Systematic Synthesis of ZnO Nanostructures

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Abstract: In this study, we report a simple solution-phase method to prepare ZnO nanostructures with controllable morphologies. By using oleylamine (OAm) and dodecanol (DDL) as solvents, zinc oxide nanocrystals with tunable sizes and diverse shapes (hexagonal pyramids, bulletlike, and pencil-like shapes) have been obtained under mild conditions. At the same time, the introduction of presynthesized gold nanocrystals can also lead to the hybrid nanostructures of gold–zinc oxide hexagonal nanopyramids. In addition, the possible formation mechanism of the as-prepared ZnO nanostructures has been investigated. Notably, the unique optical properties of the ZnO nanostructures with different sizes and shapes have also been discussed. We hope that this strategy will be a general and effective method for fabricating other metal oxide nanocrystals.

Keywords: gold · luminescence · nanostructures · synthetic methods · zinc

Introduction

Colloidal nanocrystals have been intensively investigated over the past decades because of their distinct shape- and size-dependent properties.[1–3] To gain further insight into the relationship between the crystal facets and properties of nanocrystals, the fine shape control of nanomaterials appears to be extraordinarily important.[4–6] Among semiconductor nanocrystals, ZnO nanomaterials have gained tremendous research interest on account of their wide applications in ultraviolet lasers, piezoelectric nanogenerators, light-emitting diodes, and solar cells.[7–12] In a representative work, Wang and co-workers[13] designed a piezoelectric nanogenerator based on vertical ZnO nanowire arrays, which can convert mechanical energy into electricity. Yang and co-workers[14] synthesized self-organized ZnO nanowires by using sapphire as substrates for room-temperature ultraviolet lasing. Cao et al.[15] have reported ZnO films that are used as the photoelectrodes in dye-sensitized solar cells. To date, versatile synthetic methods have been employed to fabricate ZnO nanostructures including physical vapor deposition, flux methods, chemical vapor deposition, wet chemical methods, and so on.[16–20] In comparison, the solution-based strategies are of relatively low experimental cost and are easily upscaled.[21–24] Vayssieres and Sun et al. have developed a wet-chemical approach to achieve ZnO arrays on various substrates.[25–27] However, in many instances, the synthetic processes involve high growth temperature, catalysts, or additional substrates. Therefore, it is still worthwhile to develop simple and general solution-phase procedures for the fabrication of shape-controlled ZnO nanostructures.

In this study, a facile solvothermal method has been introduced to synthesize ZnO nanoarrays with tunable size and morphologies. The synthetic processes have been conducted under mild conditions without additional substrates. It is notable that the as-prepared nanocrystals exhibit distinct shapes and good uniformity when the reaction conditions are varied. Moreover, the heterogeneous growth of hexagonal ZnO nanopyramids can also be observed by employing presynthesized gold nanoparticles as seeds. More importantly, the optical properties and the possible formation mechanism of the as-obtained ZnO nanomaterials have been well studied.

Results and Discussion

Synthesis of ZnO nanostructures: In our synthetic process, by using zinc acetate dihydrate as the starting material, various ZnO nanostructures were prepared in the presence of oleylamine (OAm) and dodecanol (DDL). The sizes and morphologies of ZnO nanostructures could be tuned by varying the reaction conditions. When zinc acetate dihydrate (0.5 mmol) was added to the mixed solvents of OAm (2 mL) and DDL (7 mL) and heated to the appropriate temperature (160–180°C), a milky white suspension appeared immediately.

Figure 1 presents the representative TEM images of the as-prepared ZnO nanostructures. It can be seen that truncated ZnO nanopyramids were produced. The individual nanoparticles possess a uniform hexagonal basal plane with an edge length of ap-
proximately 29 nm (Figure 1a). The high-resolution TEM (HRTEM) image (Figure 1c) and the corresponding fast Fourier transform (FFT) pattern (Figure 1d) reveal that the hexagonal basal plane of the truncated ZnO nanopyramids is perpendicular to the \( c \) axis of the hexagonally structured ZnO. Similarly, if the reaction proceeded with zinc acetate dihydrate (3 mmol) in the presence of OAm (3 mL) and DDL (6 mL), truncated ZnO nanopyramids with an average edge length of approximately 62 nm were also obtained (Figure 2a). It is notable that hexagonal bases can be observed (Figure 2b). As shown in Figure 2c, the hexagonal ZnO bases with an extended lamellar structure are perpendicular to the TEM copper grid. Figure 4a (see below) shows the X-ray diffraction (XRD) pattern of the as-prepared product. The corresponding diffraction peaks can be readily indexed to the hexagonal wurtzite structure of ZnO (JCPDS card no. 36-1451). In contrast, when 0.5 mmol zinc acetate dihydrate was used in the above reaction system and the reaction time was prolonged to five minutes, ZnO nano-crystals with a perfect pyramid-like morphology were achieved. The SEM image (Figure 2d) indicates that the ZnO nanopyramids possess uniform size with a mean edge length of approximately 95 nm. From the above experimental results, we deduced that the formation of the as-prepared nanopyramids might begin with the hexagonal bases, which further evolved into the truncated pyramids and ultimately transformed into perfect pyramids.

