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Influence of pH on hydrothermally derived ZnO nanostructures

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A B S T R A C T

Zinc oxide (ZnO) nanostructures with numerous morphology was prepared by using hydrothermal method. The effect of pH on structural, optical and photocatalytic activity of ZnO was investigated systematically. The prepared ZnO samples were characterized by various characterization techniques. The X-ray diffraction study revealed that the crystalline hexagonal phase of ZnO nanostructures was observed. Scanning electron microscopic observations revealed that the variation of pH significantly alters the morphology of the grown ZnO nanostructures. The UV–vis spectrum shows an optical bandgap was not significantly influenced by pH of reactant solution. Photoluminescence studies at room temperature for different pH values revealed a weak band edge emission altogether with strong defect-related visible emission peaks. Photocatalytic activity of methylene blue (MB) under visible light illumination was studied. Maximum degradation of 99% was observed in 100 min for ZnO nanostructure prepared at pH 11.

1. Introduction

Control over the size and shape of ZnO nanostructures is a great challenge for researchers. This is because the structural, optical and morphological properties of ZnO can be tuned by varying size, shape and morphologies of nanostructures. For this reason, numerous methods were used to synthesize ZnO such as chemical vapour deposition [1], microwave method [2], hydrothermal method [3] and spray pyrolysis [4]. Among these various methods, the hydrothermal method is widely used to synthesize ZnO micro/- nanostructures. The hydrothermal method has many advantages such as simple, environmentally benign, less hazardous, and low cost [5].

Water pollution is major threat which causes serious damage of flora and fauna life [6]. Numerous methods are used for water treatment such as flocculation, floatation, ozonization, electrochemical deposition, adsorption, etc. These methods are less efficient with formation of secondary sludges. Photocatalysis is promising and efficient method for wastewater treatment. These method involved the removal of organic and inorganic compounds from water. Waste water from industries are important source of MB dye. MB have various adverse effect on environment and human beings.

ZnO is very promising catalyst and effectively used for degradation of MB dye. It is most widely studied semiconductor material because of its properties that include cheapness, chemically and thermally inert, non-toxic, abundantly available in nature at low cost. Many researchers are interested in optical properties of ZnO because of its wide band gap (3.37 eV)

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and high exciton binding energy (60 meV) and hence ZnO plays a crucial role in electrical, optical and biological applications [7]. It has been also studied that numerous morphology of ZnO effect the photocatalytic degradation of MB [8–10].

In this research work, we reported the growth of ZnO nanostructures by hydrothermal method and subsequently studied the effect of pH on crystallographic, morphological and optical properties of ZnO nanostructures. We were also interested to examine the influence of various morphology of ZnO nanostructures on photocatalytic activity.

2. Experimental section

2.1. Experimental procedure

All chemicals used were AR grade and purchased from S. D. Fine Chem. Ltd. and used without further purification. In the present synthesis process, 70 ml of an aqueous solution of Zn $(CH_3COO)_2{\cdot}2H_2O$ (0.05 M) and 70 ml of an aqueous solution of NaOH (1 M) was prepared. Then an aqueous solution of NaOH was gradually added into the an aqueous solution of $Zn(CH_3COO)_2{\cdot}2H_2O$ with constant stirring so as to adjust pH at 12. Initially, by adding the NaOH solution gradually $Zn(OH)_2$ white precipitate was obtained. After adding a sufficient amount of NaOH solution $Zn(OH)_2$ completely dissolved in solution and solution becomes clear containing $Zn(OH)_4{}^{2-}$ growth units. The resultant aqueous solutions were transferred to the Teflon containing stainless steel autoclave and heated at a temperature of 200 °C for 24 h. After 24 h the autoclave was allowed to cool at room temperature. Further, the experiment was repeated by adding the appropriate amount of NaOH solution to adjust the pH at 8, 10, 11 without changing other parameters. The final product was dried at 80 °C for 6 h and used for further characterizations.

2.2. Characterizations

X-ray diffraction (XRD) pattern was recorded by Rigaku, Miniflex-II X-ray diffractometer using monochromatized CuKα radiation (λ = 1.5405 Å) keeping scanning rate 5° min^{-1}. FEI Quanta FEG-200 high resolution scanning electron microscope (SEM) attached with an energy-dispersive X-ray analyzer (EDXA) was used to observe the morphology of synthesized ZnO and to determine the elemental compositions. X ray Photoelectron Spectroscopy (XPS) was recorded with PHI Versa probe- II photoelectron spectroscope. Optical absorption was measured with a UV–visible spectrophotometer (PerkinElmer Lambda 750). Fluorescence spectrophotometer (PerkinElmer LS 55) was used to study room temperature photoluminescence properties.

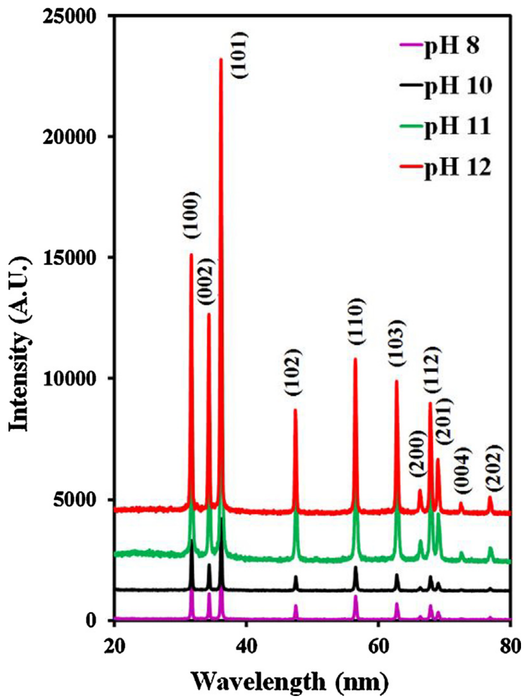

Fig 1. XRD pattern of ZnO nanostructures at (a) pH 8, (b) pH 10, (c) pH 11, (d) pH 12.