Reverse Micelle-assisted Route to Control Diameters of ZnO Nanorods by Selecting Different Precursors

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A reverse micelle-assisted route was reported to prepare ZnO nanorods from two different precursors, $Zn(NH_3)_4{}^{2+}$ and $Zn(OH)_4{}^{2-}$, respectively. The reverse micelles were used as microreactors, which lead into anisotropic growth of ZnO crystals during a simple solvothermal process.

Controlling the shape of nanostructures at the mesoscopic level is one of the most challenging issues presently faced by synthetic inorganic chemists.[1] Especially, in the past few years, one-dimensional (1D) objects have attracted particular interest owing to their unusual properties and potential applications.[2–9] Many methods have been used to prepare 1D objects, such as electrochemistry,[2] template (mesoporous silica, carbon nanotubes, etc.),[3] emulsion or polymetric system,[4] arc discharge,[5] laser-assisted catalysis growth,[6] solution,[7] vapor transport,[8] organometallic, and coordination chemistry methods.[9] In addition to these methods, reverse-micelle technique has also attracted particular interest because of its simplicity and expedience.[10,11]

Being a wide bandgap semiconductor with a large excitation binding energy, ZnO has been extensively investigated for its promising applications in short-wavelength light-emitting, transparent conductor, piezoelectric materials and room temperature ultraviolet (UV) lasing.[12] ZnO nanomaterials with 1D structure, such as nanowires or nanorods, are especially attractive for their tunable electronic and optoelectronic properties, and the potential applications in the nanoscale electronic and optoelectronic devices.[12–14] Some methods have been developed to synthesize 1D ZnO nanostructures such as physical vapor deposition approaches,[13] chemical vapor transport,[12] ligand-assisted[14] and anodic alumina membrane templates[15] etc.

Despite the synthesis development of 1D ZnO nanostructures, seeking a simple, mild and lost-cost synthetic route is still of great significance, because of the importance of this material. Reverse-micelle technique has been widely used to synthesize monodisperse nanoparticles or 1D nanostructures in recent years, in which the reverse micelles act as microreactors. The aggregation of reverse micelles can be adjusted by many experimental parameters such as the type of surfactant or cosurfactant, the intensity of electrolyte, the temperature, etc. Rodlike reverse micelle is one of the aggregations of reverse micelles, which can be used as good templates to obtain 1D nanostructures. Electrolyte also can influence some properties of surfactant, such as critical micelle concentration (CMC) or hydrolyzation. Thus, different diameters of 1D nanostructures are possibly obtained when different reactants were used in rodlike reverse micelles. In this paper, we provide an ethanol–SDS–heptane reverse micelle system to obtain ZnO nanorods. Two different precursors, $Zn(NH_3)_4{}^{2+}$ and $Zn(OH)_4{}^{2-}$ can be directly transformed to ZnO nanorods with different diameters via a simple solvothermal process.

A typical five-component reverse micelle is formed as follows: 2 mL of $Zn(NH_3)_4{}^{2+}$ solution prepared from $Zn(CH_3COO)_2{\cdot}2H_2O$ (2.2610 g, 10.3 mmol), $NH_3{\cdot}H_2O$ (28 wt%; 3 mL) and 10 distilled water, absolute ethanol (5 mL), sodium laurylsulfonate (SDS) (1.25 g, 4.6 mmol), octanol (1.5 mL, 9.5 mmol), and heptane (20 mL). The mixture was stirred for about 5 min and then loaded into a 30-mL stainless Teflon-lined autoclave. The autoclave was sealed, warmed up at a speed of 3 °C/min and maintained at 140 °C for 24 h, and was then cooled to room temperature on standing. The white precipitate (product **A**) was filtered off, washed with absolute ethanol and distilled water for several times respectively, and then dried in vacuum at 60 °C for 4 h. Another parallel experiment (product **B**) was carried out with the same reaction parameters and process except the precursor, which was replaced by 2 mL of $Zn(OH)_4{}^{2-}$ solution prepared from $Zn(CH_3COO)_2{\cdot}2H_2O$ (2.1731 g, 9.9 mmol) and NaOH (0.2025 g, 50.6 mmol) dissolved in 10-mL distilled water.

The X-ray diffraction (XRD) pattern of as-obtained products is shown in Figure 1.[16] All the peaks of both products can be indexed to wurtzite ZnO (JCPDS card No. 36-1451, $a = 3.249$ Å, $c = 5.206$ Å) with fine crystallinity. From this figure, one can see the relative intensity of peaks in the two products is very similar, which may result from their close microcosmic structures. Employing Scherrer equation, the diameters of nanorods obtained from two precursors, $Zn(NH_3)_4{}^{2+}$ and $Zn(OH)_4{}^{2-}$, are estimated to be 50 and 30 nm, respectively.

