



Template-Free Synthesis and Growth Mechanism of Flower-Like ZnO Submicrospheres†

RONGCHUN NIE^{1,*}, CHUYANG XU², YANFEN WANG² and BENXIA LI²

¹School of Chemical Engineering, Anhui University of Science & Technology, Huainan 232001, Anhui Province, P.R. China

²School of Materials Science and Engineering, Anhui University of Science & Technology, Huainan 232001, Anhui Province, P.R. China

*Corresponding author: Fax: +86 554 6668643; Tel: +86 554 6634072; E-mail: rchnie@aust.edu.cn

AJC-9551

Nano-ZnO semiconductor materials have attracted much attention because of their remarkable physical properties and huge potential application on optical devices. Recently, the research and preparation of nano-ZnO with different morphologies have been a hot spot in the material science communities. In the present work, the preparation and performance analysis of novel three-dimensional (3D) flower-like ZnO submicrospheres built up by many uniform nanosheets are reported. At the same time, the growth mechanism of the product is also discussed briefly.

Key Words: ZnO, Three-dimensional flower-like, Submicrospheres, Homogeneous coprecipitation.

INTRODUCTION

Recently, the research and preparation of nanomaterials with odd shape have attracted much interests. Compared with the traditional materials, the nanostructured materials have a wider range of applications in mechanics, magnetism, optics, catalysis and biological activity because of their special performance, such as the light-sized effect, superficial effect, the macroscopic quantum tunnel effect and so on.

Zinc oxide (ZnO), as one of the most important functional semiconductor materials, has very important application in the filed of electronic components, solar battery, sensors and field emission display fields for its wide band gap (3.37 eV) and large excitonic binding energy (60 eV)¹⁻⁴. Due to nano-ZnO with outstanding photocatalytic activity and photosensitivity, it has been expected that have potential applications as the photocatalytic degradation of organic pollutants, purify air, deodorant and antiultraviolet^{5,6}. Therefore, ZnO nanostructured materials with different morphologies have become a focus for researchers in recent years. Up to now, there are a lot of ways to develop nano-ZnO^{7,8} and their morphology are also different⁹, such as nanowires, nanotubes, nanobelts, nanodisks, hierarchical nanostructures and so on. In spite of these successes, it is still a great challenge to fabricate novel-morphology and high-quality ZnO nanomaterials by the developing of a general, convenient, economic method.

Reasoning from the above considerations, herein we report a low-temperature one-step homogeneous coprecipitation

method, without any template or surfactant, to obtain uniformly dispersed and novel 3D flower-like ZnO submicrospheres by many reticular assembled nanosheets with average diameter 500 nm and thickness 15 nm. At the same time, the growth mechanism and optical property are discussed briefly.

EXPERIMENTAL

Nanostructure ZnO were prepared by mixing aqueous solution containing NaOH (0.4000 g) and ZnCl₂ (0.2726 g) (all from Shanghai Chemical Company) dissolved in glass bottle with 30 mL of deionized water. The mixing solution sealed was aged at 100 °C for 24 h and made cool off at room temperature. The resulting precipitate was separated with centrifuge, washed with deionized water, dried at 100 °C for 24 h.

The X-ray diffraction (XRD) were carried out on a Japan Rigaku D/max- λ A X-ray diffractometer equipped with graphite monochromatized high-intensity CuK α source ($\lambda = 1.54178 \text{ \AA}$); the field emission scanning electron microscopy (FESEM) was performed on JEOL JSM-6700F. The UV-vis diffuse reflectance spectra (DRS) were performed on a DUV-3700 DUV-vis-NIR recording spectrophotometer of Shimadzu Corporation.

RESULTS AND DISCUSSION

Fig. 1 shows the XRD pattern of the prepared samples. From the curve, it can be clearly observed that all the diffraction

†Presented to the 4th Korea-China International Conference on Multi-Functional Materials and Application.

