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Low temperature synthesis of fluorescent ZnO nanoparticles

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ABSTRACT

Fluorescent ZnO nanoparticles have been prepared by mixing aqueous solutions of zinc nitrate and ammonium carbonate in the presence of a non-ionic surfactant, Tween-80. Increased concentrations of the surfactant were found to affect both the morphology and purity of the synthesized ZnO nanoparticles. XRD, SEM, FTIR, TGA and Confocal laser scanning microscopy were employed to characterize the as-prepared samples. ZnO nanoparticles ranging in particle size from 11 to 15 nm were formed at the reaction temperature of 70–80 °C. The results of FTIR and TGA analysis indicate the self assembly of Tween molecules on the surface of ZnO nanoparticles. A bright emission in the visible region from the as-prepared ZnO nanoparticles was recorded using confocal laser scanning microscopy. This property of the as-prepared nanoparticles may find potential application in bio-imaging.

1. Introduction

ZnO nanostructures have been the subject of considerable research interest in the scientific community because of their unique optical, electronic and piezoelectric properties. They find potential applications in solar cells [1], biosensors [2], catalysts for photo-catalytic degradation [3] and composite materials [4–5].

Recently, there are increasing reports on the use of ZnO nanostructures for biomedical and bio-imaging applications instead of conventional organic dyes due to their low toxicity, superior emission characteristics and high photo stability [6–8]. ZnO eliminates the need for fluorescent labeling and provides an opportunity to detect real time binding events through UV or visible peak emission [9]. The use of ZnO nanoparticles greatly enhances the fluorescence signal collected from the biological samples once ZnO is incorporated into the bio system. However for biomolecular complexing, the surfaces of ZnO nanostructures must be chemically functionalized for subsequent biochemical conjugation. Various methods for surface modification of the polar ZnO surfaces have been developed, such as post modification of particles through adsorption of certain polymers [10–12], coverage of ZnO surface with silanes [13] and surface modification with low molecular weight surfactants [14–16]. Surfactants are added not only to control the shape and prevent the growth of particle size, but their presence on the surface of ZnO can be used to tailor the photoemission properties of ZnO nanoparticles. Polyoxyethylene sorbitan monooleate, commercially known as Tween-80, is a popular non-ionic surfactant used widely in cosmetics, foods, pharmaceutical products, and in biochemical research. Its use for the synthesis of metallic nanoparticles of silver [17–18], nickel [19], copper [20] and gold [21] has already been established.

In this work, we report a facile, low temperature method for the synthesis of spherical ZnO nanoparticles in the presence of Tween-80. Fourier transform infra-red (FTIR) spectroscopy and thermo gravimetric analysis (TGA) revealed the self assembly of Tween molecules on the surface of ZnO nanoparticles. Scanning electron microscopy (SEM) has been used to monitor the effect of temperature and Tween concentration on the morphology of the as-prepared ZnO nanoparticles. Confocal fluorescence microscopy confirms the fluorescent nature of the as-prepared nanoparticles.

2. Experimental

2.1. Materials

Zinc nitrate hexahydrate ($ZnNO_3.6H_2O$), ammonium carbonate ($(NH_4)_2CO_3$), Tween-80, and sodium hydroxide were used as starting materials. Doubly distilled water and absolute ethanol were used throughout the experiments. All chemicals used were analytical grade.

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2.2. Synthesis of ZnO nanoparticles

Zinc nitrate hexahydrate ($ZnNO_3.6H_2O$) and ammonium carbonate [$(NH_4)_2CO_3$] were dissolved in doubly distilled water to prepare 0.25 M solutions respectively. In a typical synthesis, 2 ml Tween-80 was added to the 50 ml of $ZnNO_3.6H_2O$ solution with vigorous stirring on a hot plate. The stirring was then continued for 30 min at the same temperature followed by drop by drop addition of 50 ml of $(NH_4)_2\ CO_3$. After the mixture stirred for 30 min at 50 °C, the pH of solution was adjusted to 10 by the addition of 1 M NaOH aqueous solution. The mixture was vigorously stirred for another 1 h at a temperature of 60, 70 or 80 °C separately. The precipitated powders were thoroughly washed with distilled water and absolute ethanol and collected by centrifugation. Same procedure was adopted for the synthesis of ZnO nanoparticles without Tween-80. Finally all the samples were dried in vacuum at 60 °C for 24 h.

2.3. Characterization

X-ray powder diffraction analysis of the samples was performed on a Rigaku diffractometer using Cu $K\alpha_1$ radiation ($\lambda = 1.5406$ Å). FTIR (NICOLET, 6700) transmittance spectra of the powders were recorded in the range of 400–4000 cm^{-1} using KBr pellet method. For thermal gravimetric analysis (TG-DSC-Q 600), samples were heated in a flow of nitrogen at a constant rate of 10° per min to 700 °C. Particle morphology of the samples was characterized by Scanning Electron Microscopy (JSM-5910, JEOL). Confocal fluorescence imaging of the samples were performed on a commercially available confocal laser scanning microscope (LSM 510, Carl Zeiss).

