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Correlation of morphology and luminescent properties of ZnO nano particles to different surfactants via hydrothermal method

ABSTRACT

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Nanocrystalline Zinc Oxide (ZnO) powders with different morphology have been successfully synthesized by using different surfactants such as Cetyl Trimethyl Ammonium Bromide (CTAB), Sodium Dodecyl Sulphate (SDS), and Tri Ethanol Amine (TEA) via hydrothermal method. The products were characterized by means of powder X-ray diffraction (XRD), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), UV-visible absorption and Photoluminescence (PL) spectroscopy. The sheets, rods, and spherical morphologies of the prepared SDS, CTAB, and TEA mediated ZnO were observed in the SEM micrographs..

Keywords: Zinc Oxide (ZnO); Surfactant; Photoluminescence; Hydrothermal method; Transmission Electron Microscopy (TEM).

INTRODUCTION

At present the growth, processing, and characterization of nanorods and nanoparticles is of global interest. There is an intensive research for controlling and manipulating nanostructured materials. This is of interest for both fundamental understanding as well as for potential technological and medical applications. Nanostructured ZnO materials have received broad attention due to their distinguished performance in electronics, optics and photonics. From the 1960s, synthesis of ZnO thin films has been an active field because of their applications as sensors, transducers and catalysts. In the last few decades, the shape control of semiconductor nanostructures has attracted considerable attention for potential applications due to their physical and chemical properties which are determined by morphology, size and dimensions [1–3]. Thus, the shape control of semiconductor nanostructures has been the topic of intensive investigation in recent materials chemistry.

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ZnO is one of the most important multifunctional semiconductors with its wide direct energy band gap of 3.37 eV and its large exciton binding energy (about 60 meV). As a result, various ZnO nanostructures, including nanowires, [4–9] nanorods, [10–15] nanobelts, [16–19], and nanodisks, [20] have been reported for potential applications [21–24].

With reduction in size, novel electrical, mechanical, chemical and optical properties are introduced, which are largely believed to be the result of surface and quantum confinement effects. ZnO nanostructures have been fabricated by various methods, such as thermal evaporation, [16] metal– organic vapor phase epitaxy, [13] laser ablation, [25] hydrothermal synthesis, [26] and template-based synthesis [27].

Among the above methods to prepare ZnO, hydrothermal synthesis route, as an important method for wet chemistry, has been attracting material chemists' attention. The hydrothermal processing is an alternative to calcination for the crystallization of ZnO under mild temperature. However, it was still difficult to control the size of nanoparticles. Recently, it has been noted that anionic, cationic and nonionic surfactants can be used to assist the formation of nanoscaled materials.

The addition of organic surfactants or structure directing agents (SDA) in the growth solution is extremely important due to their influence on morphological and structural properties of the materials [1]. They are commonly used to control the crystal shape and size, in order to synthesize high quality materials [28]. The major role of the SDA is to modify the morphology of the materials by virtue of site selective adsorption on the specific site of the materials during the growth process [29-33]. Various organic surfactants have been successfully used by many researchers for enabling directional growth of the nanomaterials ZnO more desirable. In the present work, we have grown vivid ZnO nanostructures from aqueous solution using various surfactants.

The main purpose of the present research is to study the influence of the surfactants on the morphology, size and hence, photoluminescence properties of the synthesized nano particles were investigated. The quality of the resulting compounds has been characterized by scanning electron microscopy (SEM), energy dispersive X-

rays (EDX), X-ray diffraction (XRD), UV-Visible and photoluminescence (PL) spectroscopy.

EXPERIMENTAL

In a typical synthesis, 0.0005 mol ZnCl₂ and 0.001 mol KOH were dissolved in 2ml of distilled water, respectively. Then a white calcic floccule immediately appeared as soon as they were mixed. After 5 min stirring, 0.00025 mol CTAB was introduced under stirring at room temperature. The PH was mentioned at about 8-9 during the reaction. The system was transferred into a Teflon-lined stainless steel autoclave of 15 ml and filled by 11ml distilled water. Hydrothermal treatments were carried out at 120 °C for 5 h. After that, the autoclave was allowed to cool down naturally. White precipitates were collected and washed with distilled water and ethanol several times to remove impurities. Finally, the precipitates were dried at 50 °C for 5 h in oven. The same procedure was followed for the preparation of ZnO using SDS and TEA surfactants.

The XRD pattern of the ZnO powder was recorded by using a powder X-ray diffractometer (Philips w1800) using CuKα ($\lambda=0.154$ nm) radiation at a scanning rate of 0.04° s⁻¹, with a diffraction angle between 4 and 90°. The crystallite size was determined from the broadenings of corresponding X-ray spectral peaks by using Debye Scherrer's formula. Scanning Electron Microscopy (SEM) studies were carried out on Philips XL30. UV-Vis absorption spectra for the samples recorded using a Varian Cary 100 spectrophotometer in the range of 200-800 nm for the powder samples. The photoluminescence (PL) spectra of the ZnO were recorded by Perkin-Elmer lambda 900 spectrophotometer with a Xe lamp as the excitation light source.

