

## Selected-Control Synthesis of ZnO Nanowires and Nanorods via a PEG-Assisted Route

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Long-chain polymer-assisted growth of one-dimensional (1D) nanostructures has been investigated in previous research. This kind mild method has lots of merits such as not requiring complex procedures, without template supporting etc. Can the short-chain polymer also be used to grow long nanowires? In the present work, a short-chain polymer (PEG400) was found to promote the formation of 1D ZnO nanostructures, which cannot be obtained by long-chain polymers (such as PEG10000). Moreover, nanowires and nanorods can be selectively synthesized by using short-chain polymers. The influence factors for the formation of 1D ZnO nanostructures were also investigated in detail. The XRD, Raman spectrum, XPS, SEM, TEM, ED, HRTEM, EDXA, and PL spectra have been provided for the characterization of the as-obtained nanowires and nanorods.

### Introduction

One-dimensional (1D) nanostructures such as nanorods and nanowires have attracted considerable attention in recent years.<sup>1</sup> Especially, in the past few years, 1D objects have stimulated particular interest, due to their unusual properties and potential applications.<sup>2–9</sup> Many methods have been used to prepare 1D objects, such as electrochemistry,<sup>2</sup> template (mesoporous silica, carbon nanotubes, etc.),<sup>3</sup> emulsion or polymeric system,<sup>4</sup> arc discharge,<sup>5</sup> laser-assisted catalysis growth,<sup>6</sup> solution,<sup>7</sup> vapor transport,<sup>8</sup> and organometallic and coordination chemistry methods.<sup>9</sup> Controlling the diameter and length of 1D objects is a challenging goal of contemporary materials science.<sup>10</sup> On the other hand, inquiry into reaction conditions that affect the growth of 1D materials also throws light on the growth mechanism of the 1D materials.

ZnO nanomaterials with 1D structures, such as nanowires or nanorods, are especially attractive due to their tunable

electronic and optoelectronic properties, and the potential applications in the nanoscale electronic and optoelectronic devices.<sup>11–13</sup> Recently, a few studies on ZnO nanowires prepared by chemical vapor transport,<sup>11</sup> physical vapor deposition approaches,<sup>12</sup> anodic alumina membrane templates,<sup>13</sup> etc. were reported. Generally, the preparation methods mentioned above involve complex procedures, sophisticated equipment, and rigorous experimental conditions. Thus, the development of mild and lost-cost synthetic routes to ZnO nanorods or nanowires was of great significance. Hitherto, mild methods used to synthesize 1D ZnO nanoparticles mainly focus on the micelle technique<sup>14,15</sup> and electrical deposition,<sup>13</sup> and the latter still need a membrane to support the structure.

In previous research, it was convenient to use polymers to assist the formation of 1D nanoscale materials. This kind mild method needs no complicated procedure, without template supporting and relatively low temperature.<sup>16,17</sup>

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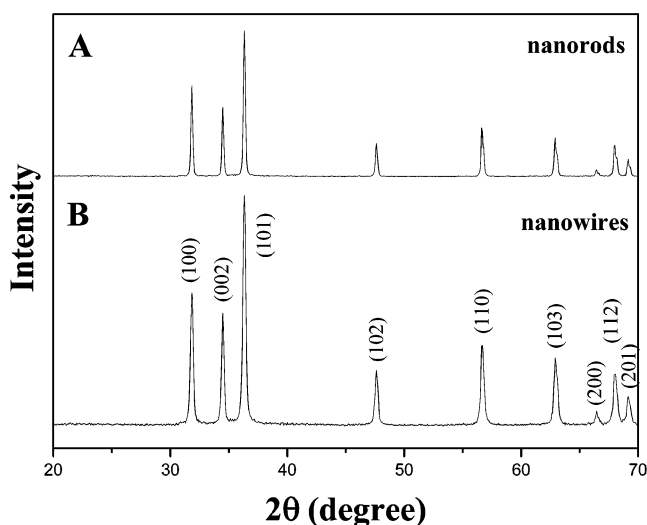
Generally, long-chain polymers help the growth of 1D nanostructures, but their characteristic intertwisting nature is also notable in lots of systems and limits their practical usage. Can a short-chain polymer also be used to assist the formation of long nanowires? It is a new and beneficial work to determine if a short chain will greatly decrease the possibility of intertwisting. If a short-chain polymer adsorbs on the surface of a growing colloid, confining some area of the colloid, this should lead into anisotropic growth of the growing crystal. Thus it is feasible that short-chain polymers can also promote the formation of 1D nanostructures if the growth of colloid is confined by adsorbed short-chain polymer. With shorter length, short-chain polymers may have the unique ability to synthesize shorter length 1D nanostructures. Therefore, we can use short-chain polymers to selectively control synthesis of different 1D nanostructures with different length. In the present work, a short-chain polymer, poly(ethylene glycol) (average molecular weight 400, abbreviated as PEG400) is found to selectively promote the formation of 1D ZnO nanowires and nanorods, respectively. Up to now, there has been no report about using mild methods to selectively control ZnO 1D morphologies (nanowires and nanorods). This method develops a new route to controllably synthesize other 1D scale materials.

