Control of ZnO Morphology via a Simple Solution Route

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By decomposing $Zn(OH)_4^{2-}$ or $Zn(NH_3)_4^{2+}$ precursor in various solvents at suitable reaction conditions, zinc oxide with a diversity of well-defined morphologies was synthesized. Flowerlike ZnO built up by nanorods was obtained by treating $Zn(OH)_4^{2-}$ precursor in water at 180 °C for 13 h. Whereas a replacement of the solvent by *n*-heptane yields snow flakelike ZnO. The prismlike and the prickly spherelike ZnO were also prepared, respectively, by decomposing $Zn(NH_3)_4^{2+}$ or $Zn(OH)_4^{2-}$ in ethanol at 100 °C for 13 h. The rodlike ZnO was produced at 180 °C under the same condition for preparing prickly spherelike product. Besides these typical samples, ZnO in other morphologies was studied manipulatively by changing the reaction conditions of our solution route. Systematical condition-dependent experiments were compared comprehensively to reveal the formation and detailed growth process of ZnO nanosized crystallites and aggregates. The experimental results studied by X-ray diffraction, transmission electron microscopy, and scanning electron microscopy indicated that the solvent, precursor, solution basicity, and reaction temperature as well as time are responsible for the variations of ZnO morphologies.

Introduction

ZnO, an exceptionally important material for applications in pigments, rubber additives, gas sensors, varistors, and optical devices,[1] has been attracting attention in both fundamental research and practical studies. Methods for the synthesis of ZnO particles or films were reported in recent years, to fine-tune its properties for potential application.[2] Recently, room-temperature UV lasing from ZnO nanorod arrays[3] was obtained by Yang et al., highlighting the prospects of corresponding research interests in the fabrication of ZnO-based candidate materials. From this aspect, it is rationally expected that some types of morphologies of ZnO would be promising candidates for room-temperature UV laser utilization or other interesting phenomena involving excited states. Therefore, development of a morphologically controllable synthesis of ZnO nanoparticles is urgently important to answer the demand for exploring the potentials of ZnO.

In addition to the conventional solid-state process, many other synthetic routes, such as precipitation,[4] hydrolysis,[5] pyrolysis,[6] and hydrothermal methods,[7−10] have been introduced to prepare nano- or microscaled ZnO particles in various sizes and morphologies over the past few years. Among all these methods, the simple solution synthesis, by thermal treatment of the reactant in different solvents, may be the most simple and effective way to prepare sufficiently crystallized materials at relatively low temperatures, while exempted from further calcination. Besides this, the benefits of a utilizing solution-based method have also involved the considerable influence of reaction species on the final size and morphology of the as-prepared samples. In this aspect, most of the previous investigations on ZnO prepared by this route, however, mainly utilized zinc hydroxide or salts as precursors and water as reaction media. Further, systematic studies on the morphological modulation of ZnO by using $Zn(OH)_4^{2-}$ or $Zn(NH_3)_4^{2+}$ as precursor are still inadequate. Therefore, it seems necessary to study the relationship between reaction conditions and ZnO morphologies for exploring an effective and simple route to control the morphology of ZnO for practical applications.

We have recently devoted time to synthesizing ZnO with controllable morphologies in order to study its morphology-dependent optical properties. The solution route has been successfully employed to prepare tubular ZnO with exceptional photoluminescence.[11] With the

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Table 1. Summarized Morphologies and Reaction Conditions

morphology	reaction media	pH[a]	temp (°C)	reaction time (h)
flowerlike	1.2 mL of $Zn(OH)_4^{2-}$ solution/13.2 mL of H_2O	14	180	13
snowflakelike	1.2 mL of $Zn(OH)_4^{2-}$ solution/13.2 mL of *n*-heptane	14	180	13
prismlike	1.2 mL of $Zn(NH_3)_4^{2+}$ solution/13.2 mL of ethanol	10	100	13
prickly spherelike	1.2 mL of $Zn(OH)_4^{2-}$ solution/13.2 mL of ethanol	14	100	13
rodlike	1.2 mL of $Zn(OH)_4^{2-}$ solution/13.2 mL of ethanol	14	180	13

[a] The pH of $Zn(OH)_4^{2-}$ or $Zn(NH_3)_4^{2+}$ precursor solutions.

assistance of surfactants, this route can also be used to synthesize ZnO nanowires.[12] Therefore, it is expected that this route will be of assistance in modulating the morphology of ZnO.

