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Synthesis, characterization and photocatalytic activity of annealing dependent quasi spherical and capsule like ZnO nanostructures

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ABSTRACT

Quasi spherical and capsule like ZnO nanostructures have been successfully synthesized via a simple precipitation route without the assistance of external capping agents. The effect of annealing temperature on the properties of ZnO was investigated. In all cases, hexagonal wurtzite crystalline structure of phase pure ZnO was obtained. The crystallinity was found to be gradually increasing with annealing temperature. At low annealing temperatures, more or less spherical ZnO nanoparticles were clearly observed, whereas they tend to grow as nanocapsules with increasing the annealing temperature. The formation of single crystalline nanocapsules was observed at 600 °C. The photoluminescence spectra indicated the annealing dependent emission features, especially in the spectral intensity. The dye pollutant methylene blue was found to be completely degraded under UV light irradiation over the ZnO nano photocatalysts. The highest photoactivity was shown by nanocapsules obtained at 600 °C and was found to be highly reusable.

1. Introduction

Dyes are one of the most important hazardous water pollutants with a detrimental effect on the ecosystem [1]. In recent years, many remedial techniques have been investigated. Among the various methods, the adsorption and photodegradation caught a much special attention for the treatment of dye polluted waste water [2,3]. Photocatalytic degradation of dyes using semiconductor metal oxides such as TiO_2, ZnO, Co_3O_4, etc. is an area of current research interest, since adsorption is not a fully validated method to remove the dyes completely [4,5]. The creation of electron–hole pairs by the excitation of electrons from valence band to the conduction band, caused by the light absorption of semiconductor metal oxides constitutes the basis of photocatalysis [6]. The as-created electron–hole pairs enter the surface of the catalyst and initiate redox reaction with water and oxygen, which results in the degradation of organic dye molecules adsorbed on the surface of the photocatalysts [7].

ZnO is one of the most extensively studied semiconductor photocatalysts with a versatile application due to its wide band gap energy of 3.37 eV and a binding energy of 60 meV [8]. In addition to the photocatalytic usage, it also have promising applications in various optoelectronic devices, actuators, gas sensors, solar cells, photo detectors, etc. [9–12]. For the synthesis of size and morphology controlled ZnO nanoparticles, much effort have been made by the researchers, since it has a direct influence on the electrical and optical properties of ZnO. Recently many synthetic methods such as hydrothermal, solvothermal, sol gel, chemical vapour deposition, precipitation, solid state mixing, sonochemical, thermal decomposition, etc. have been reported to fabricate ZnO nanoparticles with various morphologies including nanorods, nanospheres, nanocones, nanoflakes nanowires, nanobelts and different types of nano and micro flower-like structures [13–20]. Also been investigated that, a slight variation in the synthetic condition has the impact to alter its structural and morphological properties and also its bulk properties [21]. However the use of additional templates, surfactants and capping agents for the control of size, morphology and properties have been also investigated in detail [22,23].

Among the aforementioned synthetic routes, the precipitation method forms a simple and efficient method for the low cost and industrial scale production of ZnO without the use of special

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precursors and equipments [24,25]. There are numerous reports in literature about the synthesis of ZnO nanostructures by precipitation route using different precursors. However, the properties were found to have an influence on the synthesis conditions such as counter ions, solvents, pH, precipitants, etc. [26–29].

Annealing temperature is one of the important parameters concerning the synthesis and photocatalytic properties of ZnO. Previously Lv et al. [30] studied the effect of annealing temperature on the photocatalytic activity of ZnO thin films prepared by the sol–gel method. As per their report, the ZnO annealed at a temperature of 800 °C provided highest photocatalytic activity for the degradation of methyl orange under UV irradiation, due to the increased surface-to-volume ratio, roughness, grain size and oxygen defects density. Fan et al. [31] also studied the effect of annealing temperature on the photocatalytic activity of ZnO–TiO_2 based composite nanotubes. They reported that, among a set of annealed samples, the sample annealed at 600 °C showed highest catalytic activity due to the enhanced formation rate of hydroxyl radicals by the increased crystallinity of the sample. As per the report, the recombination of electron–hole pair is reduced due to the decreased crystalline defects with increase in annealing temperature [32]. Lv et al. [33] also studied the influence of annealing temperature on the photocatalytic activity of TiO_2 nanosheets and reported that, with increasing annealing temperature from 200 °C to 600 °C, the photocatalytic activity was decreased due to the reduced surface area by sintering, whereas at an annealing temperature of 700 °C, it showed a maximum photocatalytic activity due to the enhanced crystallization of the sample rather than specific surface area. Yu et al. [34] studied the same with photoactive TiO_2 prepared by a liquid phase deposition method and reported that, with increase in the annealing temperature, the photocatalytic activity was gradually increased due to the improved crystallization of the active anatase phase and a highest activity was shown by the sample calcined at 700 °C.

