Facile Hydrothermal Synthesis of Hierarchical ZnO with Lignosulphonate and Its Photo Luminescence Property

Yali Xiao, Mingjie Ding, Chongrui Guo, Xiaoguang Lian, Qi Wang, Yuanru Guo*
a Key Laboratory of Bio-based Material Science & Technology (Ministry of Education), College of Material Science and Engineering, Northeast Forestry University, Harbin 150040, China
xiaoyledu@163.com; dingmingjie72@163.com
*guoyrnefu@163.com; b* panqiitc@163.com

Keywords: ZnO nanocrystal, hydrothermal method, sodium lignosulphonate, Hierarchical nonsostructure

Abstract. series of ZnO nanomaterials were synthesized by assistant of sodium lignosulphonate (SLS) using hydrothermal method. And nanoplates, nanoflowers structures of ZnO have been fabricated successfully. XRD、SEM and PL were applied to characterize the prepared ZnO. XRD analysis indicated that prepared ZnO had preferential growth along the c-axis. The effection of synthesis conditions on ZnO crystal growth were studied by SEM. And the result showed that the concentration of Zn2+ and SLS play an important role on the formation of morphology of ZnO. The results of photolumiscience studies show that hierarchical nanoflowers-like ZnO prepared with SLS has a weaker visible emission. This indicated that the presents of SLS can deduced the defects concentration during ZnO crystal growth.

1. Introduction

ZnO is an important wide band gap(ΔE=3.37eV) semiconductor material, which has been widely used in ceramics, sensors, solar cells , chemical sensors , photocatalysis and optoelectronic devices(Mishra et al. 2015, Nam and Boo 2016). Up to now, nanostructures of ZnO including prismatic, needle-like, ellipsoidal, tetra-pod-like, nanorod, nanofiber, nanobeltsand nanotubes have been prepared by various physical and chemical methods (Kim et al. 2016, Park et al. 2012).

As one of the most abundant natural polymers on the earth, Lignin has attracted a lot of attention (Glasser et al. 2000). As an important bio-resource, lignin is always obtained as a byproduct in bio-refinery operations and a second generation bio-ethanol from lignocelluloses(Jiang et al. 2010). Lignin is regard as cheap and renewable resource and more and more research try to find its practical application. It has been widely used as technical surfactants with dispersing, stabilizing, and adhesive abilities(Bertoniere et al. 1992, Glasser and Sarkane 1989, Mao and Wu 2013). Sodium lignosulphonate is an amorphous aromatic biopolymer, which massively arises as a byproduct of pulping industry. The use of lignin as a precursor in the fabrication of new materials has been widely studied (Pu et al. 2011),(Liu et al. 2007).

In this paper, SLS was used to prepare ZnO nanomaterials. Compared our previous study of preparation ZnO from SLS(Miao et al. 2013), here in this work the hydrothermal method was applied other than precipitation method. And nanoplates, nanoflowers, no-nanoflowers structure has been fabricated successfully.

2. Materials

The Sodium lignosulphonate (industrial purity) (pH = 4.5–6.0, water content≤8.5 %, insoluble matter ≤1.0 %, sugar content≤12.0 %, Ca and Mg content≤1.5 %, and inorganic salt (Na2SO4) ≤5.0 %) was supplied by Qianjin Fuli Limited Company in the Jilin province of China. Zinc acetate [Zn(CH3COO)2·2H2O] (Baker, crystals, 99% purity) and sodium hydroxide (NaOH, flakes, 97% purity) were used as the Zinc source and precipitant, respectively. All the chemicals were used as
received without any further purification.

2.1. Experiment

In a typical process, SLS was put into 30 mL Zn$^{2+}$ solution under ultrasonic oscillating. Then the solution was added by 30 mL 2 molL NaOH and 20 mL ethanol. The mixture was transferred to the teflon-lined stainless autoclave and maintained at 130°C for 14 h. After cooled to room temperature, the obtained products were washed with deionized water for several times and then the as-fabricated products were collected. The obtained ZnO then was calcined at 550°C for 2h (heating rate: 5°C·min$^{-1}$) in the air.

2.2. Results and analysis

2.2.1. XRD

Figure 1 presents XRD results of as-synthesized samples with and without Sodium lignosulphonate. All the diffraction peaks are attributed to the hexagonal wurtzite phase of ZnO (JCPDS card NO. 36-1451). No characteristic peaks of impurity, such as Zn, ZnOH and ZnCO$_3$ were observed. As we see from the XRD patterns, the peak width of ZnO prepared by SLS increased compare to ZnO prepared without SLS. According to the Scherrer formula $L(hkl) = \frac{0.9λ}{Δ(hkl)\cosθ}$, the crystallite sizes of ZnO prepared without and with SLS were 61.8 and 30nm, respectively. This indicated that the present of SLS limited the growth of ZnO crystals and lead to the decrease of ZnO crystallite size. Compare to the ZnO prepared without SLS, the ZnO prepared with SLS show stronger intensity of (002), it implies ZnO has preferential growth along the c-axis when SLS was used.