In this paper, we described the preparation of ZnO with a diversity of well-defined morphologies via the referred simple solution route. The influences of solvent, precursor, reaction temperature and time, and solution basicity on the size and morphology of ZnO were investigated. It was revealed by scanning electron microscope (SEM) and transmission electron microscope (TEM) images that the morphology of ZnO can be effectively controlled as flower-, snowflake-, prismlike, prickly sphere-, and rodlike. X-ray diffraction (XRD) measurements showed that all ZnO samples are of an hexagonal phase structure, consistent with the electron diffraction (ED) results. The room-temperature photoluminescence of the as-prepared ZnO significantly depends on the crystallinity as well as the morphology. The growth process of ZnO was demonstrated by the condition-dependent experiments.

Experimental Section

All chemicals (analytical grade reagents) were purchased from Beijing Chemicals Co. Ltd. and used as received without further purification. Water was distilled twice. $Zn(OH)_4^{2-}$ precursor solution was prepared by mixing 0.5 mol/L $ZnAc_2$ and 5 mol/L NaOH solutions (volume ratio, v/v 1:1, pH ~14), while $Zn(NH_3)_4^{2+}$ precursor was prepared by mixing 0.5 mol/L $ZnAc_2$ and fresh ammonia (pH ~10).

The preparation of ZnO with typical morphologies as flower-, snow flake-, prism-, prickly sphere-, and rodlike is described as follows. First, $Zn(OH)_4^{2-}$ or $Zn(NH_3)_4^{2+}$ precursor solution and the solvent were mixed, to a volume ratio of 1:11, in a vessel under constant stirring. The mixture was then transferred into a 25-mL Teflon-lined autoclave and maintained at a given temperature for certain time, before they was slowly cooled to room temperature. The white precipitate deposited in the bottom of the autoclave was collected and washed several times with absolute ethanol and distilled water. Finally, the ZnO samples were obtained by centrifugation and dehydration of the precipitate in a vacuum at 60−70 °C. The reaction parameters for each series were summarized in Table 1. Time- and temperature-dependent experiments were carried out to investigate the growth processes of ZnO with these five types of morphologies. Additionally, the volume ratio of $ZnAc_2$ and NaOH solutions was changed from 1:1 to 1:2 to investigate the influence of solution basicity on the ZnO morphology.

The size and morphology of ZnO samples were characterized by SEM (Amary, FE-1910 and JEOL, JSM-6700F) and TEM (Hitachi, H-9000NAR) operating at 200-kV accelerating voltage. A small drop of the sample redispersed by ethanol was deposited on silicon substrate for SEM observation and on a copper grid that was precoated with a film of carbon then dried in the air for TEM characterization. Dry powder samples were used for the XRD (Rigaku, Dmax-2000, Cu Kα radiation) structural measurements . The room-temperature photoluminescence spectra were performed on a Jobin Yvon-Labram spectrometer with a He−Cd laser focused to ~1 μm as the excitation source (λ_{ex} = 325 nm).

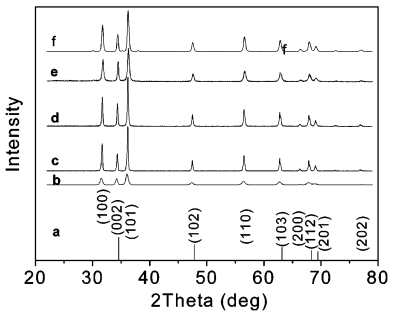

Figure 1. XRD patterns of (a) standard ZnO (JCPDS No. 36-1451), (b) flowerlike, (c) snowflakelike, (d) prismlike, (e) prickly spherelike, and (f) rodlike ZnO samples.

Results and Discussion

Structure and Morphology. All obtained ZnO samples are of wurtzite structure (hexagonal phase, space group $P6_3mc$). In the XRD patterns of ZnO with typical morphologies, shown in Figure 1, all the diffraction peaks are well assigned to hexagonal phase ZnO reported in JCPDS card (No. 36-1451).