In this paper, we report on the synthesis, characterization and photocatalytic activity of ZnO nanoparticles obtained by the conventional precipitation route and the effect of annealing temperature on the structural, morphological and optical properties of ZnO was evaluated. Its influence on the photoactivity was also studied using methylene blue degradation under UV light irradiation over a low catalyst loading.

2. Experimental

2.1. Synthesis of ZnO nanoparticles

All of the chemicals used in the experiments were of analytical grade (R&M chemicals, UK) and were used as received without further purification. In the typical procedure, 200 ml of 0.1 M NaOH solution was added drop wise to a beaker containing 1000 ml 0.1 M zinc nitrate solution. After the complete addition of precipitant, the solution was stirred for 1 h. Then the solution was kept for a while and clear solution was decanted. The precipitate was washed several times with distilled water, filtered and dried at 100 °C for an overnight. Finally, it was annealed at different temperatures from 300 °C to 600 °C with an interval of 100 °C to obtain ZnO nanoparticles.

2.2. Characterization of ZnO nanoparticles

The synthesized ZnO nanoparticles were characterized by powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), selected area electron diffraction (SAED), Brunauer–Emmet–Teller (BET) and Barrett–Joyner–Halenda (BJH) analysis. The XRD analysis was carried out in a Bruker D8 Focus powder diffractometer with Cu Kα radiation wavelength of 0.15406 nm. The samples were scanned from 10° to 80° with a step size of 0.025°. The mean crystalline size of the samples was calculated from the full width at half maximum (FWHM) of the intense diffraction peaks using Scherrer's equation. The FT-IR spectra of the dried and calcined samples were recorded in transmission mode using a thermoscientific NICOLET 6700 IR spectroscope in the region of 400–4000 cm^{-1}. The FESEM images for the determination of surface morphology were done on a Zeiss SUPRA 55 scanning electron microscope. The scanning electron micrographs were obtained at an operating voltage of 3 kV. The TEM studies of the calcined samples for the determination of internal morphology and particle size were carried out in a Philips CM-12 instrument at an accelerating voltage of 100 kV. The SAED analysis was performed in a HITACHI-88, HT 7700 TEM instrument, operated at 120 kV. The BET/BJH analyses were carried out in a Micrometrics ASAP 2010 instrument by nitrogen adsorption–desorption analysis at 77 K. The samples were degassed at 300 °C for 6 h prior to the analysis. The specific surface area was assessed by BET method and the pore size and pore volume distributions were determined by the BJH method. The optical properties of the calcined samples were studied using UV–vis absorption and photoluminescence (PL) spectroscopy. The UV–vis absorbance spectra of the samples dispersed in water were recorded in a Perkin-Elmer Lambda-35 UV–vis spectrophotometer using water as the reference solvent. The PL spectra were taken in a PL-FLSP920 Edinburgh instrument, with an excitation wavelength of 300 nm.

2.3. Photocatalytic activities

The photocatalytic activity of ZnO nanoparticles was investigated by the photocatalytic degradation of methylene blue in aqueous solution. The degradation experiments were carried out in a photoreactor (Rayonet type Photoreactor, Associate Technica, India) with 16, 8 W UV lamps (λ = 352 nm, Hitachi 8 Watt, Hittach, Ltd., Tokyo, Japan). In the typical procedure, 50 ml of methylene blue dye solution (15 mg/L) was taken in a vertical tube of 100 ml capacity and 0.05 g ZnO photocatalyst was dispersed in it using an aerator for 20 min, so that the suspension attain adsorption–desorption equilibrium prior to degradation. Then the solution was irradiated under UV-light with continuous air bubbling as the potential oxidizing agent. After a particular duration of reaction, the suspension was centrifuged and its absorbance was measured to calculate the percentage of photodegradation using a UV–visible spectrophotometer (Varian Cary, Perkin Elmer Lambda-35). The absorbance spectra were taken from 200 nm to 800 nm. The photodegradation efficiency was calculated according to the following equation: Degradation (%) = $((A_0 - A)/A_0) \times 100$, where A_0 represents the initial absorbance of the dye solution and A represents the highest absorbance after UV irradiation.

3. Results and discussion

3.1. Characterization of ZnO nanostructures

Fig. 1 represents the XRD pattern of the samples at different annealing temperatures. All of the diffraction peaks can be directly indexed to a hexagonal wurtzite crystalline structure of ZnO with the lattice parameters a = 0.3249 nm and c = 0.5206 nm and P63mcz space group (JCPDS: 01-036-1451). No other peaks were detected, indicating the high phase purity of the dried and calcined products. The sharp and strong diffraction peaks confirmed the high crystalline quality of the calcined samples. It is clear that the diffraction