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Investigation of morphologies, photoluminescence and photocatalytic properties of ZnO nanostructures fabricated using different basic ionic liquids

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ABSTRACT

ZnO nanostructures were synthesized in methanol-water reaction media using different basic ionic liquids [BILs] by hydrothermal approach at 150 °C. ZnO nanoparticles obtained from BILs consists of different morphologies, such as, hexagonal disks, hexagonal rings assembled by nanoparticles, hexagonal disks-aggregated flower-like structure and nanospheres. The effect of these basic ionic liquids on morphology, particle size and properties of as-synthesized ZnO nanostructures was investigated. The obtained nanoparticles have been characterized by X-ray diffraction, TEM, SEM, UV–vis absorption spectroscopy and photoluminescence (PL) studies. The XRD study of as-synthesized ZnO nanostructures confirmed the existence of hexagonal wurtzite structure. The maximum around 371 nm was observed in UV–vis absorption spectrum and the calculated band-gap energy is in the range of 3.07-3.10 eV. The photoluminescence spectra exhibited blue and blue-green emissions. ZnO nanoparticles prepared in choline hydroxide showed higher photocatalytic activity, which was accounted for due to high surface area, the smaller size of nanoparticles and low electron-hole recombination effect.

1. Introduction

Room-temperature ionic liquids have unique properties such as good dissolving ability, low melting point, high thermal stability, non-volatile nature, designable structures and wide liquid temperature range [1,2] and have attracted great interest due to their environment friendly properties. Ionic liquids (ILs) being highly structured liquids have been used for the synthesis of metal oxide nanostructures with controllable morphologies and properties as solvents and templates [3,4].

Recently, according to the requirements of a particular reaction, the preparation of task specific ILs or functionalized ILs with special functions has become an attractive field due to their adjustable features and advantages of being reusable ILs with green credentials. Among these, the BILs presented great potential for the synthesis of metal oxide nanoparticles by replacing conventional bases such as KOH, NaOH, K_2CO_3 and $NaHCO_3$ as they are non-corrosive, non-volatile and flexible. BILs have been reviewed by Hajipour and Rafiee for application in base-catalyzed processes [5], organic synthesis [6] and more recently in material synthesis [7,8]. BILs as environment friendly ILs which offer a new pathway for developing nanomaterials due to the advantage of their reusability, easy separation and stability in air and water. Ying et al. synthesized Cobalt oxide (Co_3O_4) nanoparticles using basic ionic liquid [Bmim]OH as structure assisting agent through a solution oxidation route at room temperature [7]. Toprak et al. presented a novel environmental friendly method for the synthesis of Mn_3O_4 nanoparticles using an ionic liquid [Bmim]OH [8]. Movahedi and co-workers synthesized different flower-like morphologies of ZnO using task specific dibasic ionic liquid, $[mmpim]_2[OH]_2$ via hydrothermal method, in which ionic liquid plays an important role for the fabrication of ZnO structures. Room temperature PL spectrum of the product exhibited strong ultraviolet emission at about 391 nm and weak blue-green emissions at about 450 and 500 nm [9].

ZnO is an important versatile semiconductor with a wide band gap of 3.37 eV appropriate for photonic applications and has high exciton binding energy of 60 meV at room temperature [10]. ZnO is used in different areas ranging from large scale products to

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advanced applications. Zinc oxide is used in rubber industry for vulcanization process, sunscreens, pharmaceutical products, white pigment in paints and heterogeneous catalyst in chemical industry to mention a few [3]. The synthesis of hexagonal wurtzite ZnO nanostructures with high density and well-defined morphology is essential for their practical applications, which has attracted a vast technological interest for its size and shape dependent properties different from bulk ZnO material. These properties provide enhanced and smart functional building blocks for a variety of nanodevice applications such as in solar cells, lithium ion batteries, sensors, piezoelectric transducers, and photocatalysis [11–13]. The absence of a centre of symmetry in Wurtzite structure of ZnO results in strong pyroelectric and piezoelectric properties resulting in turn use of ZnO in mechanical actuators and piezoelectric sensors. ZnO is biodegradable, biosafe and a green material, which can be used for environmental, biomedical and variety of possible practical applications.

The morphology and size of ZnO nanoparticles have great influence on their performance and are the most tested materials in photocatalysis [14]. Although synthesize of ZnO nanostructures with different structures and improved properties are well explored using various ionic liquids [15–21]. However, synthesis of these nanostructures in Basic Ionic Liquids needs more exploration. Numerous methods have been developed to attain ZnO nanostructures such as chemical vapour deposition, ultrasonic, thermal evaporation, hydrothermal and template assisted chemical process to mention a few [22–25]. Among these, hydrothermal synthesis is becoming popular because it is cost effective and simple for large scale preparation of ZnO. Many researchers have synthesized hexagonal ZnO micro disks and rings by using surfactants and a polymer template [26,27]. However, complete removal of these templates requires washing with suitable solvent or calcination of the products at high temperature. Therefore, there is a requirement to develop an environmentally benign approach to synthesize ZnO nanostructures with different morphologies.