The summarized morphologies and reaction conditions are illustrated in Table 1 and the representative SEM and TEM images are shown in Figures 2 and 3. Decomposing soluble $Zn(OH)_4^{2-}$ precursor in H_2O solvent at 180 °C for 13 h, gives flowerlike ZnO with an average size of ~1.5 μm, as shown in Figure 2a. The branches of flowerlike ZnO route from the individual crystalline nucleus, as further confirmed by the TEM image shown in Figure 2b. The ED pattern inset in Figure 2b indicates the single crystalline nature of the sample, and its hexagonal phase, which is consistent with the results of XRD characterization. From the ED pattern, it is also concluded that the flower-shaped ZnO is not a simple aggregation of small crystallites, but is composed by monocrystallines of nanorods growing homocentricly. A similar morphology of ZnO was previously observed by Chittofrati and Matijevic.[13] Panels c and d of Figure 2 are the magnified SEM images of two individual flowerlike ZnO particles marked by white boxes in Figure 2a, which display the detailed features of two different aggregation patterns. When the polar solvent of H_2O was replaced by the nonpolar solvent *n*-heptane, snowflakelike ZnO was achieved (Figure 2e and f). When the reaction media containing $Zn(NH_3)_4^{2+}$ precursor was heated at 100 °C for 13 h, ZnO with prismlike morphology was formed. The mean diameter and length of the prism, as can be seen from SEM image in Figure 3a, are about 500 nm and 1 μm, respectively.

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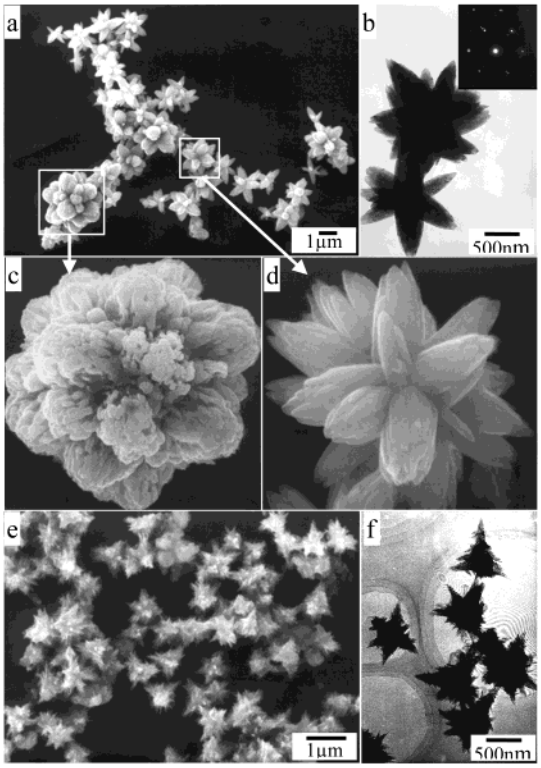

Figure 2. SEM (a, c, d, e) and TEM (b, f) micrographs of ZnO obtained by the solution route. (a) and (b) show ZnO sample with a flowerlike shape prepared by using H_2O as solvent (180 °C, 13 h), and the inset of (b) is an ED pattern; (c) and (d) are the magnified images of two individual flowerlike ZnO marked with a white box in image a; (e) and (f) show the snow flakelike sample synthesized by using *n*-heptane as solvent (180 °C, 13 h).

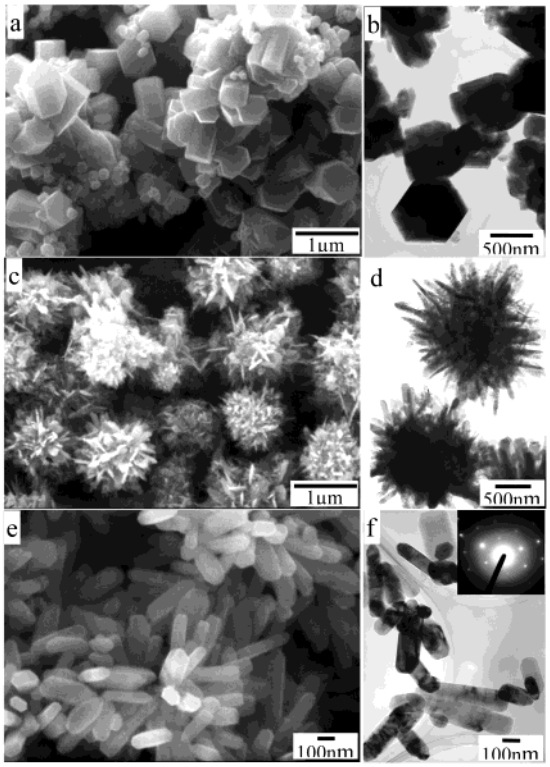

Figure 3. SEM (a, c, e) and TEM (b, d, f) micrographs of ZnO prepared by using ethanol as solvent. (a) and (b) show a prismlike sample (100 °C, 13 h); (c) and (d) are a prickly spherelike sample (100 °C, 13 h); (e) and (f) are rodlike ZnO (180 °C, 13 h); the inset of (f) is the ED image.