## Experimental Section

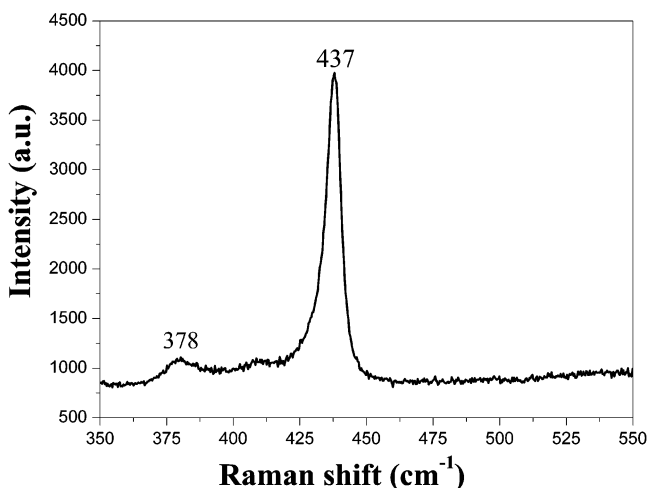
**Synthesis of ZnO Nanowires.**  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  (1.100 g, 5.02 mmol) was dissolved in 10 mL of distilled water, and then solid NaOH (3.2 g, 40 mmol) was slowly added into the solution and stirred for about 10 min and formed a transparent  $\text{Zn}(\text{OH})_4^{2-}$  solution. Then 2 mL of the above solution was loaded into a 30 mL Teflon-lined autoclave, which was then filled with 5 mL of PEG400 and absolute ethanol (20 mL) up to 90% of the total volume. The autoclave was sealed and maintained at 140 °C for 24 h and then cooled to room temperature naturally. The precipitate was filtered off, washed with absolute ethanol and distilled water several times, and then dried in a vacuum at 60 °C for 4 h.

**Synthesis of ZnO Nanorods.** A mixture of  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  (0.4522 g, 2.06 mmol) and 5 mL of PEG400 was put into a beaker containing 25 mL of absolute ethanol. The mixture was stirred for 5 min and then loaded into a 30 mL Teflon-lined autoclave, which was filled with solid NaOH (0.156 g, 3.90 mmol). The autoclave was sealed and maintained at 140 °C for 24 h, and the followed procedures acted as the synthesis of ZnO nanowires. The difference between the synthesis of ZnO nanorods and nanowires lay in the amount and addition sequence of NaOH, namely, the element Zn exists as  $\text{Zn}^{2+}$  and  $\text{Zn}(\text{OH})_4^{2-}$  before the reaction, respectively.

