Optik 127 (2016) 174–177

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo

Synthesis of zinc oxide nanoparticles with different pH by aqueous solution growth technique

Neha Singh, Fozia Zia Haque*

Optical Nanomaterials Lab, Department of Physics, Maulana Azad National Institute of Technology, Bhopal 462051, India

ARTICLE INFO

Article history:
Received 30 September 2014
Accepted 6 September 2015

Keywords:
Zinc oxide
Aqueous solution growth technique
Benzyltrimethylammoium hydroxide IL (BTMAH)
Atomic force microscopy
Photoluminescence

ABSTRACT

Highly dispersible zinc oxide nanoparticles were produced via a simple aqueous solution growth technique. The effect of concentration of ionic liquid [benzyltrimethylammoium hydroxide IL (BTMAH)] and pH on morphology and optical properties of zinc oxide nanoparticles has been extensively investigated. The average crystalline size of ZnO nanoparticles decreases with increasing pH. A sharp visible emission was observed in as-prepared ZnO nanoparticles. Crystallinity, phase purity, nanostructures and average grain size were confirmed by X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM) and atomic force microscopy (AFM). Hexagonal wurtzite phase structure of ZnO nanoparticles was obtained in the form of spheres for all the three samples. pH increased, the broadening (FWHM) of the diffraction peaks increased and the intensities of diffraction line decreased. The emission wavelength was observed through photoluminescence spectroscopy.

1. Introduction

In recent years, synthesis of inorganic materials with specific size and morphology has attracted significant attention due to their possible use in different fields [1–4]. As one of the vital wide-band-gap (3.4 eV at 2 K) metal oxide semiconductors (MOS), ZnO is an important semiconductor material with extensive application in electronics, sensor and photoelectronic device owing to its wide band gap of 3.37 eV and large exciton binding energy of 60 meV [5–7].

It is necessary to achieve control over the ZnO nanoparticle size and size distribution; it is still difficult to control the size and shape in a simple way. Most of the properties of ZnO strongly depend on its structures, including the morphology, size and aspect ratio [8–11]. Various methods have been reported, for the synthesis of ZnO particles with controlled crystalline morphology, orientation and surface architectures to fine-tune its properties for potential application. Aqueous solution growth technique is also one of the types of wet chemical technique.

Which technique is a promising alternative synthetic method. The aqueous solution growth technique has several advantage over other growth processes such as use of simple equipment, low cost, large area uniform production, environmental friendliness and less hazardous. This method has also been successfully employed to prepare nanoscale ZnO and other luminescent materials [12,13].

If we are looking surfactant like ionic liquids, they are also useful as stabilization of nanoparticles, they are better than conventional surfactants as they have better surface activity and solubility in medium.

Nowadays inorganic nanomaterials have attracted much attention for their unique chemical and physical properties compared with the bulk solids. Because of the size and shape-dependent properties of the inorganic nanomaterials, synthesis of inorganic nanomaterials with controlled size and shape becomes a hot scientific research area. As a new green solvent and surfactant, ionic liquids have some specific functions. Ionic liquids can be used to fabricate inorganic nanomaterials with unprecedented and sometimes unique structures and properties, thus they will open a new way for the preparation of nanomaterials. Ionic liquid are composed of cations and anions having low melting point (<100 °C), while the cations may be organic and anions are inorganic [14–17]. However, the formation mechanism of the inorganic nano-materials grown in ionic liquids and their properties are still in the primary stage. In some cases, ILs and the related IL crystals combine these functions and serve unique system as solvent–reactant–templates, or ionic liquid (crystal) precursors as reported in many studies [18,19]. The use of ILs in such cases provided easy synthesis of inorganic nanomaterials and surfaces with novel or improved properties, sometimes resulting into otherwise inaccessible structures with unique properties, and it is also used as a structure directing/stabilizing agent.

* Corresponding author. Tel.: +91 9300687943; fax: +91 755 2670562.
E-mail address: foziazia@rediffmail.com (F.Z. Haque).

http://dx.doi.org/10.1016/j.ijleo.2015.09.024
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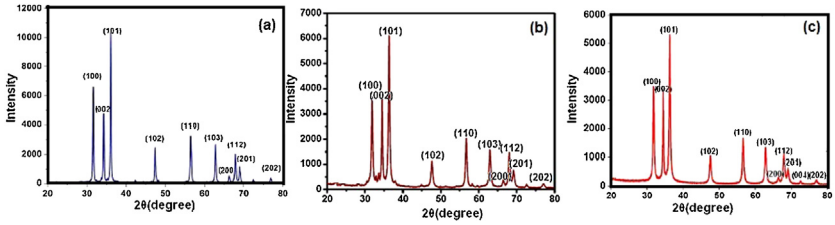

Fig. 1. The XRD pattern of the sample product is crystalline with a hexagonal wurtzite phase (a) pH 8, (b) pH 9 and (c) pH 10.

