Microchemical Journal 100 (2012) 61–65

Contents lists available at SciVerse ScienceDirect

Microchemical Journal

journal homepage: www.elsevier.com/locate/microc

Size-controllable synthesis of spherical ZnO nanoparticles: Size- and concentration-dependent resonant light scattering

Jun Ye [a], Ronghui Zhou [a], Chengbin Zheng [a], Qun Sun [b], Yi Lv [a], Chongying Li [c,*], Xiandeng Hou [a,*]

[a] College of Chemistry, Sichuan University, Chengdu, Sichuan 610064, China
[b] College of Life Sciences, Sichuan University, Chengdu, Sichuan 610064, China
[c] College of Materials and Chemistry & Chemical Engineering, Chengdu University of Technology, Chengdu, Sichuan 610059, China

ARTICLE INFO

Article history:
Received 25 August 2011
Accepted 3 September 2011
Available online 10 September 2011

Keywords:
Resonant light scattering
ZnO nanoparticles
Temperature-tunable size

ABSTRACT

A new and simple direct precipitation method assisted with ultrasonic agitation was proposed for the preparation of spherical ZnO nanoparticles. The size of the ZnO nanoparticles, 10 nm to 85 nm, was tuned through controlling the calcination temperature and changing the ratio of the reactants. The resonant light scattering (RLS) of the ZnO nanoparticles dispersed/suspended in aqueous solution of Triton X-100 was studied under room temperature. It was found that the ZnO nanoparticles of different size or concentration all have a characteristic RLS peak at 387 nm. Under optimal conditions, the RLS intensity was proportional to the ZnO concentration in the range of 7.3×10^{-8}–1×10^{-4} mol L^{-1}, while the cubic root of the RLS intensity was found to be proportional to the size of ZnO nanoparticles. Further, the quantitative relationship of the size of the ZnO nanoparticles *versus* the calcination temperature was derived, and this could be used to forecast/control the nano-size in the nano-ZnO preparation.

1. Introduction

Nanophase and nanostructured materials are attractive to researchers in varied areas because of their wide potential applications in areas such as electronics [1], optics [2], catalysis [3], ceramics [4], magnetic data storage [5] and nanocomposites [6]. In contrast to their good behaviors, many unpredictable problems and challenges impacted on the environment will certainly appear with large-scale applications of nanomaterials [7]. The unique properties, toxicity, and transportation in the environment of nanomaterials are largely determined by their size, surface structure and concentration. Hence, it is important to quick monitor the size and concentration of nanomaterials in the environment, for example, environmental waters.

In the past, the sizes of nanomaterials were usually characterized by transmission electron microscopy (TEM) [8], atomic force microscopy (AFM) [9], and X-ray diffraction (XRD) [10]. However, these are very expensive in-laboratory techniques, and not every organization can afford them. Therefore, it is of importance to establish a simple and cost-effective method to monitor the size and concentration of nanoparticles. Resonant light scattering (RLS) has many unique merits such as high sensitivity, selectivity, simplicity and quickness. This technique has been applied to the analysis of biomacromolecules [11–18], nanomaterials [19–21], organic compounds [22–24], and trace metals [25]. Because the size of nanoparticles is very close to that of most biomacromolecules, it is feasible to use RLS to monitor the size and concentration of nanoparticles. In this work, therefore, a simple, quick, and inexpensive method based on RLS was proposed to monitor the size and concentration of solid-state ZnO nanoparticles dispersed in aqueous solution.

Nano-ZnO was chosen for the study in this work, because it has special properties such as high chemical activity, and novel optical, mechanical, electromagnetic, thermodynamic and electrodynamic properties, and exhibits a wide spectrum of applications including gaseous sensors [26], fluorescent materials [27], photocatalysts [28] and additives in many industrial products [29]. Various strategies such as chemical vapor deposition [30,31], electrochemical deposition [32–34], hydrothermal solution synthesis [35–37] and sol–gel processing [38] have been developed for the synthesis of ZnO nanomaterials. As one of the most effective synthesis methods, emulsion or ultrasonic routine has been wildly used for the preparation of ZnO nanomaterials. However, there are some limitations in conventional emulsion or ultrasonic approaches. In this study, emulsion coupled with ultrasonic technique [39] was used to synthesize ZnO nanoparticles. It was found that expected size nanoparticles can be obtained through monitoring the calcination temperature or the ratio of the reactants.

