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Conversion of ZnO microrods into microdisks like structures and its effect on photoluminescence properties

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Abstract

ZnO microstructures were synthesized by the hydrothermal method. Scanning electron microscopy (SEM) revealed the formation of ZnO microrods in absence of trisodium citrate and hexagon-shaped ZnO microdisks in presence of trisodium citrate. The length and width of ZnO microrods were 3–5 μm and 500 nm–1 μm, respectively and they were tapered at both ends, whereas ZnO microdisks were 1–2 μm in diameter. Crystal growth mechanism suggested that citrate suppressed the growth of ZnO along c-axis which resulted into the formation of microdisks like structure. Photoluminescence (PL) spectroscopy showed a weak ultraviolet (UV) and strong green emission in ZnO microrods but a strong UV and very weak green emission in ZnO microdisks. It was suggested that the green emission in ZnO microrods was due to structural defects present at polar planes which was reduced in microdisks with reduction in polar planes.

Keywords: ZnO; Microstructures; Hydrothermal synthesis; Photoluminescence

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1. Introduction

The relationship between morphology of inorganic materials and their properties is well studied and it is well established that their properties significantly depend on their morphology. Therefore, many researchers are focusing on this morphology–structure–function relationship for the fabrication of highly functional materials for practical applications. It results in the progress of synthesis of inorganic materials with controlled morphology on a nano/micrometer scale in the past decade. Among several attractive materials studied so far, ZnO exhibits the widest varieties of nano/micro morphologies [1–8]. These morphologies with different shape, size, orientation etc. could have a crucial effect on certain properties. Many researchers report that the morphology of ZnO plays an important role in determining properties. For example, Gao and co-workers investigated the effect of morphology on catalytic activity of ZnO [9]. They found that the polar planes of ZnO are important for the activity, because they favor forming more oxygen vacancies responsible for catalyzing the N-formylation reaction. In our previous study, we synthesized two different kinds of ZnO microstructures, composed of rod like ZnO building block units with different diameters [10]. It was found that the flower-like ZnO, composed of thinner ZnO nanorods showed significantly better sensing performance due to high quantity of surface atoms, resulting in a larger quantity of adsorbed oxygen than those composed of thicker nanorods. However, for the attractive material, there is still a great deal of unanswered questions regarding the relationship between morphology and properties.

ZnO nano/micro structures with different morphologies are synthesized by several methods including physical and chemical methods. Among them, the wet chemical method is more popular due to their low cost. However, in most of the cases one-dimensional ZnO nano/micro structures are formed due to its highly anisotropic growth character along the *c*-axis. Therefore, the development of a morphologically controlled synthesis of ZnO nano/micro structure is urgently needed to satisfy the requirements for exploring the potential applications of ZnO materials. It is well known that crystal growth of ZnO is highly sensitive to crystal growth modifiers. Therefore, it is possible to synthesize the ZnO nano/micro structures with controlled morphology from an aqueous solution at low temperatures using crystal growth

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modifiers. Here, we developed a low-temperature, environmentally benign hydrothermal approach to synthesize ZnO microrods and microdisks, in the absence and presence of sodium citrate as crystal growth modifiers. A possible growth mechanism of the ZnO microstructures based on growth modifier and ZnO crystals interactions in aqueous solution is also given. Furthermore, the effect of morphology change on PL property is also investigated.

2. Experimental

For the synthesis of the ZnO microstructures, aqueous solutions of 5 mM zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), 5 mM hexamethylenetetramine (HMT; $C_6H_{12}N_4$), and 0.25 mM trisodium citrate were prepared. Growth solution for ZnO microrods were prepared by mixing zinc nitrate and HMT solution and stirred thoroughly. The mixture solution (25 ml) was transferred in 40 ml Teflon-lined autoclave and left undisturbed in the oven at 95 °C for 1 h to synthesize ZnO microrods. ZnO microdisks were synthesized by the similar method by adding 3 ml of the trisodium citrate solution to the growth solution. The product was centrifuged and washed with deionized water and ethanol several times before being dried.

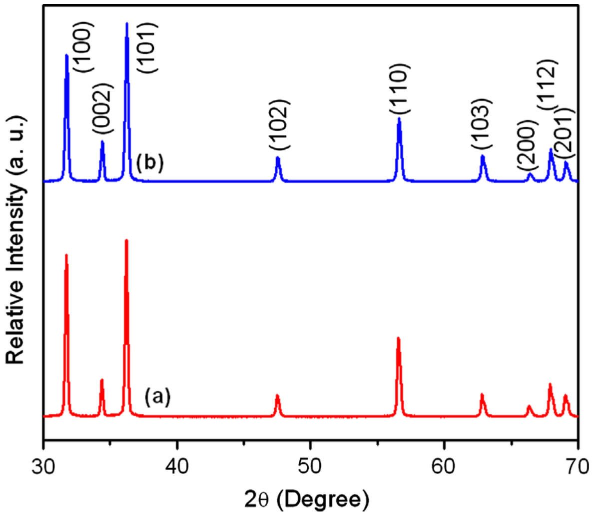

Fig. 1. XRD profiles of ZnO; (a) microrods and (b) microdisks.

