found that the morphology of the zinc oxide is greatly influenced by the alkali metal hydroxide, which should be attributed to the different ionic radius of the octahedrally coordinated cations Li^+, Na^+, K^+ and their charge density [28]. Additionally, the sizes of the rods tend to be uniform upon the erosion effect of extra base as reported [29]. Therefore, when the concentration of KOH is reduced the sizes of petals become nonuniform due to the lower concentration of OH^- (Fig. 5).

3.4. Growth process and mechanism

To reveal the morphological evolution and formation mechanism of ZnO on Cu substrate time-dependent experiments were carried out. The morphological evolution of sample 2 with 0.55 M NaOH on Cu substrate can be clearly observed by varying the hydrothermal reaction time (Fig. 8). When the reaction time is 10 min, irregular aggregations with different sizes were obtained (Fig. 8a). When the reaction is prolonged to 20 min, the early forms of flower-like ZnO with a diameter about 1 μm were observed. The products mainly

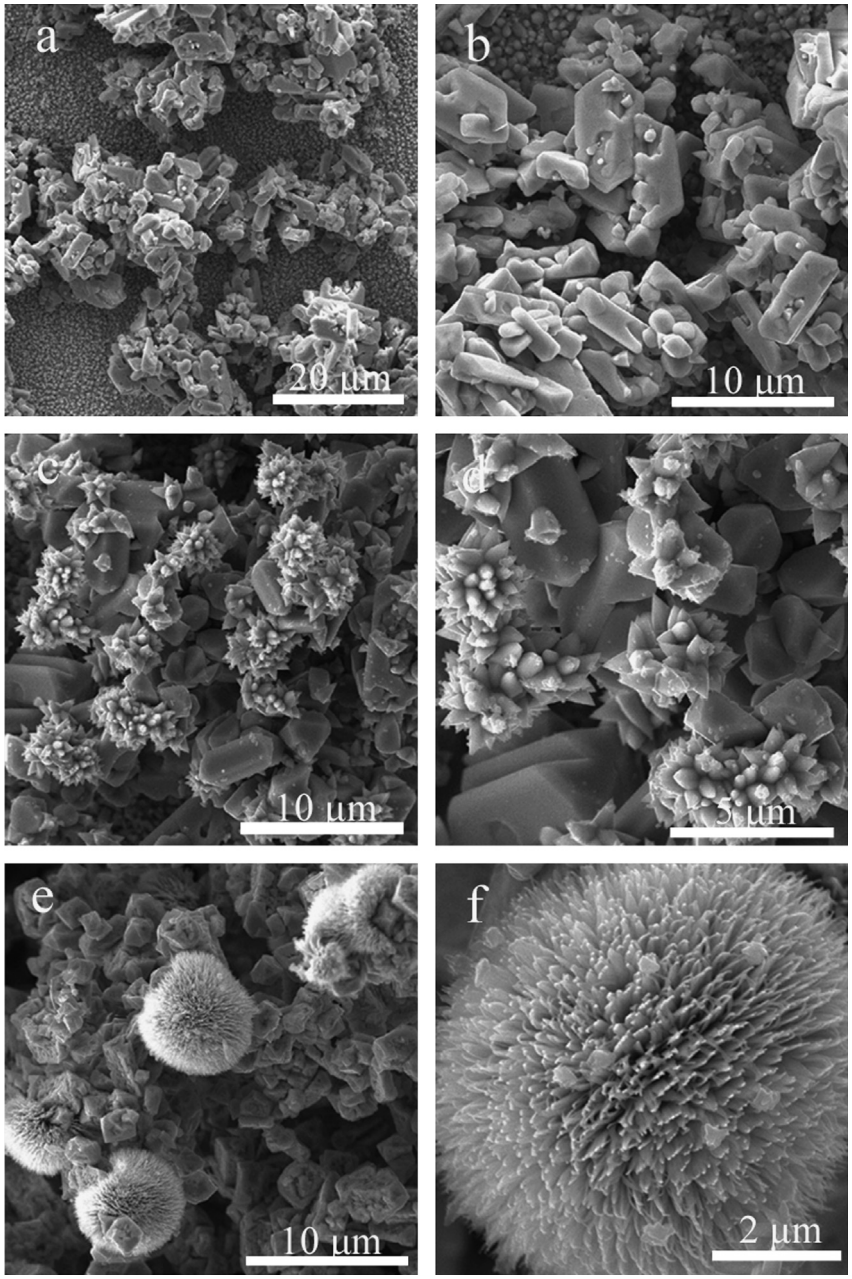

Fig. 6. Typical SEM images of ZnO prepared on Cu substrate (a, b) sample 11; (c, d) sample 12; and (e, f) sample 13.