2. Experimental

2.1. Instrumentation and reagents

The RLS spectra were obtained with a model F-4500 spectrofluorimeter (Hitachi, Japan). Nanoparticle X-ray diffraction (XRD) patterns were

* Corresponding authors.
E-mail addresses: lichy@cdut.edu.cn (C. Li), houxiandeng@yahoo.com.cn (X. Hou).

0026-265X/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.microc.2011.09.002

obtained with a model Ricoh D/max-rA X-ray diffractometer (Ricoh, Japan). TEM photographs were taken with a model JEM-100CX microscope (NEC, Japan). An ultrasonic disintegrator was used for agitation.

$ZnSO_4 \cdot 7H_2O$ (AR, Shengyang Chemical Reagent Factory, Shengyang, China), absolute ethanol (AR, Shanghai Chemical Reagent Research Institute, Shanghai, China), NH_4HCO_3 (AR, Shantou Xilong Chemical Co. Ltd, Shantou, China) and Triton X-100 ($C_{34}H_{62}O_{11}$, CP, Shantou Xilong Chemical Co. Ltd, Shantou, China) were used to prepare ZnO nanoparticles.

2.2. Preparation procedure

Solution A was prepared by adding appropriate amount of $ZnSO_4 \cdot 7H_2O$ and 0.2% (v/v) Triton X-100 into doubly distilled water (DDW), while solution B was prepared by dissolving appropriate amount of NH_4HCO_3 and 0.2% (v/V) Triton X-100 into DDW. Solution A (2 L) was added dropwise into solution B (2 L) under vigorous stir. During the addition, the reaction mixture turned white and the viscosity increased. After stirring for 5 h, the reaction mixture was allowed to leave still overnight. Then, the precipitate was separated from the reaction mixture (the supernatant was discarded), and taken into a beaker to ultrasonicate for 1 h. Then, the precipitate was filtered and washed with DDW in order to remove the residual SO_4^{2-}; the resultant precipitate was vacuum dried at 90 °C for 2 h to obtain the precursor of small crystallite proved to be $ZnCO_3 \cdot 2Zn(OH)_2 \cdot H_2O$ by TG-DTA. Finally, the precursor was calcined for 2 h at different temperature in the range of 300–800 °C to obtain different size of ZnO nanoparticles. The main chemical reactions occurred in the preparation process are supposed as follows:

$$3Zn^{2+} + CO_3^{2-} + 4OH^- + H_2O \rightarrow ZnCO_3 \cdot 2Zn(OH)_2 \cdot H_2O\downarrow$$

$$ZnCO_3 \cdot 2Zn(OH)_2 \cdot H_2O \rightarrow 3ZnO + 3H_2O + CO_2\uparrow.$$

Different sizes of ZnO nanoparticles can also be obtained through altering the molar ratio of the reactants.

2.3. Analytical procedure

100 ml absolute ethanol, 10 ml 2×10^{-4} (v/v) Triton X-100 solution and appropriate mass of ZnO nanoparticles were successively added into a 250 ml beaker. After ultrasonicating for 20 min at room temperature, the mixture was measured with the spectrofluorimeter. All RLS spectra were obtained with the excitation and emission synchronously throughout the wavelength range of 200–900 nm. The RLS intensities were measured at $\lambda = 387$ nm in a 1.00 cm fluorescence quartz cell with a slit width of 2.5 nm. The RLS intensities of the nano-ZnO were represented as $\Delta I_{RLS} = I_{RLS} - I^0_{RLS}$, and here I_{RLS} and I^0_{RLS} were the intensities of the systems with and without ZnO nanoparticles, respectively. This simply means that the RLS intensities were blank corrected.