X-ray diffraction (XRD) patterns were carried out on a Japan Rigaku D/max rA X-ray diffractometer equipped with graphite-monochromatized high-intensity Cu  $\text{K}\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ). The accelerating voltage was set at 50 kV, with 100 mA flux at a scanning rate of 0.06°/s in the  $2\theta$  range 20–70°. The Raman spectrum was obtained at room temperature with a LABRAM-HR Confocal Laser MicroRaman spectrometer. The X-ray photoelectron spectra (XPS) were collected on an ESCALab MKII X-ray photoelectron spectrometer, using nonmonochromatized Mg  $\text{K}\alpha$  X-ray as the excitation source. The field emission scanning electron microscopy (FE-SEM) images were taken on a JEOL JSM-6700FSEM. The transmission electron microscopy (TEM) images and electronic diffraction (ED) patterns were taken on a Hitachi



**Figure 1.** Powder XRD patterns of the products: (A) nanorods; (B) nanowires.



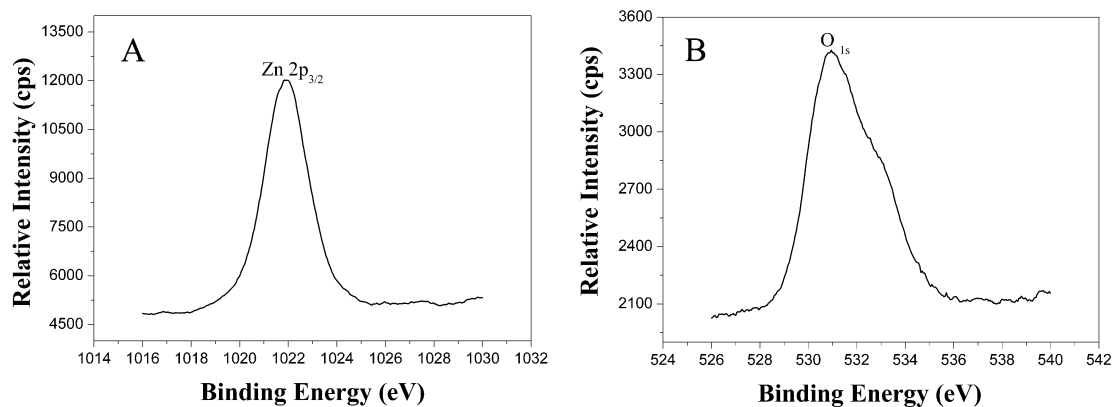
**Figure 2.** Raman spectra of the nanowires.

model H-800 instrument with a tungsten filament, using an accelerating voltage of 200 kV. The high-resolution transmission electron microscopy (HRTEM) image and energy-dispersive X-ray analysis (EDXA) were recorded on a JEOL-2010 TEM at an acceleration voltage of 200 kV. The room temperature photoluminescence (PL) spectra were performed on a Jobin Yvon–Labram spectrometer with a He–Cd laser.

## Results and Discussion

**X-ray Diffraction Patterns (XRD) of the Products.** The XRD pattern of the as-obtained nanowires and nanorods is shown in Figure 1, respectively. All the peaks of both nanowires and nanorods can be indexed to the wurtzite ZnO (JCPDS card No. 36-1451,  $a = 3.249 \text{ \AA}$ ,  $c = 5.206 \text{ \AA}$ ) with high crystallinity. Employing the Scherrer equation, the sizes of nanowires and nanorods are 40 and 60 nm, respectively, which correspond to their diameters observed by TEM. No characteristic peaks were observed for the other impurities such as  $\text{Zn}(\text{OH})_2$ .

**Raman Spectrum.** Wurtzite ZnO with  $C_{6v}$  or  $6mm$  symmetry has the characteristic Raman spectrum which was shown in Figure 2 (ZnO nanowires). The Raman peaks at



**Figure 3.** XPS analysis of the nanowires: (A) Zn region; (B) O region.

378 and 437  $\text{cm}^{-1}$  are attributed to the A1 mode and the E2 mode of ZnO, respectively.<sup>18</sup> The broadening asymmetry Raman peak at 437  $\text{cm}^{-1}$  is typical of ZnO Raman active branches, which is also one of the characteristics of ZnO nanoparticles.<sup>13</sup> The Raman spectrum of ZnO nanorods is similar to that of nanowires. Clearly, the Raman spectrum reveals that the as-obtained ZnO nanowires and nanorods are composed of ZnO with wurtzite structure.