consisted of several leaflike crystal structures around a single center (Fig. 8b). And the size of the widest petal is about 500 nm. By increasing the reaction time to 30 min, flower-like ZnO with more petals were formed (Fig. 8c). The diameters of the petals do not vary significantly. Until now, we can conclude that the flower-like structure of ZnO could be produced when the reaction time is above 30 min. Using the reaction time of 1 h, well-defined flower-like structures were observed (Fig. 8d). It is worth to mention that the largest diameter of the flower-like ZnO is 2 μm and the size of the widest petal decreased to about 400 nm. In particular, a layer of CuO crystallites on the surface of Cu substrate appeared. However, the sizes of CuO crystallites ranged greatly. When the reaction time is 2 h, flower-like structures comprised of nonuniform petals with diameters about 2–3.5 μm were obtained. Nevertheless, the largest diameter of the petals had no significant change (Fig.8e). Moreover, it is obvious that the sizes of CuO crystallites became large. Further extending the reaction time to 4 h, more flower-like structures were formed so that the CuO almost cannot be observed (Fig. 8f). And the diameters of petals become more uniform and the numbers of petals become more and more. However, the sizes of products and the largest diameter of petals increased to about 3.5–4 μm and 500 nm, respectively. When the reaction time is 6 h, the sizes of polyhedron CuO became large and the largest diameter can reach 1 μm (Fig. 8g). However, the sizes of flower-like ZnO and petals had no evident change. When the reaction time is 12 h, CuO crystallites almost cannot be observed due to