The TEM image (Figure 3b) shows the top view of the prism, which clearly reveals the regular hexagonal shape. When the reaction was performed at 100 °C for 13 h by decomposing $Zn(OH)_4^{2-}$ in ethanol, the shape of ZnO changed from prismlike to prickly spherelike, as shown in Figure 3c and d. The average diameter of prickly spherelike ZnO deduced from the SEM image (Figure 3c) is ∼1.5 μm. The TEM image (Figure 3d) indicates that the surface of the prickly spherelike ZnO is built up by needlelike rods of several tens of nanometers in width. When maintaining the reaction conditions for preparing prickly spherelike ZnO sample but increasing temperature to 180 °C, rodlike ZnO with uniform size was achieved (Figure 3e and f). The mean diameter of the rodlike ZnO is ∼100 nm and the aspect (length/width) ratio is about 5 to 1. The ED pattern (the inset of Figure 3f) showed that the preferred growth orientation of rodlike ZnO is along the *C* axis of hexagonal phase, which is the nature of the ZnO crystal growth.[14]

Growth Process. In the present case, we planned to fabricate ZnO particles by the decomposition of soluble $Zn(OH)_4^{2-}$ or $Zn(NH_3)_4^{2+}$ precursor directly under thermal conditions, in various solvents, to follow the growth habit of ZnO. This preparation route gives an alternative choice from high temperature and transitional intermediate of the zinc hydroxide to obtain well-crystallized ZnO, for $Zn(OH)_4^{2-}$ is proposed to be the growth unit and is directly incorporated into ZnO crystallites under given conditions.[15] This route also enhances the influence of solvents and reaction conditions on the morphologies of products and, therefore, pushes the need to investigate the morphology variations of materials with different precursors, solvents, and other conditions.

The crystal formation process can be divided into two stages of nucleation and crystal growth. External conditions may stress tremendous effects on the size and morphology of a given crystal by participating in the nucleation and growth, in which many overall factors integrate to dominate the process. Meanwhile, the real behavior of crystal growth in nanocrystalline semiconductors may vary between fractal aggregation in the inauguration period and the subsequent diffusion process. Here we expected to shed some light on the growth mechanism of the as-prepared ZnO crystallites by forcing controls in the reaction parameters and introducing a series of comparisons in the resulting images.

With respect to the large lattice energy of ZnO, rearrangement and diffusion of ZnO crystallites has been limited to a certain extent under the present reaction temperature during the reaction stage of invariance of reactant concentration. The limited concentration of the aggregated ZnO also favors the diffusion-limited aggregation (DLA) theory.[16−18] The diffusion

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process, as observed in the present case, appears obvious only in the latter morphology-reforming period, when raw materials become scarce in the prolonged reaction time. This is to say, at the initial reaction period, reaction time affects merely the overall size of the aggregation instead of the morphology. But, with the reactant concentration decreasing gradually during a further extension of reaction time, the effects of diffusion process, which are sensitive to the reaction temperature, have to be taken into account.

The sticking coefficient[18] is also an important factor in the DLA model. The solvents H_2O, ethanol, and heptane enable a smooth control of such parameter, making practically achievable the fractal patterns as flower, prickly sphere, and snowflake, shown in Figures 2 and 3. ZnO obtained in these three reaction solvents respectively indicate decreased fractal dimension and increased density. However, since the main point of this article is to discuss the thermodynamic effects of solvents, precursors, reaction time, and temperature, as well as basicity, we are going to publish our investigation on the fractal patterns of ZnO aggregation in future articles.