RESULTS AND DISCUSSION

XRD analysis

The XRD pattern of the as-obtained zinc oxide nanoparticles is shown in Fig.1. All of the peaks in Figure 1a (TEA), 1b (SDS) and 1c (CTAB) can be well indexed to the hexagonal structure of ZnO (zincite 36-1451) with high

crystallinity. No characteristic peaks of impurities, such as SDS, CTAB and TEA or other Zinc oxides were observed, indicating the high purity of the products. In Figure 1a (TEA), it is noted that the peak intensity of the samples was notably higher and broader than that of the intensities in Figure 1c (CTAB) and 1b (SDS) due to larger particle size. Using Debye Scherrer's formula, the crystallite sizes of ZnO nanoparticles can be determined. The average particle size and morphology of as-synthesized zinc oxide nanoparticles are tabulated in Table 1.

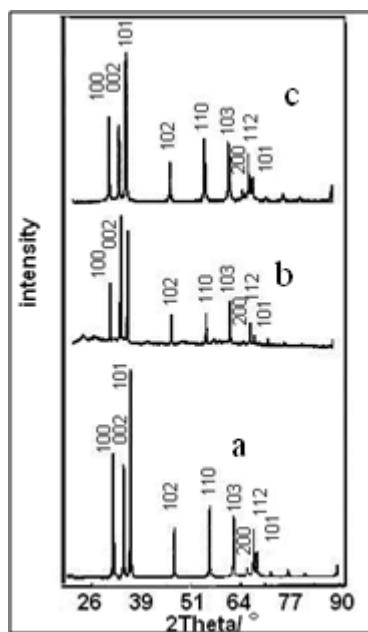


Fig. 1. XRD patterns of Zinc oxide nanoparticles (a) TEA, (b) SDS, and (c) CTAB

Table 1. The size and morphology of different surfactants assisted zinc oxide nanoparticles.

Zinc oxide samples	FWHM _i	Particle size (D) nm	Morphology
SDS	0.2018	23	sheet
CTAB	0.2362	38	Rod
TEA	0.2755	68	spherical

SEM analysis

The surface morphology of the samples obtained using SDS, CTAB and TEA as examined

by SEM is shown in the Figure 2(a-c). The SEM micrographs clearly show remarkably different morphologies for ZnO prepared by different surfactants. Spherical morphology was observed for the sample (a) (TEA) whereas the shape of the agglomerated particles of the sample (b) (SDS) looked like the sheets or narrow plates. In an aqueous system, CTAB ionize completely and result in cation with tetrahedral structure. The electrostatic interaction takes place between CTA⁺ cations and Zn(OH)₆²⁻ anions, the cation CTA⁺ condense into aggregates in which counter ions Zn(OH)₆²⁻ are interrelated in the interfaces between the head group to form CTA⁺-Zn(OH)₆²⁻ pair. The rod-like morphology was observed for sample (c) (CTAB). TEA being a non-ionic surfactant ZnO formation was not possible due to the electrostatic interaction and was due to weak Vander wall's interaction [13]. The lower particle size and different morphology reveals the key role of individual surfactants in controlling the nucleation and crystal orientation.

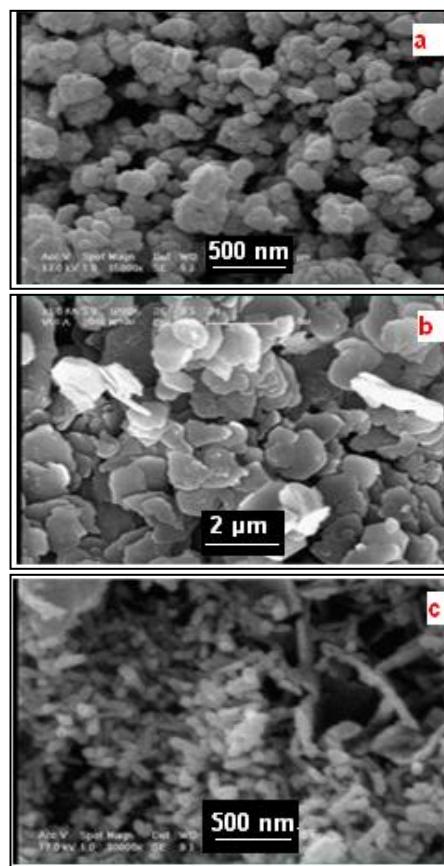


Fig. 2. SEM images of ZnO nanoparticles (a) TEA, (b) SDS, and (c) CTAB.