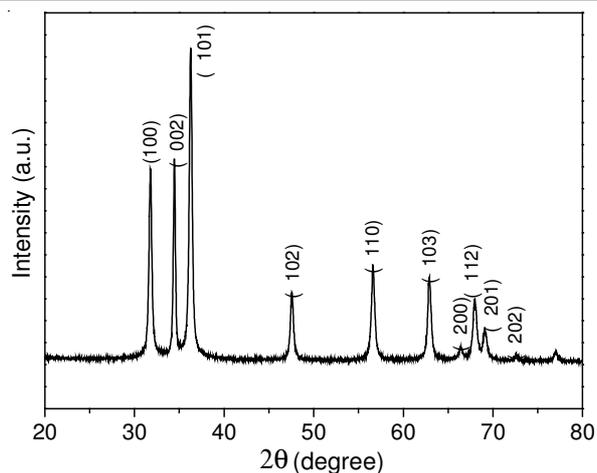


Fig. 1. XRD pattern of the as-obtained nano-ZnO samples

peaks corresponding to ZnO in the literature (JCDPS card, 36-1451) are detected, proving that the ZnO product is the hexagonal wurtzite structure with lattice parameters of $a = 0.3249$ nm and $c = 0.5206$ nm. There is no other impure peaks appeared in figure, indicating the high purity and well crystallinity of the product.

Field emission scanning electron microscopy (FESEM) measurements have also been carried out in order to further investigate the structure and morphology of nano-ZnO samples, as shown in Fig. 2. From the typical panoramic image of Fig. 2(a), it is observed that the products are composed of a large number of ZnO submicrospheres with uniformity in size and well-dispersion. The further observation from the higher magnification of FESEM images in Fig. 2(b-d), reveals that these ZnO submicrospheres uniformity in size are assembled by many net-like compactly arranged nanosheets with average diameter of 500 nm and thickness of 15 nm and these nanosheets interlace with each other to form 3D flower-like nano-ZnO structure with a diameter of *ca.* 1 μm .

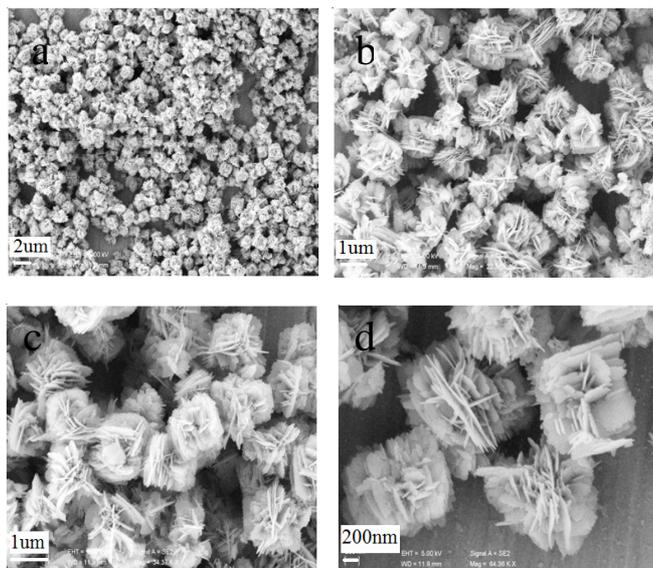


Fig. 2. FESEM images of the as-obtained nano-ZnO samples

Fig.3 shows the light absorption performance of the samples. From the figure, we can see that the flower-like nano-

ZnO exhibits a broad absorption at a wavelength of *ca.* 200-400 nm in the UV region, indicating that the products have a strong absorption in ultraviolet area near the visible light area. This can be attributed to the 3D flower-like ZnO submicrospheres with the wide band gap as well as the high specific area and open, porous surface layers, which is closely related to the activity of photodegradation. Therefore, the product may have important application value as photocatalyst.