Solvents. In our case, three solvents with different polarity and saturated vapor pressure are used as reaction media, each producing a distinguished morphology of obtained ZnO. The polarity and saturated vapor pressure of the solvents were found to affect the products under thermal conditions, by giving adjustments to the homogenization of the reactants in reaction medium, the amount of individual nucleus formation, and the amalgamation and direction preference of growing nucleus. For instance, when the reaction takes place in H_2O, the reactants disperse more homogeneously than in *n*-heptane, and the growth of the crystal nucleus is subject to less confinement in a boiling droplet of solvent. Therefore, it is liable to form a flowerlike morphology of ZnO in H_2O but form a snowflakelike morphology in *n*-heptane. Furthermore, the orientation growth of the ZnO crystal is more obvious and the size is a little bigger. When a solvent with a higher saturated vapor pressure such as ethanol is utilized as reaction media, the amalgamation of the nucleus is not intense due to the higher boiling point of the solvent, in comparison with other solvents with lower saturation vapor pressure such as H_2O and *n*-heptane. So it is easier to form an individual pattern such as prism- and rodlike ZnO than dendritic or fractal patterns such as flowerlike or snowflakelike ZnO. Of course, as we mentioned above, since the factors influencing the morphology of ZnO are generally the same, so when different precursors are placed in the same solvent, the morphologies of ZnO are vitally determined by the precursors. This is confirmed by morphological discrepancies between the prismlike and prickly spherelike ZnO in the present case. Some additional investigations on the effects of solvents on the morphology of ZnO also indicate the tendency described above.

Precursors. Compared with the conventional solid-state process, the fabrication of ZnO via the solution route, by decomposing $Zn(OH)_4^{2-}$ or $Zn(NH_3)_4^{2+}$ precursor, is mild. The precursor, $Zn(OH)_4^{2-}$, can be used as

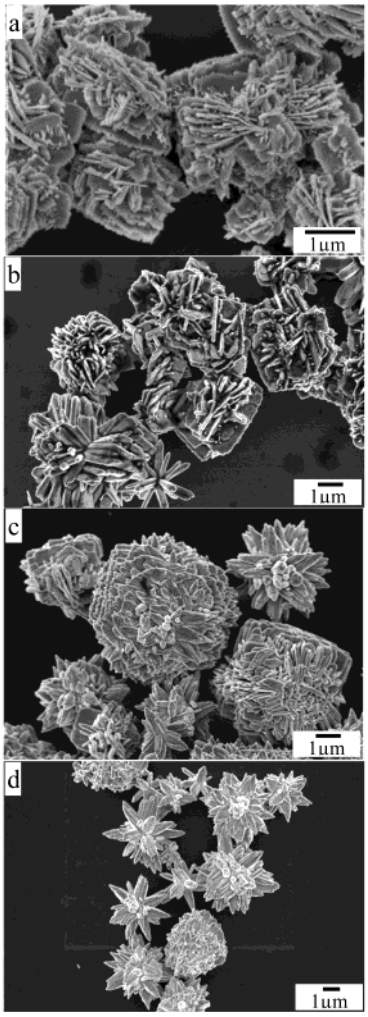

Figure 4. SEM images of morphological evolution of ZnO sample with typical flowerlike shape heated at 180 °C for (a) 10 min, (b) 2 h, (c) 4 h, and (d) 8 h.

the growth unit to incorporate into ZnO crystallites directly.[15] From the point of reaction process, the reactions for the formation of ZnO by using the different precursors experience distinct routes according to the following reactions:

$$Zn(NH_3)_4^{2+} + 2OH^- \rightarrow ZnO + 4NH_3 + H_2O$$

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

where NH_3, as one of the byproducts, can prevent the amalgamation of the nucleus in the supersaturated solvents during the reaction process, thus leading to dispersed morphology such as prismlike rather than prickly spherelike. Therefore, to obtain ZnO with prismatic morphology, the precursor $Zn(NH_3)_4^{2+}$ can be adopted. From the viewpoint of growth behavior, the formation of this morphology is mainly attributed to weak basicity afforded by ammonia and the $Zn(NH_3)_4^{2+}$ cation, which cause the crystal face along the *C* axes to grow slightly faster than any other axes to form a regular polyhedral shape. On the other hand, $Zn(OH)_4^{2-}$ precursor plays an important role in determining the morphologies of ZnO crystallites due to the concentration of OH^- in the reaction solution, which should be a key factor for controlling the growth rate of different