**The X-ray Photoelectron Spectra (XPS).** Further evidence for the quality and composition was obtained by the XPS of the products, and the XPS spectra of ZnO nanowires and nanorods are identified. The binding energies obtained in the XPS analysis were corrected for specimen charging by referencing the C 1s to 284.60 eV. Figure 3 shows XPS spectra taken from the Zn and O regions of the ZnO nanowires. In Figure 3A, there is a strong peak at about 1022 eV, which is attributed to Zn 2p<sub>3/2</sub>. In Figure 3B, we can see that the O 1s profile is asymmetric, indicating that two oxygen species are present in the nearby region. The peak at about 531 eV can be indexed to the O(-2) in the ZnO, whereas the weaker shoulder peak at about 532 eV is due to chemisorbed oxygen caused by surface hydroxyl, which corresponds to O-H bonds.<sup>19</sup> No obvious peaks for other elements or impurities were observed. The atomic composition of Zn and O (excluding OH) was calculated by using the integrated peak area and sensitivity factors, and the atomic ratio of Zn:O is 1:1.10, close to the composition of ZnO.

**Morphologies of the Nanowires and Nanorods.** Typical SEM images of as-obtained wurtzite ZnO nanowires and nanorods are shown in Figure 4 as well as the TEM images and ED pattern for detail illustration. Figure 4A shows the SEM image of the as-obtained nanowires with diameters ranging from 30 to 50 nm, while Figure 4B is that of nanorods with diameters of 50–80 nm. The diameters of the products are in good agreement with those calculated by XRD patterns. The TEM images of the nanowires and the nanorods are shown in Figure 4C and Figure 4D, respectively. It reveals the nanowires with lengths up to 2  $\mu\text{m}$  and the nanorods with lengths of 800 nm. The ED

patterns (insets in Figure 4C and Figure 4D) indicate that both of them are single-crystalline. HRTEM images provide the structural details of the products, in which the interplanar spacings of the crystalline stripes (Figure 5A,B) are both about 4.2 Å and can be indexed to the (204) plane. It indicates that both nanorods and nanowires exhibit a preferred growth orientation along the (204) plane. The EDXA image of nanowires (Figure 6) showed that components of the crystals are Zn and O with a ratio of 1.05:1. The Cu signal is attributed to the copper meshes for HRTEM.

**Photoluminescence (PL) Spectra of the Nanowires and Nanorods.** ZnO exhibited a wide direct band gap with a large excitation binding energy, which is suitable for effective UV emission. The room temperature PL spectra of the as-obtained ZnO nanowires and nanorods were examined and are shown in Figure 7. The excited wavelength was 325 nm, and no filter was used. Strong emission at  $\sim 380$  nm was observed in both nanowires and nanorods, which comes from recombination of excitonic centers in the 1D nanoparticles.<sup>20</sup> The green emission ( $\sim 510$  nm) of ZnO comes from the recombination of electrons in singly occupied oxygen vacancies with photoexcited holes.<sup>21</sup> From the figure, we can see that the nanowires have a more intense green emission than the nanorods, which suggested that the photoexcited holes in the nanowires have a better chance of finding an oxygen defect because the holes in a thin and longer 1D nanostructures can access more total ZnO volume.<sup>11</sup>

**Possible Formation Mechanism and Influence Factors.** PEG with uniform and ordered chain structure is easily adsorbed at the surface of metal oxide colloid, which has been investigated in previous reports.<sup>22,23</sup> When the surface of the colloid adsorbs this type of polymer, the activities of colloid will greatly decrease.<sup>22</sup> From the view of kinetics of colloid growth, if the colloid adsorbs the polymer on some area of its surface, the growth rate of the colloids in some certain direction will be confined. Therefore, the addition of PEG in the metal oxide colloids will modify the growth