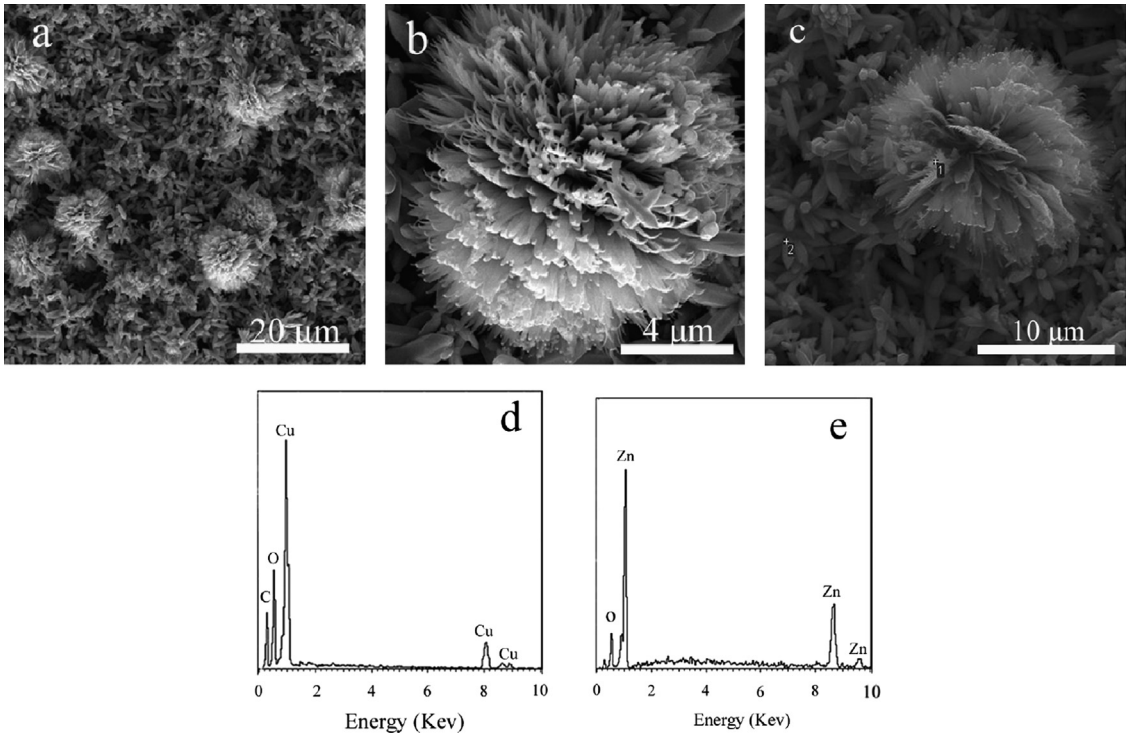

Fig. 7. SEM images of sample 14 prepared with 0.25 M LiOH on Cu substrate (a, b, c) SEM images and EDS spectrums of point 1 (d) and point 2 (e). Sample coated with carbon.

the formation of a large amount of flower-like ZnO (Fig. 8h). Further increasing the reaction time to 24 h makes the flower-like ZnO structures more defined in the function of Ostwald ripening mechanism (Fig. 8i) [30]. Finally, the sizes of flower-like ZnO increased to about 4–5 μm and the diameters of petals became more uniform, whereas the wider petals can be observed occasionally.

Based on the above experiments, it can be concluded that flower-like ZnO and the polyhedron CuO crystallites were obtained when the reaction time is 30 min and 1 h, respectively. Regarding the formation of rod-like and flower-like ZnO, the concentrations of Zn^{2+} and OH^- must have played key roles, since no template, organic additive, or surfactant existed in the reaction system. Therefore, we propose the following explanation for the formation of the rod-like and flower-like ZnO microstructures and polyhedron CuO on Cu substrate, and the schematic illustration of the formation process and mechanism is presented in Fig. 9.

At the early stage of the reaction, when the concentration of NaOH is 0.65 M, both nucleation and crystal growth are very fast so that ZnO nuclei with high surface energy grow along *c*-axis, which leads to the formation of numerous ZnO nanorods randomly distributed (Fig. 1a and b). When the concentration of sodium hydroxide is decreased from 0.65 M to 0.55 M (0.45 M and 0.35 M), both the nucleation rate and crystal growth of the ZnO crystal became relatively slower than ones with 0.65 M sodium hydroxide. In general, slow crystallization is required to form products with a thermodynamically stable structure because the crystallizing partners would aggregate and follow the lowest-energy path [31]. Consequently, at the beginning of the reaction, Zn^{2+} reacts with sodium hydroxide to produce a suitable quantity of growth unit of $Zn(OH)_4^{2-}$(Eqs. 1 and 2). Afterwards, $Zn(OH)_4^{2-}$ would transform into very tiny ZnO particles in situ via the dehydration reaction under the hydrothermal conditions at stage B (Eq. 3). With the reaction extending, ZnO nucleates spontaneously form the solution of $Zn(OH)_4^{2-}$ to multinuclei aggregates (Step C). The multinuclei aggregates serve as the sites for the growth of one dimension ZnO nanostructures along the direction of [0001] to form early forms of flower-like ZnO nanostructures under hydrothermal conditions (Step D). However, the diameters of petals are very large and nonuniform. Then, with reaction time proceeding, Cu reacted with oxygen and H_2O and formed $Cu(OH)_2$ (Eq. 4). However, $Cu(OH)_2$ is a metastable phase which would transform into more stable CuO in NaOH solutions (Eq. 5) [32,33], and it occurred more readily at higher temperature because of the activated nature of this process. It is reported that during the solution synthesis of CuO, the composition and morphology of final product are largely dependent on the synthesis condition, such as alkalinity and solvent, and the solid precursors including $Cu(OH)_2$ may exist only momentarily or may not exist at all [34]. Therefore, polyhedron CuO subsequently was obtained at stage E. In the meanwhile, fast growth of ZnO in the *c*-axis causes a situation of metastability, which is thermodynamically favorable for a large crystal to small one. As a consequence, the wide petals of the flower-like ZnO transformed into thinner ones. Then, some small and thin petals grew out and the sizes of the nanorods tend to be uniform at the erosion effect of extra alkali at step F [35,36]. Moreover, NaOH is a strong