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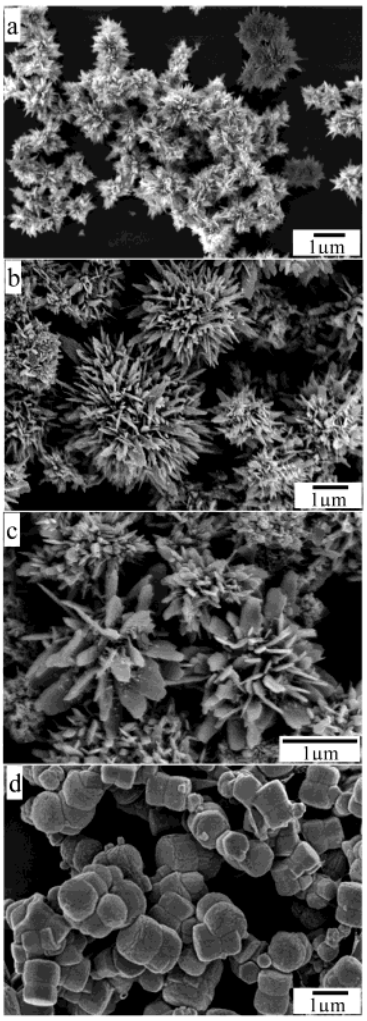

Figure 5. SEM images of morphological evolution of (a) snowflakelike, (b) prickly spherelike, (c) rodlike, and (d) prismlike ZnO. Reaction time is 10 min.

crystal faces and thus lead to the formation of an anisotropic particle such as rod shape or the flower-, snowflake-, and prickly spherelike morphology.

Time and Temperature. To investigate morphological evolution of ZnO with flowerlike morphology as shown in Figure 2a, time-dependent experiments were carried out. The ZnO sample heated for 10 min exhibits the complicated shape consisting of aggregates of sheetlike branches (Figure 4a). When the heating time is prolonged for 2 h, some sheetlike branches evolve into rodlike forms (Figure 4b). Meanwhile, the whole aggregates are evolved into small flowerlike particles. When heated for 4 h, the shape of ZnO is close to flowerlike. It is clearly that the bigger ones are aggregated by a large number of rods growing homocentrically, while the smaller ones are composed of a small amount of rods (Figure 4c). When the reaction time is increased to 8 h, the crystal shape is well-developed into a flowerlike form (Figure 4d). It seems that the size of ZnO obtained at 4 h (Figure 4c) is a little bigger than that obtained in 8 h (Figure 4d), which arises from the split of bigger aggregates into smaller ones to satisfy the spatial requirements of the crystal growth during the "Ostwald ripening" process.

Time-dependent experiments for other ZnO samples (Table 1) were also conducted. When the reactions were performed for 10 min, the initial shapes of snowflake-, prickly sphere-, and rodlike ZnO are analogous to that of the flowerlike ZnO sample (Figure 5a−c), but the morphology of the prismlike ZnO sample displays the twin hexagonal nutlike form (Figure 5d), which can further disassemble and evolve into a prismlike shape after heating for 13 h.

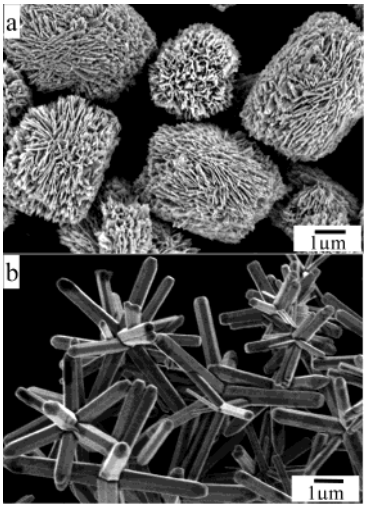

Figure 6. SEM images of ZnO particles prepared by heating $Zn(OH)_4^{2-}$ precursor [$ZnAc_2$/NaOH = 1:2 (v/v)] in H_2O at 180 °C for (a) 10 min and (b) 2 h.

The temperature-dependent experiments at 100 and 140 °C were also carried out for flowerlike ZnO samples. It is shown that the temperature has no obvious influence on the morphology but only affects the size slightly.