The phase formation and crystal structure of the powder were studied by powder X-ray diffractometer (XRD; D/Max 2005, Rigaku). Particle morphology was investigated by scanning electron microscopy (JSM 5900 JEOL). PL property was studied by Cd–He laser source with 325 nm excitation.

3. Results and discussion

3.1. Structural analysis

The XRD pattern of ZnO microrods and microdisks are shown in Fig. 1a and b, respectively. All the diffraction peaks are indexed to the hexagonal phase of ZnO (JCPDS 36-1451) and no other crystalline phases are detected. The intensity of diffraction peaks is slightly higher for microrods compared to microdisks. The characteristic peaks with high intensities corresponding to (100), (002), (101) planes and lower intensities corresponding to (102), (110), (103), (200), (112) and (201) planes, indicate the product is of high-purity hexagonal ZnO wurtzite structure.

Fig. 2 shows SEM images of the as prepared ZnO microstructures. Hexagon-shaped ZnO microrods with tapered

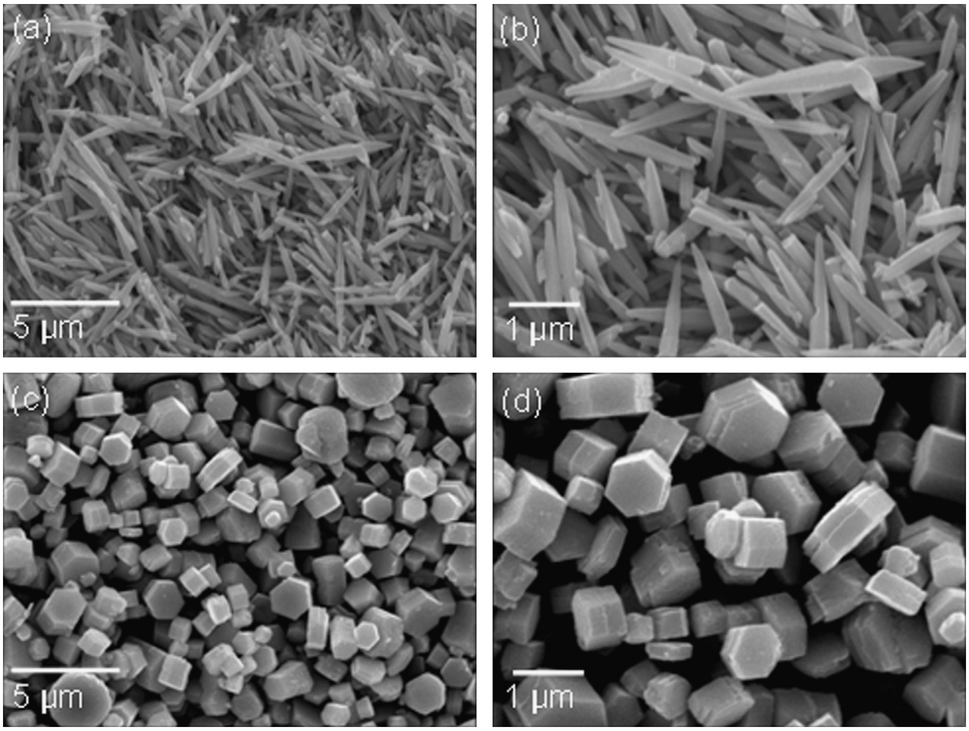

Fig. 2. SEM images of ZnO; (a and b) microrods and (c and d) microdisks.

end could be clearly observed in the Fig. 2a and b. The average diameter and length are about 800 nm and 4 μm, respectively. Hexagon-shaped ZnO microdisks, with an average diameter of 1–2 μm, could be clearly observed in Fig. 2c and d. The average thickness of the ZnO microdisks was about 500 nm–1 μm. These results show that in the absence of citrate, ZnO preferentially grew along *c*-axis and formed ZnO microrods, whereas the addition of citrate suppressed the growth along *c*-axis which resulted in the formation of microdisks.