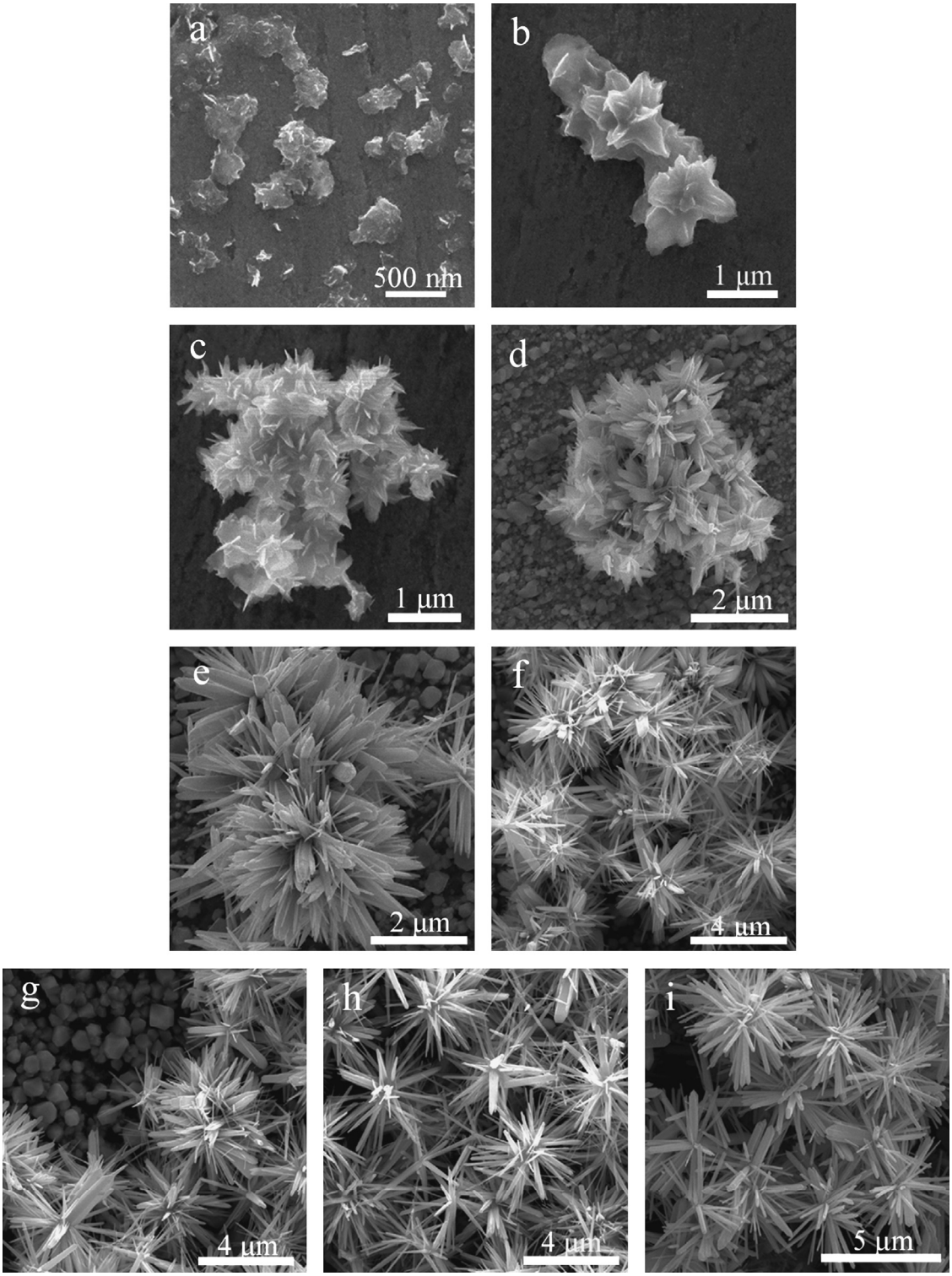

Fig. 8. Typical SEM images of sample 2 obtained with different reaction time: (a)10 min; (b)20 min; (c)30 min; (d) 1 h; (e) 2 h; (f) 4 h; (g) 6 h; (h) 12 h; and (i) 24 h.

electrolyte, and it may neutralize the surface charges of the CuO, preventing them from possible crystallite aggregation [37]. Thus, dispersed CuO formed and the sizes of CuO crystallites became larger. Finally, the sizes of petals did not become very uniform due to shortage of base and flower-like ZnO with nonuniform petals was also formed at stage F. However, it is worth to note the polyhedron CuO cannot be observed due to the formation of a great number of flower-like ZnO.