The morphologies and sizes of both ZnO nanorods can be seen from the FE-SEM images, shown in Figure 2 (A and B).[16] From Figure 2a (for product **A**), one can see the diameters of these nanorods are about 50 nm with variation of no more than 10 nm. In Figure 2b (for product **B**), it was found that

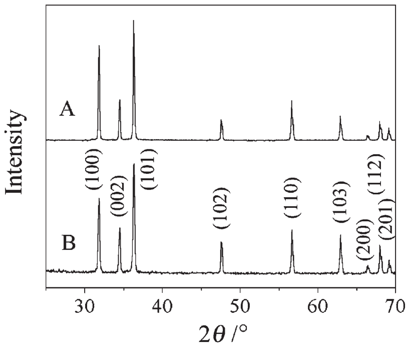

Figure 1. XRD pattern of as-obtained ZnO nanorods. (a) Product **A** from precursor $Zn(NH_4)_4{}^{2+}$; (b) Product **B** from precursor $Zn(OH)_4{}^{2-}$.

the nanorods are longer than product **A**, and the diameters range from 20 nm to 40 nm. The average diameters of these two type nanorods are 50 nm and 30 nm, respectively, which correspond to their calculated diameters by the XRD patterns. The structural details of the nanorods (product **A**) also have been provided and shown in HRTEM image (Figure 2c),[16] in which the crystalline stripes can be clearly seen and the interplanar spacings are about 1.6 Å corresponding to (110) plane. It indicates that the nanorods exhibit a preferred growth orientation along the (110) plane. The ED pattern (inset of Figure 2c) also showed the high crystallinity of these nanorods. The nanorods in product **B** have the same preferential growth and similar structures details as product **A**.

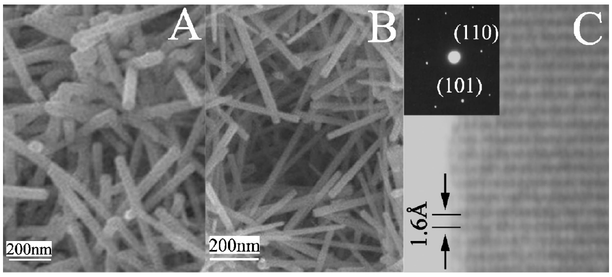

Figure 2. Morphologies of as-obtained products. (a) FE-SEM image of product **A**; (b) FE-SEM image of product **B**; (c) HRTEM image and ED pattern of product **A**.

Both the experiments without surfactant produce no 1D nanostructure, which indicates the surfactant SDS in our experiments was indispensable to the morphologies of final products. The possible formation mechanism of as-obtained ZnO nanorods with different diameters is proposed as follows. When the concentration of the surfactant is ten times the critical micelle concentration (cmc) or more, the surfactant will form both hydrophilic and hydrophobic rod-like structures.[17] That the ionic surfactant SDS with the cosurfactant octanol can form rod-like micelle or reverse micelle have been verified in the previous research.[11,18] In this case, some SDS reverse micelles were thought to form rod-like structures, which provide 1D microreactors for some of $Zn(NH_3)_4^{2+}$ or $Zn(OH)_4^{2-}$ ions to initially transform to $Zn(OH)_2$ during the warming process. Then the newly formed $Zn(OH)_2$ in the microreactors led into succedent anisotropic growth of ZnO crystals when the temperature continuously increased. Meanwhile, the reverse micelles gradually collapsed at higher temperature, but the anisotropic growth of ZnO crystals continued, which resulted in larger diameters of final products than those of the 1D microreactors. The average diameters of these nanorods in products **A** and **B** were different, which may result from the fact that the latter system has stronger basicity, restraining hydrolyzation of SDS to some extent, and favored the formation of smaller dimeters of products, since it would keep the rod-like reverse micelles for a longer time.

The reason that we chose ethanol rather than water as reaction solvent is for the consideration of slowing the speed of crystal growth. ZnO nanorods with irregular lengths also can be obtained when water instead of ethanol used as solvent, which is due to the fact that the precursors transformed to $Zn(OH)_2$ rapidly in water. On the other hand, ethanol is a suitable solvent for the intermediate $Zn(OH)_2$ transforming to ZnO through dehydration. The result also indicates that suitable solvent helps the well growth of 1D ZnO nanostructures. Comparing experiments with different concentration of surfactant and precursors were also done, and show that the concentration of surfactant has little influence on the morphologies of final products, while higher concentration of precursors, especially $Zn(OH)_4^{2-}$, leads into smaller diameters of ZnO nanorods. The results conformed that basicity is the key to the different diameters of as-obtained ZnO nanorods.

In summary, a suitable reverse micelle system was successfully promoted to synthesize ZnO nanorods under a simple hydrothermal reaction process. Different diameters of ZnO nanorods can be directly obtained from the precursors, $Zn(NH_3)_4^{2+}$ and $Zn(OH)_4^{2-}$, respectively. The formation mechanism was also provided.

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References and Notes

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