By varying the concentration of zinc acetate dihydrate and the reaction time, the sizes and morphologies of ZnO nanostructures were tunable. With an increased amount of zinc acetate dihydrate (1 mmol) and longer reaction time (1 h), ZnO hexagonal pyramids with well-defined facets were prepared. As shown in Figure 3a, the as-obtained ZnO pyramids are uniform in size with a basal edge length of approximately 156 nm. When the amount of zinc acetate dihydrate was increased to 4.5 mmol and heated for about 5 min, truncated cylinderlike ZnO nanostructures were produced (Figure 3b and Figure S1 in the Supporting Information). Notably, the as-prepared truncated cylinders with a hexagonal base parallel to the substrate preferentially lay flat on the SEM silicon wafer. As depicted in Figure 3d, by further increasing the reaction time to 1 h, fine ZnO hexagonal cylinderlike structures were also obtained. Furthermore, upon decreasing the volume of the solvents while maintaining the other reaction conditions, the reaction produced ZnO with
an incomplete cylinderlike structure in the presence of OAm (1.5 mL) and DDL (3 mL; see Figure S2 in the Supporting Information). Figure 4 shows that the XRD patterns of the as-prepared products are also in good agreement with hexagonal wurtzite ZnO (JCPDS card no. 36-1451). On the other hand, the composition of the reaction solvent also plays a significant role in controlling the morphology. As illustrated in Figure 3c, bulletlike ZnO nanostructures could be achieved by using the mixed solvent of OAm (3 mL) and DDL (7 mL). In contrast, by adding zinc acetate dihydrate (1 mmol) into the mixed solvent of OAm (1 mL) and DDL (8 mL), when the reaction mixture was heated to 160–180°C for 1 h, pencil-shaped ZnO nanorods was produced. The SEM image in Figure 5c indicates that the resulting pencil-like ZnO nanorods present uniform shape with an average length of approximately 160 nm. From the HRTEM image (Figure 5a) and the corresponding FFT pattern (Figure 5b) of the selected area, it can be observed that the as-prepared ZnO nanorods have good crystallinity and grow along the <001> direction.

Furthermore, the heterogeneous growth of ZnO nanopyramids on the presynthesized gold nanoparticles was also investigated. The TEM image in Figure 6a shows the as-prepared Au–ZnO hybrid nanoparticles. The corresponding high-angle annular dark-field scanning TEM (HAADF-STEM) image further demonstrates that the hybrid nanoparticles possess good homogeneity (Figure 6b). From the UV-visible spectrum in Figure 7, two absorption peaks can be observed, which are assigned to the absorption bands of ZnO and gold, respectively.[11]

**Growth and shape evolution mechanism:** To better understand the formation mechanism, pure oleylamine and dodecanol were chosen for the synthetic process. When the sole

![Figure 4](image_url) XRD patterns of the as-obtained samples: a) truncated ZnO nanopyramids with an average edge length of approximately 62 nm, b) ZnO nanopyramids with a mean edge length of approximately 95 nm, c) hexagonal ZnO pyramids with a basal edge length of approximately 156 nm, and d) truncated ZnO cylinders.

![Figure 5](image_url) Pencil-shaped ZnO nanorods: a) HRTEM image, b) the corresponding FFT pattern of the selected area, and c) SEM image.

![Figure 6](image_url) a) TEM image and b) HAADF-STEM image of the as-prepared Au–ZnO hybrid nanopyramids.

![Figure 7](image_url) UV-visible absorption spectrum of the as-prepared Au–ZnO nanoparticles.
solvent of OAm was employed, truncated ZnO hexagonal pyramids were obtained (see Figure S3a in the Supporting Information). However, as shown in Figure S3b (see the Supporting Information), ZnO nanostructures with nearly spherical aggregates in shape were produced from pure DDL. In addition, from the corresponding SEM image, it can be observed that the individual aggregate is composed of packed small nanoparticles.