In continuation to our work [28] towards synthesis of nanomaterials using functionalized ILs, the present work explored the use of basic ionic liquids for the synthesis of ZnO nanostructures both as hydrolyzing and templating agent avoiding the use of corrosive bases as one of the major advantage of the process. Here, we report, environment friendly and low cost method to synthesize single-crystalline ZnO hexagonal disks, rings assembled by nanoparticles, hexagonal disks-aggregated flowers and nanospheres in various BILs via hydrothermal method and their effective utilization as photocatalyst for the discoloration of methyl orange dye. We mainly investigated the effect of cations of three different basic ionic liquids, 1-butyl- 3-methylimidazolium hydroxide, [Bmim]OH 1-dodecyl-3-methylimidazolium hydroxide, [C_{12}mim]OH and (2-hydroxyethyl) trimethyl ammonium hydroxide, [Ch]OH on ZnO nanostructures. The products formed were labelled as sample ZnO-IL-1, ZnO-IL-2 and ZnO-IL-3. The mechanism of synthesized materials has been discussed and their photoluminescence and photocatalytic properties have been tested.

2. Materials and methods

2.1. Reagents and chemicals

The basic ionic liquids [Bmim]OH and [C_{12}mim]OH were prepared according to the procedure reported in the literature [5]. All chemicals used in this work zinc acetate, choline hydroxide, butyl bromide, 1-bromo dodecane, 1-methylimidazole, commercial zinc oxide, ethanol, methanol and methyl orange were of analytical purity grade, supplied by Sigma-Aldrich and were used as received without any further purification.

2.2. Synthesis of ZnO

0.6 g of zinc acetate dihydrate was dissolved in 30 ml of double distilled water with stirring. An alcoholic solution of 0.5 g of basic ionic liquid ([Ch]OH, pH = 12, [Bmim]OH, pH = 9.0 and [C_{12}mim]OH, pH = 8.5) was added drop wise to the previous solution. The mixture was magnetically stirred vigorously for 30 min at room temperature. A clear and transparent homogenous solution was formed. The synthesis was performed in a Teflon-lined stainless steel autoclave (Parr Instrument, USA). The reaction mixture was transferred into a Teflon-cup enclosed in a 50 ml autoclave, which was heated in a furnace and maintained at 150°C for 15 h. After cooling the autoclave in air at room temperature, the resulting products were collected, separated by centrifugation (10,000 rpm, 15 min), washed thoroughly with distilled water (2 × 5 ml) and ethanol (3 × 10 ml) several times and dried overnight in a vacuum oven at 70 °C.

2.3. Characterisation of nanocrystalline ZnO

XRD measurements were performed using an X-ray powder diffractometer (XPERT-PRO) operated at 45 kV and 40 mA with Cu-Kα radiation (λ = 0.15406 nm) and a scan angle (2θ) of 5–80°. UV–vis spectra were recorded on spectrometer Lambda 35 (Perkin Elmer) equipped with diffuse reflectance accessory at room temperature. BET surface areas were calculated by using BET (Brunauer Emmett Teller) equation thermally heated at 180 °C for 2 h (Quantachrome Nova Win version 10.01). SEM images of samples were obtained using Model SU 8010 (Hitachi) and TEM images of samples were studied using transmission electron microscope (TEM) Hitachi (H-7500) with an accelerating voltage of 120 kV. The photoluminescence spectra were recorded at room temperature on a Hitachi F-4500 spectrophotometer equipped with Xe arc lamp.

2.4. Photocatalytic experiments

The photocatalytic activity of ZnO was investigated by degradation of methyl orange in an aqueous solution under UV irradiation. Discoloration was carried in an immersion well type photochemical reactor made of Pyrex glass with a water-circulating jacket maintained at room temperature, an opening for supply of oxygen and inlet through which the samples were taken from time to time during the experiment with the help of a syringe. The photo-reactor was placed on a magnetic stirrer. A UV lamp of 125 W was used as a light source to irradiate the solution. 60 mg of ZnO sample powder was mixed in 200 ml of 20 ppm aqueous methyl orange solution (2 g/100 ml). To attain the adsorption-desorption equilibrium, solution was stirred in the dark for 30 min 5 ml of sample was taken at regular intervals and further separated by centrifugation at 4000 rpm for 20 min. The obtained upper clear solution was analysed using a UV–vis spectrometer. The percentage degradation was determined according to Eq. (1):

$$\eta = \frac{Ao - At}{Ao} \times 100\% \quad (1)$$

where A_o and A_t are the absorbances at t = 0 and time t respectively assessed by evaluating the absorbance at 463 nm on UV–vis spectrometer.

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