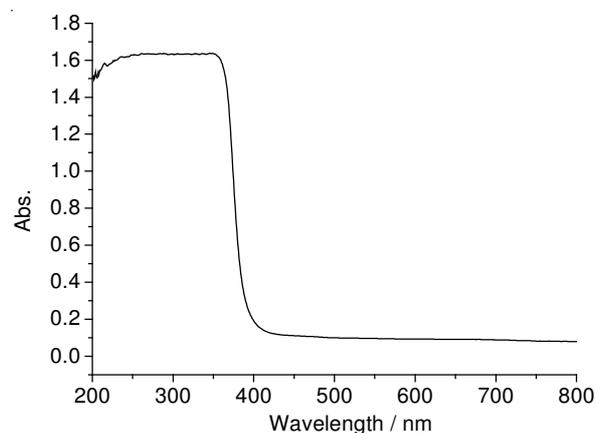


Fig. 3. UV-visible absorption spectra of the as-obtained nano-ZnO samples

In order to understand the possible formation mechanism of 3D flower-like ZnO submicrospheres as well as influences of reactive reagents on the morphology of products, under the condition of other experimental conditions unchanged, one of the reagents are changed to observe the morphology of products.

Fig. 4 is FESEM images of the prepared nano-ZnO samples by Zn piece replaced of ZnCl_2 as zinc source, while the other conditions are kept unchanged. It is found that the products are composed of one-dimensional ZnO nanorod arrays with dense and well-aligned grown on the zinc substrate. The ZnO nanorods densely packed are uniformed with 300 nm diameter and lengths ranging from 3 to 4 μm . In addition, the well-faceted end and side surfaces of the hexagonal ZnO nanorods are also observed clearly.

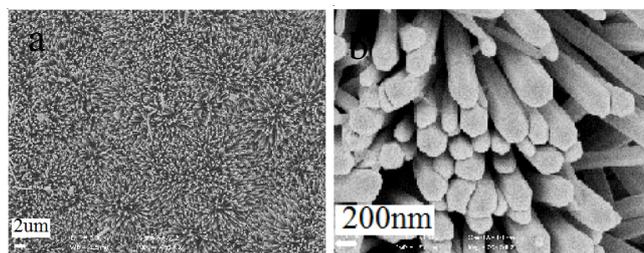


Fig. 4.. FESEM images of the prepared nano-ZnO samples obtained by Zn piece replaced of ZnCl_2 as zinc source at 100 $^\circ\text{C}$ for 24 h

These results have shown that one of the key influencing factors of obtaining 3D flower-like ZnO submicrospheres are the choice of zinc source. Besides, the alkalinity of the reaction system also shows very important influence on the morphology of nano-ZnO products.

In the reaction solution, the morphology and size of the crystal are mainly influenced and controlled by their crystalli-

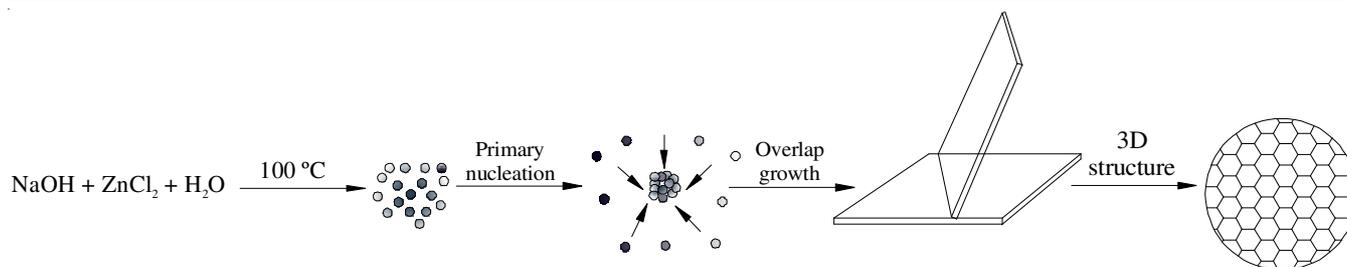
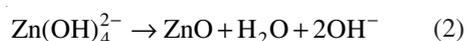
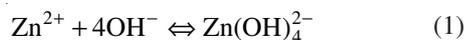


Fig. 5. Formation mechanism of the flower-like ZnO submicrospheres

zation behaviour and the crystal behaviour is usually restricted by the growing environment and conditions. In general, in an appropriate formation environment, the organic additives or surfactants added can lead energy and growth rate of the crystal planes to change by the coordination of the inorganic ions or surface adsorption of nuclei and then change the morphology of the product. However, in present reaction system, without using any templates or additives, the formation of 3D hierarchical structure primarily depends on the relative amount controlled of Zn²⁺ and OH⁻.