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \quad (1)$$

$$Zn(OH)_2 + 2OH^- \rightarrow Zn(OH)_4^{2-} \quad (2)$$

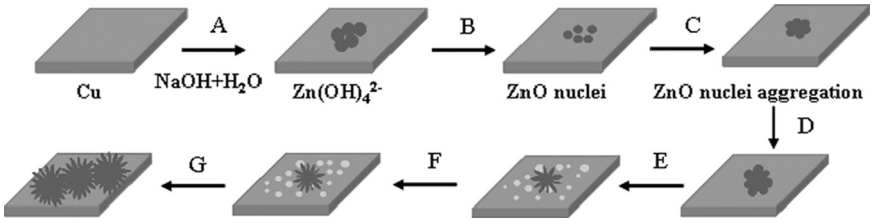

Fig. 9. Schematic diagram of the possible growth process for flower-like ZnO grown on polyhedron CuO prepared on Cu substrate.

$$Zn(OH)_4^{2-} \rightarrow ZnO + 2H_2O + 2OH^- \quad (3)$$

$$2Cu + O_2 + 2H_2O \rightarrow 2Cu(OH)_2 \quad (4)$$

$$Cu(OH)_2 \rightarrow CuO + H_2O \quad (5)$$

4. Conclusions

In summary, flower-like ZnO grown on polyhedron CuO have been hydrothermally fabricated on Cu substrate at 70 °C. The alkaline metal hydroxide plays an important role in this system. The rod-like zinc oxide would transform into flower-like ones when the concentration of sodium hydroxide is decreased. Moreover, the polyhedron CuO can be observed when proportionally decreasing the concentrations of Zn^{2+} and OH^-. The flower-like ZnO was easily formed when using potassium hydroxide compared with the equivalent sodium hydroxide. Specially, irregular ZnO and the flower-like CuO were obtained when using lithium hydroxide. Time-dependent experiments indicated that the formation of flower-like ZnO was prior to polyhedron CuO on Cu substrate. The evolution of morphology and size of ZnO and CuO depended on reaction time. The numbers and diameters of petals of flower-like ZnO changed and the sizes of polyhedron CuO became larger and larger with increasing time. On the basis of experiments, a growth mechanism was proposed to account for the growth of the flower-like ZnO on polyhedron CuO.

Acknowledgments

This work was supported in part by the Program for Taishan Scholars of Shandong Province Government, Projects from the National Natural Science Foundation of China (21071061), the Natural Science Foundation of Shandong Province (ZR2010EZ001 and ZR2009FM072), and the Science and Technology Projects of Colleges and Universities of Shandong Province (J12LA06).