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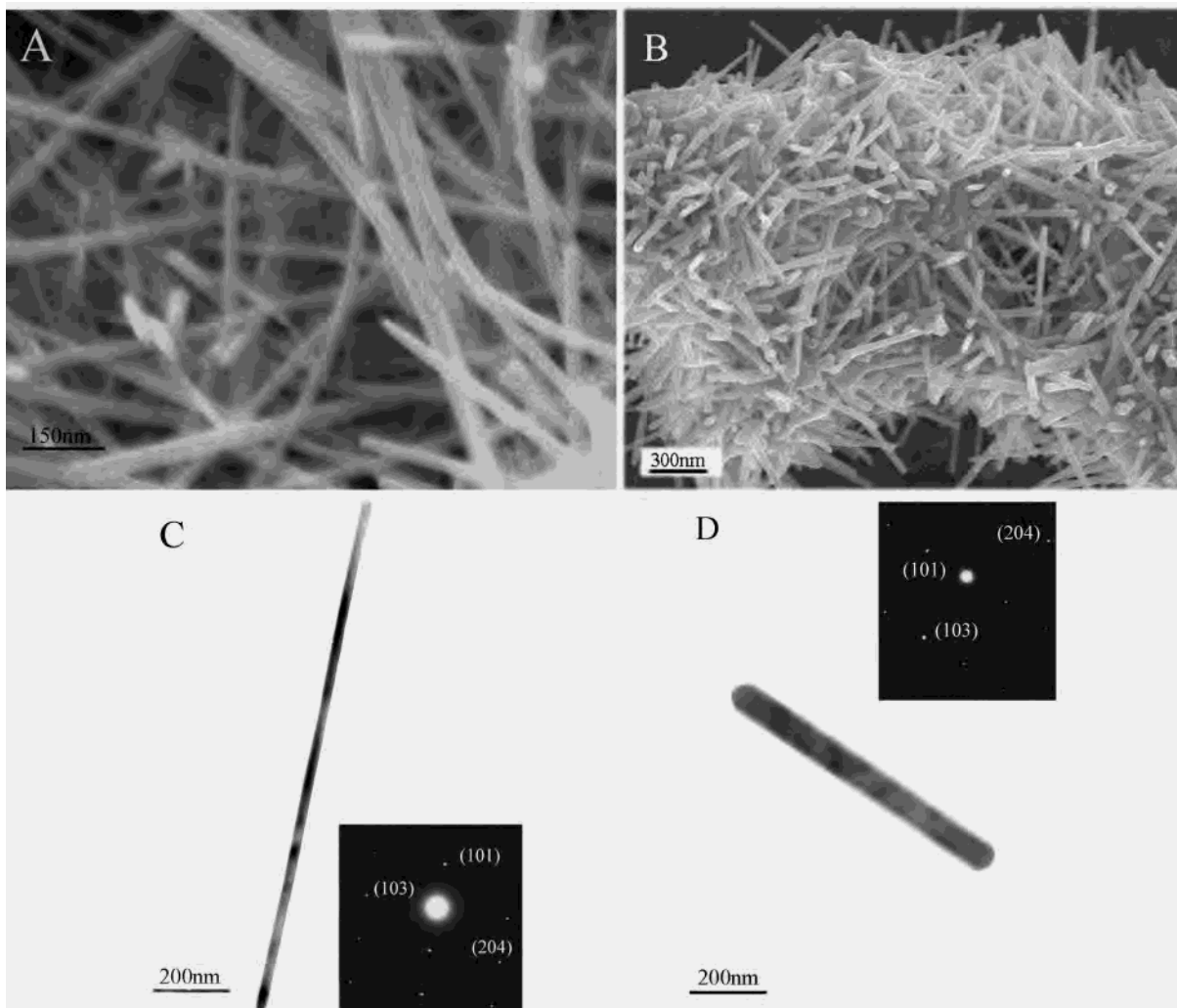
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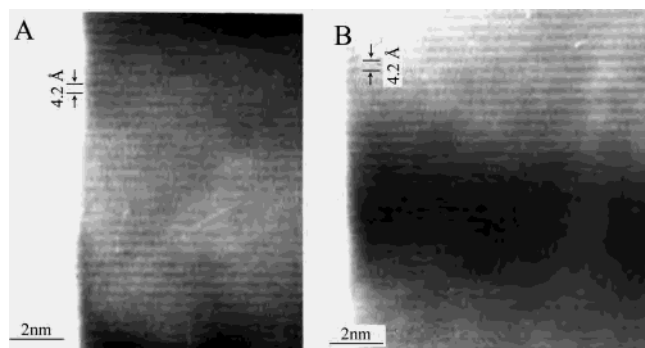
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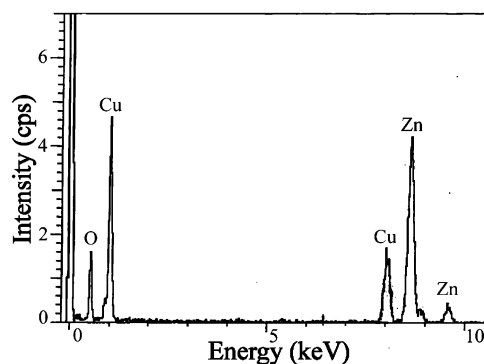