3.2. Photoluminescence properties

To characterize the optical properties of as-prepared ZnO microstructures, PL spectra is measured at room temperature and shown in Fig. 3. As can be seen, ZnO microrods show two emitting bands, including a weak UV emission and a strong visible emission. The UV emission peak is centered at 393 nm, whereas visible emission consist a broad band in the visible region with a peak position in the green region (532 nm). Compared to microrods, ZnO microdisks show strong UV emission at 393 nm and a weak visible emission. Thus, above mentioned result shows an interesting phenomenon that the change in morphology of ZnO, from microrods to microdisks, results in the reduction of defect related emission. It is well-known that the UV emission corresponds to the near band-edge emission whereas green emission peaks at 532 nm is due to radial recombination of the photo-generated hole with the electrons that belongs to the singly ionized oxygen vacancies [11]. However, the exact reasons for the origin of the green emission in ZnO are not fully understood and many researchers report that antisite defect [12] or zinc interstitials [13] are also responsible. It is also suggested that the presence of Cu impurity or $Zn(OH)_2$ on the surface of ZnO are also responsible for green emission [14,15]. Although, the type of defects responsible for green emission in ZnO is not yet clear, there is convincing evidence that they are located at the surface. The difference in the green luminescence behaviors of the ZnO microrods and microdisks show the surface-dependent properties, indicating that the green luminescence would be related to the atomic structure at the surface of the crystal. Zhou et al. investigated the luminescence property of polar and non-polar planes of ZnO [16]. Their results demonstrate that oxygen vacancies originate from a polar plane because they have a relatively high surface energy and thus, defect should present on the polar surface. Therefore, ZnO having exposed polar planes such as (000−1) and {10−11} surfaces show green emission. On the other hand non-polar {10−10} surfaces are electrically neutral. They have relatively low surface energy and thus, very low defect should be present on the surface. As, defects are known to be responsible for the green emissions, the {10−10} surfaces have very weak green emissions. Therefore, these findings can clearly explain the difference in PL properties of ZnO microrods and microdisks. Since, conversion of ZnO microrods to microdisks reduces the exposed polar planes which consequently reduce the green emission. Thus, the above results indicate that the morphology has a significant effect on PL property.

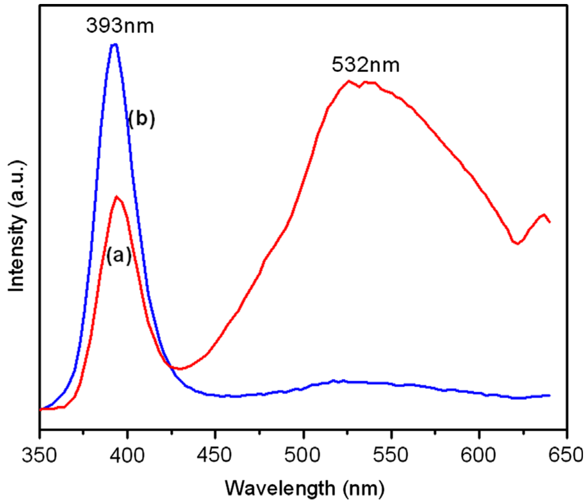

Fig. 3. Room temperature PL spectra of ZnO; (a) microrods and (b) microdisks.

3.3. Growth mechanism

The formation process for the hexagonal ZnO structure using the hydrothermal method can be expressed as follows [17];

$$(CH_2)_6N_4 + 6H_2O \leftrightarrow 6HCHO + 4NH_3 \tag{1}$$

$$NH_3 + H_2O \leftrightarrow OH^- + NH_4^+ \tag{2}$$

$$2OH^- + Zn^{2+} \leftrightarrow ZnO + H_2O \tag{3}$$

Zinc oxide has hexagonal symmetry and the absence of a center of symmetry determines the polar character of the compound along *c*-axis. This polarity of ZnO along *c*-axis determines its growth behavior which results in the formation of rod like structures. Thus, ZnO microrods are formed due to the growth habit of ZnO crystal. However, during citrate assisted hydrothermal processes, strong charge interaction between the Zn^{2+} ions of the ZnO (0001) surface and the bulky citrate ions ($C_6H_5O_7^{3-}$) occurs during ZnO growth. This binding of bulky $C_6H_5O_7^{3-}$ ions to the ZnO (0001) surface efficiently prevents the contact between the growth units and this crystal plane. This phenomenon limits the anisotropic growth of ZnO and leads to formation of ZnO microdisks [18]. This phenomenon is confirmed by synthesizing ZnO microrods with various amount of trisodium citrate and results are presented in Fig. 4. As can be seen from Fig. 4a and b, when 1 ml sodium citrate is added to the growth solution then ZnO microrods with a flat end on both sides are formed. Also, the length of these microrods decreases and width increases after addition of sodium citrate. The length and diameters of these ZnO microrods are 1–2 μm and 1 μm, respectively. It means with addition of citrate, the growth of ZnO along *c*-axis decreases and therefore, pointed end of ZnO microrods disappears. Further increase in citrate amount again reduces the growth along *c*-axis and drum like ZnO microrods are formed as shown in Fig. 4c and d. The length and diameters of these drum like ZnO microrods are almost the same and nearly