Basicity. As has been pointed out, the basicity is important for a controllable synthesis, especially for the morphologies of typical flowerlike ZnO; the experiments were conducted by changing the volume ratio of $ZnAc_2$ and NaOH solutions from 1:1 to 1:2. When solution basicity is higher, the morphology of ZnO heating for 10 min (Figure 6a) exhibits the aggregate feature of sheetlike branches, which is similar to the morphology of ZnO obtained by heating for the same time in a lower basicity solution (Figure 4a), but the sheet size is smaller and the aggregate shape is columnlike. When the reaction time is prolonged to 2 h in higher basicity solution, the columnlike ZnO totally evolves into a uniform branch rodlike shape of ∼300 nm in width (Figure 6b). The individual ZnO rod seems to grow homocentricly like the flowerlike ZnO (Figure 2a), but the diameter of the rod is smaller and the aspect ratio of the rod (length/width) is bigger. In lower basicity solution, only parts of the morphology of ZnO composed of aggregates of sheetlike branches solution evolve into flowerlike form (Figure 4b). It is believed that the growth process of the two morphologies is analogous to that of the flowerlike shape but having a different crystal growth rate along certain crystal faces due to the effects of various solution basicities on the crystal growth habit.

Optical Properties. ZnO exhibited a wide band gap at room temperature with a large exciton binding energy, which is suitable for effective UV emission. However, due to the poor crystal quality of the nanomaterials, i.e., high density of structure defects, the UV

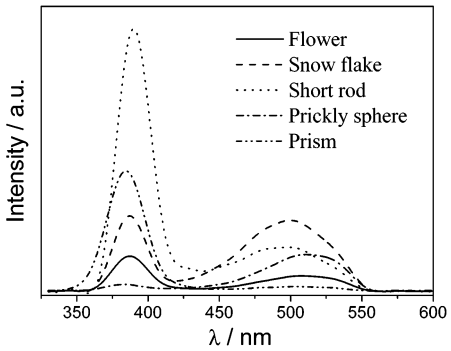

Figure 7. Room-temperature photoluminescence of ZnO with various morphologies.

emission of nanoscaled ZnO is liable to be quenched and only defect emission in visible region is detected.[19] This deficiency hinders progress for the applications of ZnO in optoelectronic and lasing devices. Therefore, how to improve the crystal quality of ZnO by synthetic processing and how to realize UV emission and lasing are still major challenges. In our case, the morphologically modulating synthesis of ZnO is carried out. The photoluminescence of the obtained ZnO (Figure 7) exhibits different features, depending on their morphological variations. Due to its regular prismatic morphology with sufficient crystallization, the prismlike ZnO shows strong UV emission at ∼385 nm, which comes from recombination of exciton, [20] and no defect emission is detected. The rodlike ZnO sample exhibits a strong UV emission with a very weak green emission (∼510 nm). The green emission of ZnO comes from the recombination of electrons in singly occupied oxygen vacancies with photoexcited holes.[21] The relative density of the oxygen vacancies can been estimated by comparing the green emission intensity. ZnO samples with three other kinds of morphologies, i.e., flower-, snowflake-, and prickly spherelike, show both the UV and green emissions, but the relative intensity of UV emission gradually decreased when the morphology changed from flower-, to snowflake-, to prickly spherelike, which is strong evidence indicating the increase of oxygen vacancies. Further research about the properties of photoluminescence is under progress and will be addressed elsewhere.

Conclusion

Nanosized ZnO with a diversity of well-defined morphologies, such as flower-, snowflake-, prism-, prickly sphere-, and rodlike samples, has been successfully fabricated by a simple solution approach. To finely modulate the morphology of ZnO, the relationship between the morphologies and reaction conditions were investigated. It is found that the variations in solvent, precursor, reaction temperature and time, and solution basicity have significant effects on ZnO morphology. The polarity and saturated vapor pressure of the solvents are key factors in directing the morphology of ZnO. The reasons for the precursors affecting the morphology of ZnO can be attributed to different reaction path and distinguished basicities of the solutions, which may influence the crystal nucleation and growth processes. Besides, the size and morphological evolution of ZnO is also dependent on the reaction temperature and time. Prospectively speaking, this work not only obtained the morphology-controllable ZnO but fundamentally afforded an effective and simple way to modulate inorganic materials into well-defined morphologies with potential applications. Further investigation on the fractal pattern of ZnO aggregation is to be published in future articles.

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