![Figure 1 XRD spectra of as-synthesized ZnO crystals samples (a) without and (b) with 2 g SLS and the standard hexagonal wurtzite phase of ZnO.](image)

2.2.2. SEM

Figure 2 presents the SEM images of prepared ZnO. From figure 2(a), we can see that ZnO prepared without SLS was shown as irregular plates. The width and length of plates was 0.5 μm and 0.7 μm, respectively. When SLS was used during preparations, the prepared ZnO with certain morphology appeared, as shown in figure 2(b, c and d). We can see in figure 2(b) that ZnO featured as flowers were prepared when 1 g SLS was used. And these ZnO flowers are made by nanoplates with the thickness of 0.09 μm. Increase the addictive amount of SLS to 2 g, fine hierarchical ZnO flowers are obtained with the thickness of 0.02 μm to sub-unit of petal plates. The diameter of these nanoflowers were about 1~2 μm. These hierarchical nanoflowers show better 3D structure by forming nanoplates interfacing with each other, which may result in larger specific surface area and better properties. However, when improved the amount of SLS (3g), nanorods were found in
figure 2(d). All the results give the evidence that SLS play an important role on formation the certain morphology of ZnO. By controlling the amounts of SLS, we can get the certain ZnO morphology.

![Figure 2 SEM of ZnO which the weight of SLS was (a)0g; (b)1g; (c)2g and (d)3g prepared by the 0.4mol·L of Zn²⁺.](image)

In order to study the effects of concentration of Zn²⁺ on preparation of ZnO, The experiments using different concentration of Zn²⁺ were carried out and their morphology are shown in figure 3. ZnO nanocrystals fabricated by 0.2 mol·L Zn²⁺ presents morphology of well dispersed nanoplates, as we can see in figure 3(a). Improving the concentration of Zn²⁺ in precursor solution, ZnO with morphology of hierarchical nanoflowers appeared. We can see these nanoflowers clearly in figure 3(b-c). The diameter of these nanoflowers were about 1~2 μm. To the ZnO prepared by 0.4 mol·L Zn²⁺, hierarchical nanoflowers show better 3D structure by more nanoplates interfacing with each other, which may result in larger specific surface area and better properties. Further increase the concentration of Zn²⁺, hierarchical nanoflowers seem to collapse, as seen in figure 3d.
2.2.3 BET

Specific surface areas of the ZnO were determined by BET method as shown in figure 4. One can see that the BET specific surface areas of ZnO are strongly affected by the added amount of SLS used in the preparation. If SLS is not added, then obtained ZnO has specific surface area as low as 14.6 m²·g⁻¹. In contrast, upon adding SLS, the specific surface area of ZnO will increase to more than 25 m²·g⁻¹. On the condition of 2g SLS, the hierarchical ZnO flowers has the largest specific surface area of 42.6 m²·g⁻¹.

![Figure 4 specific surface area of ZnO prepared with amount of SLS](image)

2.2.4 The Photoluminescence Properties

The photoluminescence (PL) properties of our ZnO were studied in figure 5. From the figure 5, we can see that all ZnO has two emission peaks. To the ZnO prepared without SLS, it shows an UV band emission at 385 nm and a strong and broad emission covered almost visible band from 400-650 nm. While to the ZnO prepared with 2g SLS, we can see a less strong emission of UV band centered at 385 nm with a weak and broad visible band emission. It is reported that visible band emission of ZnO is caused by defects of ZnO, such as Oxygen vacancies and Zn interstitials, which were formed during the formation of ZnO crystals. The visible emission became weak after adding
the SLS indicated that SLS has deduced defects concentration of ZnO.

Figure 5  Room-temperature photoluminescence emission spectra of ZnO prepared a) without SLS, b) with 2g SLS

3. Conclusion

ZnO nanocrystals were synthesized by hydrothermal method with SLS. Changing the concentration of Zn\(^{2+}\) in precursor solution, we fabricated ZnO with morphology of nanoplates and nanoflowers with SLS. The amount of SLS also plays an important role on the formation of ZnO. The SLS can limit the growth of ZnO crystals and decreased the crystallite size. By using 2 g SLS, hierarchical nanoflowers-like ZnO with high specific surface area was obtained. Meanwhile, PL spectra showed that the present of SLS during the preparation can deduce the defect concentration of ZnO.

Acknowledgements

This work was supported by the National Undergraduates Training Programs of Innovation (Northeast Forestry University) (201710225055).

References