References

[1] H.N. Wu, M.S. Xue, J.F. Ou, F.J. Wang, W. Li, Effect of annealing temperature on surface morphology and work function of ZnO nanorod arrays, Journal of Alloys and Compounds 565 (2013) 85–89.
[2] C.H. Zang, D.M. Zhang, C.J. Tang, S.J. Fang, Z.J. Zong, Y.X. Yang, C.H. Zhao, Y.S. Zhang, Optical properties of a ZnO/P nanostructure fabricated by a chemical vapor deposition method, Journal of Physical Chemistry C 113 (2009) 18527–18530.
[3] E. Fazio, A.M. Mezzasalma, G. Mondio, F. Neri, R. Saija, ZnO nanostructures produced by laser ablation in water: optical and structural properties, Applied Surface Science 272 (2013) 30–35.
[4] S.W. Chen, J.M. Wu, Nucleation mechanisms and their influences on characteristics of ZnO nanorod arrays prepared by a hydrothermal method, Acta Materialia 59 (2011) 841–847.
[5] S.J. Lee, S.K. Park, C.R. Park, J.Y. Lee, J. Park, Y.R. Do, Spatially separated ZnO nanopillar arrays on Pt/Si substrates prepared by electrochemical deposition, Journal of Physical Chemistry C 111 (2007) 11793–11801.
[6] N. Kiomarsipour, R.S. Razavi, Hydrothermal synthesis and optical property of scale- and spindle-like ZnO, Ceramics International 39 (2013) 813–818.
[7] Y. Zeng, T. Zhang, W.Y. Fu, Q.J. Yu, G.R. Wang, Y.Y. Zhang, Y.M. Sui, L.J. Wang, C.L. Shao, Y.C. Liu, H.B. Yang, G.T. Zou, Fabrication and optical properties of large-scale nutlike ZnO microcrystals via a low-temperature hydrothermal route, Journal of Physical Chemistry C 113 (2009) 8016–8022.
[8] Y.S. Lee, S.N. Lee, I.K. Park, Growth of ZnO hemispheres on silicon by a hydrothermal method, Ceramics International 39 (2013) 3043–3048.
[9] C.M. Yang, M.H. Hon, I.C. Leu, Patterned Zn-seeds and selective growth of ZnO nanowire arrays on transparent conductive substrate and their field emission characteristics, Ceramics International 38 (2012) 4277–4283.
[10] J.Y. Yang, Y. Lin, Y.M. Meng, Y.H. Liu, A two-step route to synthesize highly oriented ZnO nanotube arrays, Ceramics International 38 (2012) 4555–4559.
[11] X.D. Guo, H.Y. Pi, Q.Z. Zhao, R.X. Li, Controllable growth of flowerlike ZnO nanostructures by combining laser direct writing and hydrothermal synthesis, Materials Letters 66 (2012) 377–381.
[12] Y.M. Liu, H. Lv, S.Q. Li, G.X. Xi, X.Y. Xing, Synthesis and characterization ZnO with hexagonal dumbbell-like bipods microstructures, Advanced Powder Technology 22 (2011) 784–788.
[13] X.L. Zhang, R. Qiao, R. Qiu, J.C. Kim, Y.S. Kang, Fabrication of hierarchical ZnO nanostructures via a surfactant-directed process, Crystal Growth Design 9 (2009) 2906–2910.
[14] M. Raula, M.H. Rashid, T.K. Paira, E. Dinda, T.K. Mandal, Ascorbate-assisted growth of hierarchical ZnO nanostructures: sphere, spindle, and flower and their catalytic properties, Langmuir 26 (2010) 8769–8782.
[15] Y. Zeng, T. Zhang, L. Wang, R. Wang, W. Fu, H. Yang, Synthesis and ethanol sensing properties of self-assembled monocrystalline ZnO nanorod bundles by poly(ethylene glycol)-assisted hydrothermal process, Journal of Physical Chemistry C 113 (2009) 3442–3448.
[16] J.J. Feng, Q.C. Liao, A.J. Wang, J.R. Chen, Mannite supported hydrothermal synthesis of hollow flower-like ZnO structures for photocatalytic applications, CrystEngComm 13 (2011) 4202–4210.
[17] Z. Wang, X.F. Qian, J. Yin, Z.K. Zhu, Large-scale fabrication of tower-like, flowerlike and tube-like ZnO arrays by a simple chemical solution route, Langmuir 20 (2006) 3441–3448.
[18] C. Jia, X.H. Zhang, Y.Q. Chen, Y.S. Su, Q.T. Zhou, M.J. Xin, Y.S. Lv, W.H. Kong, Liquid phase epitaxial growth and optical property of flower-like ZnO nanosheets on zinc foil, Applied Surface Science 254 (2008) 2331–2335.
[19] Y. Lin, Q.F. Jiang, Effect of substrates and anions of zinc salts on the morphology of ZnO nanostructures, Applied Surface Science 257 (2011) 8728–8731.
[20] C.X. Xu, A. Wei, X.W. Sun, Z.L. Dong, Aligned ZnO nanorods synthesized by a simple hydrothermal reaction, Journal of Physics D: Applied Physics 39 (2006) 1690–1693.
[21] Z. Guo, X. Chen, J. Li, J.H. Liu, X.J. Huang, ZnO/CuO hetero-hierarchical nanotrees array: hydrothermal preparation and self-cleaning properties, Langmuir 27 (2011) 6193–6200.