The particle properties such as morphology and size can be controlled via the aqueous solution process by adjusting the reaction temperature, calcinations temperature [20], time, pH and concentration of precursors. This paper reports effect of pH level and concentration of ionic liquid benzyltrimethylammoium hydroxide IL (BTMAH) on the growth crystallinity and grain size of material. Ionic liquid used as a surfactant to promote a confined and stable growth to ZnO in the reaction process. It is indicated that the addition of surfactant could greatly influence the size confinement of ZnO nanostructure, which in turn affect the physical properties. Structure and surface root mean square (RMS) roughness of ZnO nano/micro structures were systematically studied by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM) and the optical behavior was analyzed through photoluminescence (PL) spectroscopy.

2. Experimental outline

2.1. Materials used

The starting materials were zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$, Scientific Ltd), sodium hydroxide NaOH (0.3 M) procured from CDH with 99% purity were used as the zinc cation precursor material, hydroxide anion precursor and pH controller respectively and benzyltrimethylammonium hydroxide ($C_6H_{12}N_4$, BTMAH, procured from Alpha Aser with purity: 99.5%, Scientific Ltd). All chemicals reagents in the experiment were of analytical grade and used without further purification

2.2. Aqueous solution growth technique for preparing ZnO micro/nano particles

All chemicals reagents in the experiment were of analytical grade and used without further purification. For the synthesis of ZnO micro/nano-particles, a stoichiometric ratio of $Zn(CH_3COO)_2{\cdot}2H_2O$ was dissolved in 75 ml distilled water with constant stirring at room temperature followed by the slow addition [benzyltrimethylammoium hydroxide] BTMAH into the solution after 5 min. The resulting reaction mixture was constantly stirred for 15 min; aqueous solution of NaOH was slowly added drop wise into the solution under the constant stirring until the pH of the solution reached to exact values. During the dropping process, the white precipitate was gradually formed in the solution; after the solution were kept in a temperature controlled oven at 95 °C for 5 h, and then solution cooled in oven. Finally the sample were washed and filtered out using DI water and ethanol after overnight aging. The samples thus collected were calcined at 200 °C for 5 h in the furnace to complete the process of oxidation of zinc.

2.3. Materials characterization

The data to analyze crystal structure of all the samples have been collected in Bruker D8 Advance X-ray powder diffractrometer with CuK_α radiation operating at 40 kV and 40 mA. Diffraction peaks of the crystalline phase were compared with those of the standard compounds reported in the JCPDS data files JCPDS: 792205 card ICSD#: 067454. Meanwhile, scanning electron microscopy (SEM, JEOL-JSM-6390) and atomic force microscopy, NT-MDT Solver NEXT, was used to determine the morphology of as-prepared samples. The optical property determined through photoluminescence (PL) spectra at room temperature and the data was recorded using fluorescence spectrometer (F-7000 Hitachi) exiting with its xenon lamp at 320 nm.

3. Result and discussion

3.1. Crystal structure and phase analysis

Fig. 1 shows X-ray diffraction pattern of ZnO samples prepared at three different pH values of 8, 9 and 10. XRD spectra of ZnO nanoparticles are shown in Fig. 1. The micro/nanorods are highly crystalline as seen in XRD patterns, in which broad peaks with high intensity are extended over the 2θ. The results indicate that the product consists of pure phase and there is no impurity reflection peaks of (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (2 0 0), (1 1 2), (2 0 1), (0 0 4) and (2 0 2) of crystal planes respectively, indicates the hexagonal wurtzite structures of ZnO [15,21], which are consistent with standard JCPDS: 792205 card ICSD#: 067454. The sharp peaks indicate that the samples were well crystallized and oriented. The broadening of the diffraction peaks gives an idea about the small particle size, which is clearly shown in Fig. 1. ZnO micro/nanoparticles samples grown for various pH values have the same hexagonal wurtzite structure. As pH increased, the broadening (FWHM) of the diffraction peaks increased and the intensities of diffraction line decreased. Crystallite size (D) was calculated by using Debye Scherrer's formula,

$$D = K\lambda/\beta\cos\theta \tag{1}$$

where K is the particle shape factor which depends on the shape of the particles and its value is 0.94 for spherical particles, λ is CuK_α radiations (1.54 Å), β is the full width at half maximum (FWHM) of the selected diffraction peak corresponding to planes, θ is the Bragg angle obtained from 2θ value corresponding to the same plane. The standard XRD pattern of ZnO and their miller indices are used for relative comparison.

$$1/d^2 = 4/3(h^2 + hk + k^2/a^2) + (l^2/c^2) \tag{2}$$

where 'a' and 'c' are the lattice parameters, h, k, and l are the Miller indices and d is the interplaner spacing for the plane (hkl). The volume (V) of the unit cell for wurtzite hexagonal system has been calculated by using the equation: $V = 1.732.a^2c/2 = 0.866\,a^2c$. The variation of lattice parameters and unit cell volume of ZnO nanoparticles is also reported in Table 1.

3.2. Williamson–Hall method

The strain induced in powders due to crystal imperfection and distortion was calculated using the formula:

$$\varepsilon = \beta_{hkl}/4\tan\theta \tag{3}$$