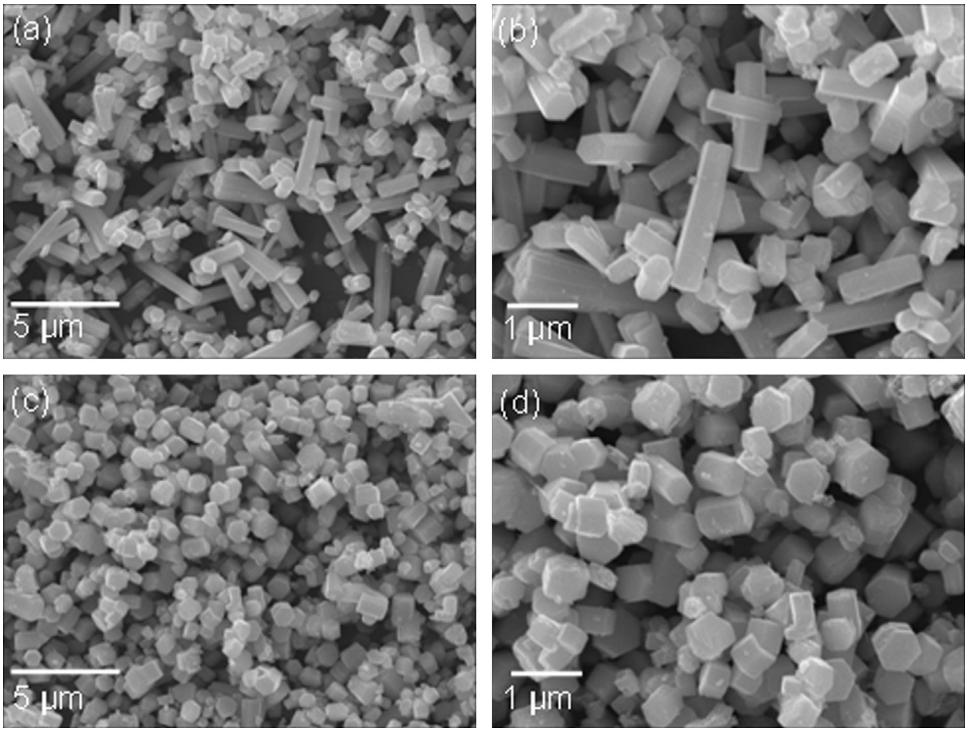

Fig. 4. SEM images of ZnO microrods with different amounts of sodium citrate; (a and b) 1 ml and (c and d) 2 ml.

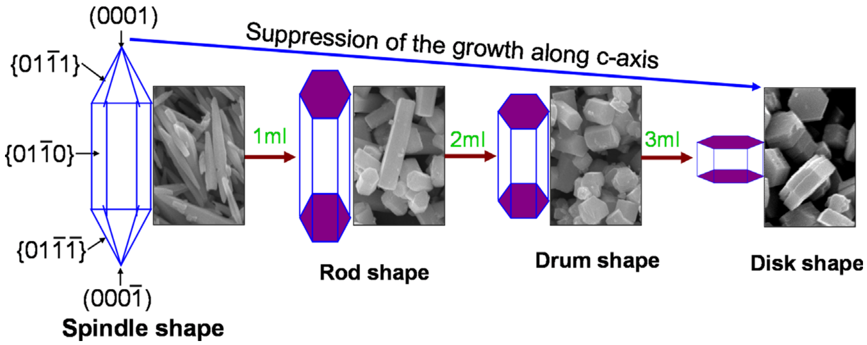

Fig. 5. Schematic presentation of conversion of ZnO microrods to microdisks.

equal to 1 μm. Further increase in citrate amount results in the formation of disk like microstructures. A schematic presentation of the conversion of ZnO microrods into microdisks is also shown in Fig. 5. Thus, the above discussion clearly indicates that the large existence of negatively charged citrate ions decrease the absolute rate of crystal growth along *c*-axis and results in the formation of disk like ZnO microstructures.

4. Conclusions

ZnO microstructures were synthesized by the hydrothermal method. These microrods were converted into microdisks like structure using trisodium citrate as a crystal growth modifier. It was found that citrate suppressed the growth of ZnO microrods along *c*-axis which resulted into the formation of microdisks like structure. PL spectroscopy showed strong UV emission compared to the green emission for microdisks while weak UV emission compared to the green emission for microrods. The presence of the green emission in ZnO microrods suggested that they have structural defect such as oxygen vacancy, whereas microdisks have no or little structural defect. The reduction in the green emission by changing the morphology from microrods to microdisks was due to a reduction in polar planes.

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