3. Results and discussion

3.1. XRD patterns

Fig. 1(a)-(c) shows the XRD patterns of ZnO samples prepared at different reaction temperatures in the presence of 2 ml Tween-80. XRD patterns of ZnO samples prepared without Tween-80 are also shown for comparison. XRD pattern of the product obtained at 60 °C in the presence of Tween-80 shows the formation of Zn $(OH)_2$ without any peaks from the ZnO. The pattern shown in Fig. 1(a) can be indexed to the pure Zn $(OH)_2$ by the peak positions in the XRD spectrum (JCPDS No.89-0138). When the reaction temperature was raised to 70 °C, crystalline peaks of hexagonal wurtzite ZnO appeared along with a small peak at 33.2° from Zn $(OH)_2$. Pure hexagonal wurtzite ZnO in the presence of Tween-80 was formed at reaction temperature of 80°C as can be seen in Fig. 1(c). All XRD peaks from phase pure ZnO were indexed to the hexagonal wurtzite phase of ZnO (JCPDS No. 36-1451). The average particle size calculated from the first three peaks using scherrer formula were found to be 11 and 15 nm for the samples prepared in the presence of 2 ml Tween-80 at 70 and 80 °C respectively. In the XRD pattern of the sample prepared at 60 °C without Tween-80 (Fig. 1d), peaks from ZnO can be seen along with peaks from Zn $(OH)_2$. At higher reaction temperatures, pure ZnO was formed. The average particle size calculated for ZnO obtained at 70 and 80 °C without adding Tween-80 to the reaction mixture was found to be 24 and 37 nm respectively. The bigger particle size for the sample prepared without Tween-80 indicates fast growth of the particles in the absence of surfactant. It may also be noticed that the presence of Tween-80 tends to retard the formation of ZnO at 60 and 70 °C. However at increased reaction temperature of 80 °C, pure ZnO is formed, as shown by XRD pattern in Fig. 1c.

Since phase pure ZnO was obtained at synthesis temperature of 80 °C, further experiments were carried out in which the amount of Tween-80 was varied and the synthesis temperature was maintained at 80 °C. The XRD patterns of the products obtained using different concentrations of Tween are shown in Fig. 2. It can be seen in Fig. 2(a-c) that pure ZnO is obtained at reaction temperature of 80 °C using up to 4 ml of Tween. The peaks labeled with star in Fig. 2(d-e) were recognized as those of $(ZnOH)_2$ which again suggests that for increased concentration of Tween-80, the conversion of $(ZnOH)_2$ to ZnO is incomplete. This inhibitory action of Tween-80 on the formation of ZnO may be due to the steric hindrance arising from the soluble Tween molecules which reduces the reaction rate and hence the conversion of $Zn(OH)_2$ to ZnO is incomplete.

3.2. Particle morphology

Fig. 3 shows typical SEM micrographs of ZnO nanoparticles synthesized at 70 and 80 °C. SEM images show that the morphology of ZnO nanoparticles is greatly influenced by the addition of Tween-80, which adsorb onto to the surface of ZnO, thereby slowing down the growth of crystal facets by reducing the surface free energy. ZnO nanoparticles prepared in the absence of Tween-80 (Fig. 3a and b) have elliptical structures with a wide size distribution from 200–400 nm. It is found that ZnO nanoparticles prepared in the

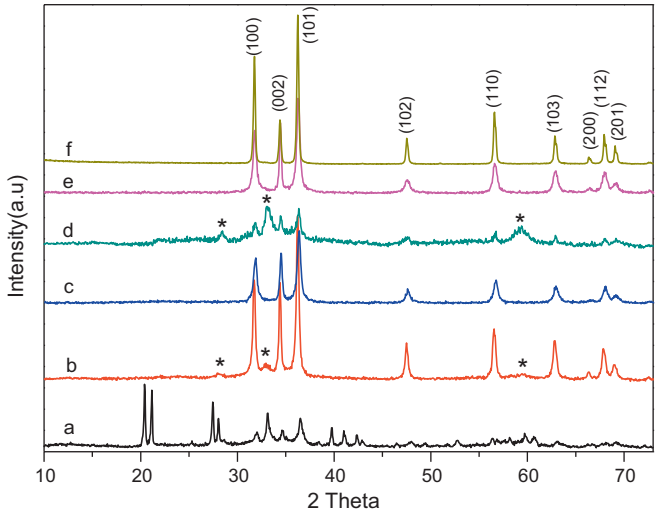

Fig. 1. XRD patterns of ZnO synthesized with 2 ml Tween-80 at (a) 60 (b) 70 and (c) 80°C. ZnO samples prepared in the absence of Tween-80 at (d) 60 (e) 70 and (f) 80°C. Peaks from Zn $(OH)_2$ are labeled with a star.

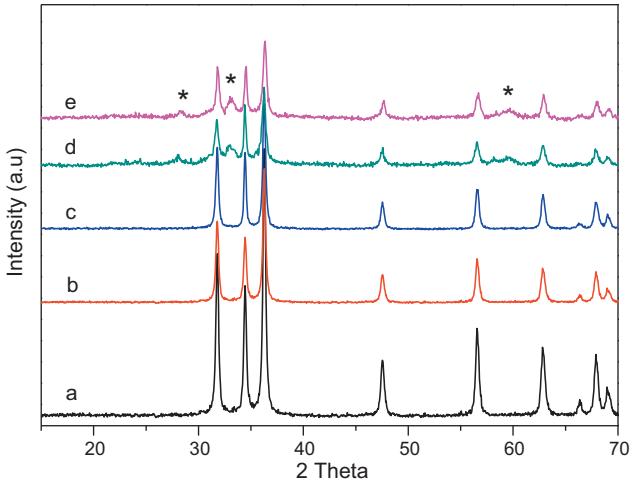

Fig. 2. XRD patterns of ZnO prepared at 80°C using (a) 1 (b) 3 (c) 4 (d) 5 and (e) 6 ml Tween-80.