[22] Y. Qin, F. Zhang, Y. Chen, Y.J. Zhou, J. Li, A.W. Zhu, Y.P. Luo, Y.T. Tian, J.H. Yang, Hierarchically porous cuo hollow spheres fabricated via a one-pot template-free method for high-performance gas sensors, Journal of Physical Chemistry C 116 (2012) 11994–12000.
[23] L.B. Chen, N. Lu, C.M. Xu, H.C. Yu, T.H. Wang, Electrochemical performance of polycrystalline CuO nanowires as anode material for Li ion batteries, Electrochimica Acta 54 (2009) 4198–4201.
[24] D.J. Shang, K. Yu, Y.S. Zhang, J.W. Xu, J. Wu, Y.E. Xu, L.J. Li, Z. Q. Zhu, Magnetic and field emission properties of straw-like CuO nanostructures, Appllied Surface Science 255 (2009) 4093–4096.
[25] A. Zainelabdin, G. Amin, S. Zaman, O. Nur, J. Lu, L. Hultman, M. Willander, CuO/ZnO nanocorals synthesis via hydrothermal technique: growth mechanism and their application as humidity sensor, Journal of Material Chemistry 22 (2012) 11583–11590.
[26] Y.W. Zhu, C.H. Sow, T. Yu, Q. Zhao, P.H. Li, Z.X. Shen, D.P. Yu, T.L. Thong, Co-synthesis of ZnO–CuO nanostructures by directly heating brass in air, Advanced Functional Materials 16 (2006) 2415–2422.
[27] S. Jung, S. Jeon, K. Yong, Fabrication and characterization of flower-like CuO–ZnO heterostructure nanowire arrays by photochemical deposition, Nanotechnology 22 (2011) 015606.
[28] N. Uekawa, R. Yamashita, Y.J. Wu, K. Kakegawa, Effect of alkali metal hydroxide on formation processes of zinc oxide crystallites from aqueous solutions containing $Zn(OH)_4^{2-}$ ions, Physical Chemistry Chemical Physics 6 (2004) 442–446.
[29] Q.P. Ding, Q.Q. Cao, H.B. Huang, S.G. Yang, X.N. Zhao, Y.W. Du, Zinc oxide microtubes prepared by optical thermal evaporation, Journal of Physics D: Applied Physics 39 (2006) 46–49.
[30] Y.J. Sun, L. Wang, X.G. Yu, K.Z. Chen, Facile synthesis of flower-like 3D ZnO superstructures via solution route, CrystEngComm. 14 (2012) 3199–3204.
[31] S. Ashoka, G. Nagaraju, C.N. Tharamani, G.T. Chandrappa, Ethylene glycol assisted hydrothermal synthesis of flower like ZnO architectures, Materials Letters 63 (2009) 873–876.
[32] Y. Zhao, J.Z. Zhao, Y. Li, D.C. Ma, S.N. Hou, L.Z. Li, X.L. Hao, Z.C. Wang, Room temperature synthesis of 2D CuO nanoleaves in aqueous solution, Nanotechnology 22 (2011) 115604.
[33] Y. Cudennec, A. Lecerf, The transformation of $Cu(OH)_2$ into CuO, revisited, Solid State Science 5 (2003) 1471–1474.
[34] C.H. Lu, L.M. Qi, J.H. Yang, D.Y. Zhang, N.Z. Wu, J.M. Ma, Simple template-free solution route for the controlled synthesis of $Cu(OH)_2$ and CuO nanostructures, Journal of Physical Chemistry B 108 (2004) 17825–17831.
[35] C.L. Yan, D.F. Xue, Conversion of ZnO nanorod arrays into ZnO/ZnS nanocable and ZnS nanotube arrays via an in situ chemistry strategy, Journal of Physical Chemistry B 110 (2006) 25850–25855.
[36] Z.T. Chen, L. Gao, A new route toward ZnO hollow spheres by a base-erosion mechanism, Crystal Growth Design 8 (2008) 460–464.
[37] Y. Chang, H.C. Zeng, Controlled synthesis and self-assembly of single-crystalline CuO nanorods and nanoribbons, Crystal Growth Design 4 (2004) 397–402.