3. Results and discussion

3.1. Characterization of ZnO nanoparticles

Fig. 1(a) and (b) is resulted from ZnO nanoparticles produced by calcining the precursor at 300 °C and 800 °C, respectively. The XRD patterns show that both have the same XRD characteristic peaks, so both have the same crystal type. The diffraction peaks can be indexed to the hexagonal phase (PDF 5–664). Meanwhile, no diffraction peaks from other species could be detected, and this indicates that the nano-ZnO is very pure. According to Scherrer's law [40], the ZnO in Fig. 1(a) has a smaller size than that in Fig. 1(b). This implies that

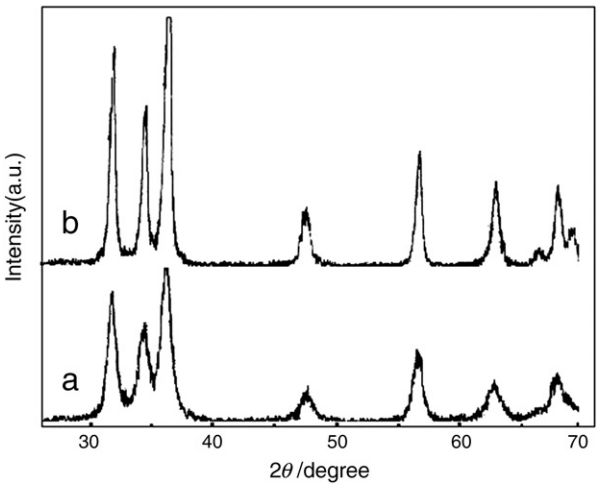

Fig. 1. XRD patterns of ZnO nanoparticles calcined at (a) 300 °C and (b) 800 °C, respectively.

ZnO nanoparticles with the same crystal type but different particle sizes can be obtained through altering the calcination temperature.

Fig. 2 further shows TEM photographs of ZnO nanoparticles prepared under different calcination temperature. The TEM photographs show that the ZnO nanoparticles are even and well dispersed. Further, it can be concluded from Table 1 that the increase in the amount of reactant NH_4HCO_3 and the calcination temperature generally led to the increase of the nanoparticles size.

3.2. RLS spectra of ZnO nanoparticles

The RLS spectra of ZnO nanoparticles in different concentrations are shown in Fig. 3. It can be seen that the RLS intensities of H_2O/Triton X-100 interface in absence of ZnO nanoparticle are very weak over the whole scanning region (the bottom trace). When nano-ZnO is present in the aqueous medium, however, a greatly enhanced RLS band appears with a maximum scattering peak at 387 nm, which is dependent of the concentration or the size of the nanoparticles. So, 387 nm was chosen as the RLS characteristic peak of ZnO nanoparticles for later use in this work.

3.3. Optimization of general analytical procedure

The optimal surfactant concentration is obtained when the surfactant adsorbed on the ZnO nanoparticle surface reaches saturation. Meanwhile, because Triton X-100 is a hydrophobic substance, Triton X-100 tiny particles will form when its concentration is higher than its saturation absorption. Triton X-100 tiny particles can also lead to RLS, thus interfering with ZnO nanoparticles' RLS. The optimal concentration of Triton X-100 was obtained by varying Triton X-100 concentration from 0 to 5×10^{-4} (v/v). The result indicated that when the concentration of Triton X-100 was less than 2×10^{-5}, the RLS intensities of the systems increased with increasing Triton X-100 concentration and decreased thereafter. Furthermore, when the concentration of Triton X-100 was more than 4×10^{-4}, many unidentified RLS peaks appear in RLS spectra. Therefore, 2×10^{-5} (v/v) Triton X-100 was selected for use in this work. Under the optimal conditions, the RLS intensity of the ZnO nanoparticles was found to be stable in 5 min.

3.4. Nano-ZnO concentration-dependent RLS intensity

The RLS belongs to synchronous luminescence, with its particularities of $\Delta\lambda = 0$ nm and no electronic excitation after absorption [41]. Previous studies show that the intensity of RLS is theoretically proportional