**Figure 4.** Morphologies of the products: (A) SEM image of the nanowires; (B) SEM image of the nanorods; (C) TEM image of a representative nanowire and ED pattern; (D) TEM image of a representative nanorod and ED pattern.



**Figure 5.** HRTEM images of the products: (A) nanowire; (B) nanorod.

kinetics of the growing colloids, which finally leads into anisotropic growth of the crystals. In the previous research, that the polymer helps the growth of 1D nanostructures has been verified.<sup>16,17</sup> In the present work, PEG400 can efficiently adsorb the surfaces of ZnO colloids;<sup>22</sup> therefore it is thought that the formation of 1D ZnO nanostructures is due to the adsorption of PEG400 leading the growth of the ZnO crystals along a certain direction. Farther investigating the relation between PEG400 and final products 1D ZnO, experiments have been done with a different concentration of PEG400



**Figure 6.** EDXA spectra of the nanowires.

under the same conditions as the synthesis of nanorods and nanowires, respectively. It is found that 1D ZnO nanostructures can only be obtained in a range of PEG400 concentration (2–10 mL) under these conditions. Irregular particles were obtained at a lower concentration of PEG (<2 mL), while spherical particles were obtained at a high concentration of PEG (>10 mL) in our experiments, which corresponds to the fact that too low a concentration of PEG400 cannot confine much area of the colloids while too high a

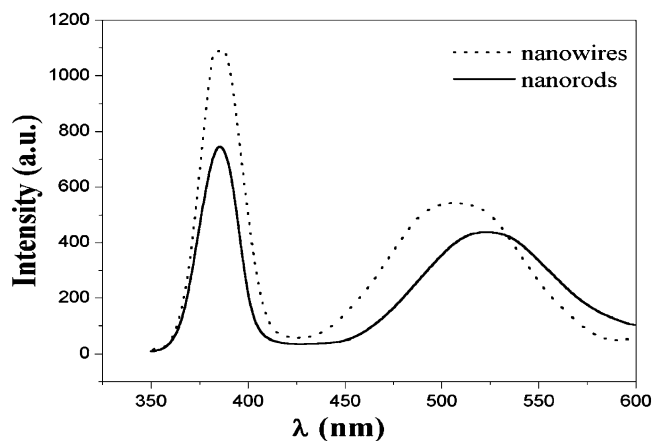


Figure 7. PL spectra of the nanorods and nanowires at room temperature.

concentration of PEG400 confined all aspects of the colloids.

In order to investigate the length of PEG on the kinetics of growth of a 1D ZnO nanostructure, experiments have been done with PEG2000 and PEG10000 under the same conditions as the synthesis of the nanowires and nanorods, respectively. It is found that lots of spherical particles are obtained, which is due to the fact that a long-length PEG can confine more than one direction of the growing colloid and finally formed spherical colloids. Further observation shows that the longer the PEG length, the larger the spherical particles obtained; this phenomena also is found in the formation of TiO<sub>2</sub> with different lengths of PEG.<sup>24</sup> Thus short-length PEG is needed for the synthesis of 1D ZnO nanostructures in our experiments although all different-length PEG chains have affinities to ZnO colloids. On the other hand, long-chain polymers are easily intertwined together, which has a disadvantage to the formation of 1D nanostructures, while short-chain polymers greatly decrease the possibilities of intertwisting under these conditions.