Therefore, on the basis of the experimental results, a possible growth mechanism can be proposed. As described in Figure 8, with the nucleation that occurs in the presence of oleylamine and dodecanol, we assumed that the hexagonal bases were readily formed at the initial growth stage. As the reaction progressed, the hexagonal bases further evolved into ZnO nanostructures with tunable morphologies by varying the reaction conditions. In our experiments, alkylamine (OAm) was critical for the formation of hexagonal nanoprisms. When a low concentration of acetate was added, the different crystal facets of ZnO nanoparticles would be coordinated by capping ligands of alkylamine with less selectivity. Thus, the hexagonal pyramid structure would be produced, in which the surface energy of various crystal facets might decrease greatly. On the other hand, maintaining higher concentration of acetate is favorable to the oriented growth along the \(<001>\) direction, the \(c\) axis of hexagonal wurtzite ZnO, which is also in accord with many reported results.\(^{[28]}\) The solvent composition is also critical for the shape evolution of ZnO nanocrystals. In our synthetic system, oleylamine might act as a stronger capping ligand than dodecanol. With the appropriate increase of the DDL-to-OAm volume ratio at certain conditions, oleylamine is insufficient and selectively coordinates onto the lower-energy crystal surfaces. Finally, the ZnO nanorods can be achieved with faster growth rate along the direction of the \(c\) axis.

**Optical properties of the ZnO nanostructures:** Also investigated were the optical properties of ZnO nanocrystals, which are usually dependent on their sizes and morphologies. Figure 9a shows the UV-visible absorption spectrum of the as-obtained truncated ZnO nanoprisms with a basal edge length of approximately 29 nm. The corresponding absorption peak at 364 nm can be attributed to the ground excitonic state of ZnO. In contrast, for the ZnO nanoprisms with an average edge length of approximately 95 nm, the absorption onset is apparently redshifted and appears at 376 nm (Figure 9b). Absorption peaks are also observed at \(\lambda = 376\) nm for the truncated ZnO nanoprisms with an average edge length of approximately 62 nm (Figure 10a) and the pencil-shaped ZnO nanorods (Figure 10b), respectively. Notably, for the as-obtained truncated ZnO cylinders, a weak absorption peak appears at 373 nm with tailing at longer wavelength (Figure 10c), which might originate from scattering of the colloidal solutions.\(^{[29]}\) Similar absorption peaks are observed for the bulletlike ZnO nanostructures (Figure 10d) and hexagonal ZnO pyramids with a basal edge length of approximately 156 nm (Figure 10e), respectively. In addition, the photoluminescence (PL) spectra of the as-prepared ZnO nanostructures are also displayed in Figure 11. It is notable that only the UV emissions around \(\lambda = 389\) nm are observed, which is related to the recombination of excitons.
In summary, we have demonstrated a facile solution-phase strategy to fabricate ZnO nanostructures. By varying the reaction parameters, zinc oxide nanocrystals with various sizes and shapes have been produced under mild conditions. Subsequently, the Au–ZnO hybrid nanostructures have been further achieved by using gold nanoparticles as seeds. In addition, the shape evolution mechanism and the optical properties related to the as-obtained ZnO nanostructures have also been explored. It is believed that this strategy can be readily extended to synthesize more transition-metal oxide nanocrystals.

**Experimental Section**

**Materials**: All chemicals were of analytical grade and were used without further purification. Oleylamine was supplied by Acros (C18-content 80–90%). Zinc acetate dihydrate, ethanol, and hexane were obtained from the Beijing Chemical Reagent Company (China).

**Synthesis of ZnO nanostructures**: ZnO nanostructures with different morphologies were achieved by varying the experimental parameters. Typically, for the synthesis of ZnO hexagonal nanopyramids (approximately 95 nm), zinc acetate dihydrate (0.5 mmol) was loaded in a flask that contained a mixture of dodecanol (6 mL) and oleylamine (3 mL). Then the above mixture was further heated to 160–180°C under agitation and maintained at this temperature for about 5 min. After that, the final products were cooled to room temperature and washed with ethanol by means of centrifugation.

**Synthesis of ZnO nanostructures in the individual solvent**: Zinc acetate dihydrate (0.5 mmol), oleylamine (3 mL), and dodecanol (6 mL), were mixed and stirred. Next, 3–5 nm gold seeds (approximately 60 mg, dispersed in hexane) were added and the above mixture was heated to 120°C to remove water and hexane. Then the resulting solution was further heated to approximately 180°C and maintained at this temperature for a few minutes. After the products were cooled to room temperature, ethanol was used to precipitate the samples, followed by centrifugation. The final samples were dispersed in hexane or cyclohexane.

**Characterization**: The morphologies of the products were investigated by SEM, TEM (JEOL JEM 1200EX operating at 100 kV), and HRTEM (FEI Tecnai G2 F20 S-Twin working at 200 kV). The phase purity was characterized using a Bruker D8 Advance X-ray powder diffractometer with Cu Kα radiation (λ = 1.5418 Å). UV/Vis absorption spectra of the samples in cyclohexane were recorded using a Hitachi U-3010 spectrophotometer. Fluorescence spectra were measured using a fluorescence spectrophotometer (Hitachi F-4500).

**Acknowledgements**

This work was supported by the State Key Project of Fundamental Research for Nanoscience and Nanotechnology (2011CBA00500) and...