UV-Visible studies

Figure 3 represents the μ UV absorption spectra of ZnO nanoparticles, and absorbance edges were observed at 360, 363, and 361 nm for different surfactants mediated like CTAB, SDS and TEA respectively (Figure 3a-c) that compare with bulk ZnO (400 nm). In all the cases, red shifts in wavelength were observed. The corresponding band gap energies can be calculated to be 3.44 eV, 3.41 eV and 3.43 eV and are larger than the bulk ZnO (3.37) according to quantum effect for nanoparticle.

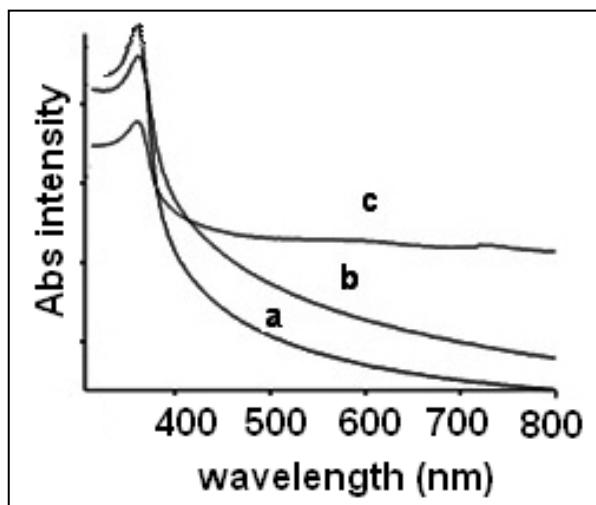


Fig. 3. Absorption spectra of ZnO nanoparticles (a) CTAB, (b) SDS, and (c) TEA.

Optical studies by photoluminescence spectroscopy (PL)

Figure 4 shows the room temperature PL spectra of the ZnO nanoparticles prepared from different surfactants, with an excitation wavelength of 325 nm. It is clear from the figure that the spectrum consists of a widened shoulder peak from \sim 350 to 600 nm and a sharp one centered at around 630 nm. Particularly, CTAB mediated ZnO nanoparticles (Figure 4a) exhibited strong high intensity UV emission than that of the SDS (Figure 4b) and TEA (Figure 4c) assisted samples. Usually, the UV emission is attributed to the near band edge emission of the wide band gap of ZnO due to the annihilation of excitons [22, 23]. Generally, the dominance of the UV emission at around 350 nm in PL spectra has been rarely observed for ZnO nanocrystals, except when their surface has been passivated by organic molecules

or when the particles from alcoholic solutions have been UV-irradiated in airless conditions. In our work, it is probable that ZnO surface in our samples was partially passivated by surfactants.

From the above experiments, one can easily find that the morphologies and absorption properties of the products can be influenced when the surfactant varied, while the PL spectra not change generally in range. In a word, the above results demonstrate that as-prepared ZnO nanoparticles are bioluminescent nanomaterials.

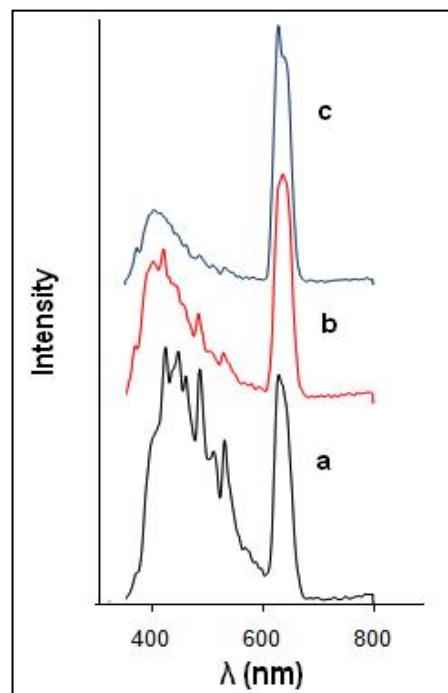


Fig. 4. Photoluminescence spectra of zincoxide nanoparticles (a) CTAB, (b) SDS, and (c) TEA.

CONCLUSIONS

Hydrothermal synthesis of nanocrystalline ZnO powders have been successfully synthesized by using different surfactants such as CTAB, SDS, and TEA. On the other hand, the morphologies of the as-synthesis ZnO nanocrystallites are dependent on the surfactant. The addition of surfactant can influence particle growth, coagulation, and flocculation. Therefore, surfactants play an important role in the preparation of metal oxide nanoparticles. Moreover, the ZnO nanoparticles have bioluminescent properties at ultraviolet and visible

wavelength range. The as-synthesized ZnO nanoparticles are promising materials will favor more reliable for fluorescence sensing. We also believe that they should be also powerful in the fluorescence detection of biomolecules because the less UV emission of them and it is under investigations now.

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