Zinc oxide is a kind of polar crystal. Its polar axis is *c*. In the crystal structure of ZnO, Zn²⁺ is surrounded by four O²⁻ and it is the same on the contrary. In the reaction solution of ZnCl₂-NaOH, [OH⁻] / [Zn²⁺] = 5. The concentration of OH⁻ ions in solution was high and zinc was mainly in the form of Zn²⁺ or Zn(OH)₄²⁻ ions present. With the reaction temperature increased, Zn(OH)₄²⁻ was decomposed into ZnO. The overall reaction could be described as shown in the following equations:



Because of the high supersaturation of ZnO in the current solution, the chemical reactant rate was so rapid. So that a large number of ZnO colloidal particles were formed instantaneously. It could be observed from the experiment that had appeared a lot of white flocculent precipitates in the solution. These colloidal particles with large specific area and high surface energy would aggregate together, making into the ZnO primary nucleation. As the reaction proceeded, Zn(OH)₄²⁻ in the solution continued to provide raw materials and ZnO primary nucleation would aggregate into ZnO growth units. At the same time, with the concentration of Zn²⁺ ions reduced, some active sites on the surface of ZnO growth units would grow along the oriented direction, making the growth of the crystal plate (0001) inhibited, while (10 $\bar{1}$ 0) fast growing and

thus hexagonal ZnO nanosheets were created. A lot of nanosheets overlapped each other and generated hierarchical net-like structure, eventually forming the 3D flower-like structure with a large number of nano-sheets (Fig. 5).

Conclusion

3D flower-like ZnO submicrospheres were successfully obtained by a low-temperature homogeneous coprecipitation route, without any template or surfactant. The analysis show products obtained are hexagonal phase wurtzite and have a good crystalline. Besides, it displays a very good responsiveness in UV-vis absorption spectra. Therefore, this work not only provides a facile route to the synthesize nanomaterials with novel morphology, but also the flower-like nano-ZnO with wide specific surface area is expected to have potential application value as photocatalyst.

ACKNOWLEDGEMENTS

This work was supported by outstanding innovative academic team's fund from Anhui University of Science & Technology and Anhui Provincial University Key Science Research Projects (KJ2010A101).

REFERENCES

1. D.M. Li, J.H. Li, X. Fang, X.H. Wang, Z.P. Wei, Y.P. Nie and C.P. Li, *Chin. J. Lumin.*, **31**, 114 (2010).
2. Y.F. Zhu, D.H. Fan and W.Z. Shen, *J. Phys. Chem.*, **112**, 10402 (2008).
3. H.X. Li, J.Y. Wang, H. Liu, C.H. Yang, H.Y. Xu, X. Li and H.M. Cui, *Vacuum*, **77**, 57 (2004).
4. L.J. Luo, G. Lu, B.H. Li, Z.H. Chen and Y.W. Tang, *J. Wuhan Univ. Nat. Sci.*, **15**, 130 (2010).
5. A.H. Yuan, X.B. Bao, L. Tang and H. Zhou, *Chem. Res. Appl.*, **20**, 122 (2008).
6. Y.M. Wang, X.G. Hou, D.H. Wang and S. Wang, *Nonferr. Met. (Extractive Metallurgy)*, **3**, 39 (2002).
7. C.J. Lin, Q. Tian and Y.S. Wang, *Phys. Exp.*, **26**, 12 (2006).
8. H.D. Yu, Z.P. Zhang, M.Y. Han, X.T. Hao and F.R. Zhu, *J. Am. Chem. Soc.*, **127**, 2378 (2005).
9. Z.L. Wang, *Mater. Today*, **7**, 26 (2004).