It was worthy to note that the solvent ethanol played a crucial role in the formation of 1D ZnO nanostructures. Experiments with water instead of ethanol as solvent were done under the same conditions as the synthesis of nanorods and nanowires, respectively. However 1D ZnO cannot be obtained in a water system, this result probably caused by the fact that water solvates the PEG400 extremely well, and the PEG400 has a too low affinity for the ZnO colloid surface. Further experiments without PEG400 were done under the same conditions as the synthesis of nanowires, one with water and one with ethanol as solvent, respectively. The results show that some short rodlike elliptical ZnO nanoparticles can be obtained in the ethanol system while irregular particles emerged in the water system. The above experiments indicate that ZnO has a natural tendency to form a rodlike colloid in ethanol; the ZnO nanowires and nanorods obtained in our experiments may result from the synergistic effect of solvent and adsorbent affinities of PEG400.

Comparing the two synthesis experiments, the amount and addition sequence of NaOH are critical to the different morphologies of 1D ZnO nanostructures under these syn-

thesis conditions. At the beginning of our experiment, the element Zn exists as Zn<sup>2+</sup> and Zn(OH)<sub>4</sub><sup>2-</sup>, respectively. It is known that a colloid can selectively adsorb cations or anions on its surface and form an electric double layer under different conditions. In the synthesis of ZnO nanorods, the growing colloids selectively adsorb Zn<sup>2+</sup> first and then chemically adsorb PEG400 on the surface and form the Stern layer of ZnO colloids. The atom O in PEG400 has coordination abilities with metal ions;<sup>25</sup> thus it has a relatively strong electrostatic attraction to Zn<sup>2+</sup> and makes PEG400 bind closely to the surface of the ZnO colloid, while, in the synthesis of ZnO nanowires, the Stern layer of ZnO colloids is made of Zn(OH)<sub>4</sub><sup>2-</sup> and PEG400, Zn(OH)<sub>4</sub><sup>2-</sup> with less attraction to PEG400 making the latter bind less closely to the surface of the ZnO colloid compared with the former system. From the view of the kinetics of colloid growth, PEG binding with different affinities to the growing ZnO colloids will result in different morphologies of the final products. The different 1D ZnO nanostructures obtained in our experiments are attributable to the fact that the closer the PEG400 binds with the ZnO colloid, the easier the length of the final 1D product is confined.

It was found that the amount of NaOH has a slight effect on the length of ZnO nanowires. When other reaction parameters were kept constant as that in the formation of nanowires, a series of experiments were developed with the mole ratio of Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O and NaOH as 1:4, 1:6, 1:8, and 1:10, respectively. It is found that the average length of ZnO nanowires in the final products increases (from 1.8 to 2.1 μm) with quantitative enhancement of the solid NaOH, which may be due to the fact that basic concentration increased the growth rate of ZnO crystals and higher basic concentration resulted in longer nanowires. These above experiments also indicated that Zn(OH)<sub>4</sub><sup>2-</sup> is the precondition to obtain long ZnO nanowires.

## Conclusion

In conclusion, a PEG-assisted route has been developed to prepare 1D ZnO nanostructures, and nanowires and nanorods can be selectively synthesized by using a short-chain polymer, PEG400. This method brings forward a new idea of using short polymer chains to synthesize nanowires and nanorods. The possible formation mechanism of the as-obtained 1D nanostructures was proposed which was further supported by the influence factors. This method needs no complicated procedure, without template supporting and low temperature, but nanowires and nanorods can be selected-control. The XRD, Raman spectrum, XPS, SEM, TEM, ED, HRTEM, EDXA, and PL spectra have been provided for the characterization of the as-obtained nanowires and nanorods.

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