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Morphology controlled synthesis and photocatalytic activity of zinc oxide nanostructures

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Abstract

Zinc oxide with different morphologies is prepared by adopting various synthetic pathways. The synthetic routes adopted include solvothermal method using polyvinylpyrrolidone (PVP), CTAB assisted hydrothermal synthesis and the direct heating of zinc nitrate hexahydrate precursor. The prepared systems are well characterized using X-Ray diffraction analysis, scanning electron microscopy, Fourier transform infra-red spectroscopy, surface area analysis by BET method and Diffuse Reflectance UV spectroscopy. Three different morphologies of zinc oxide are identified, vis., rice like short nanorods, flower like structures and hexagonal pyramid. The systems exhibited commendably high photocatalytic degradation efficiency towards rhodamine B dye. A correlation between the physical characteristics of the systems and the activity is also attempted here.

Keywords: Water pollution; Photocatalysis; ZnO; Rhoadamine B; Flower-like structures

1. Introduction

Water pollution is a major threat which we face today. Extensive use of toxic materials like pesticides, fertilizers, dyes, pigments etc. and their improper ways of treatment and discharge to water bodies are mainly responsible for the contamination of natural water resources. Conventional methods used for water treatment such as precipitation, coagulation/flocculation, flotation, ozonisation, electrochemical method, ion exchange, adsorption etc. have inherent limitations as they are less efficient and lead to the production of secondary sludge. Heterogeneous photocatalysis is gaining much importance in wastewater treatment for the past few decades. This technique can be effectively employed for the removal of organic and inorganic pollutants from water. Titania (TiO_2) is the most commonly used and effective photocatalyst for a wide range of organic chemical degradations [1,2]. However, high cost of this catalyst necessitates search for alternatives. Numerous studies have been carried out to evaluate the role of other metal oxides in photocatalysis. Among others, zinc oxide authenticates itself as a very promising photocatalyst to this effect.

Zinc oxide is a n-type semiconductor with wide direct band gap energy 3.37 eV. It has found applications in surface acoustic wave filters, photonic crystals, photocatalysis, photodetectors, light emitting diodes, gas sensors, optical modulator waveguides, solar cells and so on [3–6]. Zinc oxide has been considered as a suitable alternative of TiO_2 because of its comparable band gap energy as well as relatively lower cost of production. Some of the earlier reports suggested the higher efficiency of zinc oxide over titania in generating photoactive species [7–10]. It has been established that the morphology of zinc oxide influences its fine properties, and hence its activity also. Morphology dependant photocatalytic activity of ZnO has been studied extensively by many researchers [11–13]. Zinc oxide nanodisk has been effectively employed for the

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degradation of methylene blue in aqueous solution [14]. Photocatalytic degradation of methyl orange over zinc oxide nanorods has been discussed by Ghule et al. [15]. Wang et al. have proved that zinc oxide with flower like morphology exhibited enhanced activity towards photodegradation of 4-chlorophenol in aqueous solution under UV radiation compared with zinc oxide nanorods [11]. The photocatalytic activity of zinc oxide is highly dependent on its crystal plane orientation. Recent reports provide evidence for this fact. In order to get maximum activity, the fine tuning of growth orientation is necessary [11–12,16–17]. From the studies it has been proved that the synthetic parameters have decisive role in enhancing the photocatalytic efficiency of zinc oxide towards various pollutants.

We were interested to examine the influence of morphology and crystal planes of ZnO structures on their photocatalytic activity. Hence ZnO systems with three different morphologies have been prepared by adopting different synthesis pathways. The well characterized catalysts are employed for photodegradation of rhodamine B in aqueous solution. Rhodamine B is a widely used organic dye for various applications. Though it has wide spread applications, it is carcinogenic, neurotoxic and mutagenic. Rhodamine B also causes irritation to the skin, eyes and respiratory tract. It is toxic to aquatic organisms and may cause long-term adverse effects in the aquatic environment. The high concentrations of dyes in effluents generally interfere with the penetration of visible light into the water, resulting in a hindrance to photosynthesis and a decrease in gas solubility. All these factors necessitate the prior treatment of dye contaminated waste water.

2. Experimental methods

2.1. Materials

All the reagents were of analytical grade and were used without further purification. The precursors selected were zinc nitrate hexahydrate (Sigma Aldrich) and zinc acetate dihydrate (Merck). Sodium hydroxide (Merck), cetyl trimethyl ammonium bromide (Sigma Aldrich), polyvinylpyrrolidone (Himedia) constitute other reagents used in the synthesis. Rhodamine B (Himedia) was used for activity determination study.

2.2. Preparation of the catalysts

Three different methods were adopted for the preparation of catalysts, namely solvothermal method, hydrothermal method and direct heating of the precursor salt.

2.2.1. Solvothermal method using polyvinylpyrrolidone (PVP) as capping agent

Zinc acetate dihydrate (18 g) and polyvinylpyrrolidone (15 g) were separately dissolved in 45 mL methanol. The two solutions were mixed thoroughly and NaOH solution in methanol was slowly added to the above mixture. The reaction mixture was transferred to a 500 mL Teflon lined autoclave and was kept in an oven at 70° C for 24 h. The precipitate obtained was washed with de-ionised water and acetone to remove excess PVP. The final product was dried at 70 °C for overnight and was ground to form a fine powder [18]. The oxide powder was then subjected to calcination at 400 °C for 2 h.

2.2.2. CTAB assisted hydrothermal synthesis

A transparent solution of CTAB and NaOH in distilled water was prepared by vigorous stirring for 15 min. Aqueous solution of zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) was added drop wise to the above solution and was stirred thoroughly for 2 h. The resultant solution was transferred to a 500 mL teflon lined stainless steel autoclave and heated at 90 °C for 15 h. The white product obtained was separated from the solution by centrifugation. Washed four times with distilled water and absolute ethanol respectively, and dried in air at 80 °C. The final product was calcined at 400 °C for 2 h.

2.2.3. Direct heating of salt precursor

In this procedure, zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) was used as the precursor. A weighed quantity of $Zn(NO_3)_2 \cdot 6H_2O$ was kept in a silica crucible and directly heated in a muffle furnace at 500 °C for 2 h. Light yellow powder of zinc oxide was obtained.

The samples were named after the preparation method adopted for the respective systems. Thus the catalysts were named as follows: ZnO-PVP for solvothermal method using polyvinylpyrrolidone (PVP) as capping agent; ZnO-CTAB for CTAB assisted hydrothermal synthesis and ZnO-DH for direct heating of zinc nitrate hexahydrate.

2.3. Characterisation

The crystalline nature and purity of the prepared ZnO samples were examined by X-Ray diffraction (XRD) study using Rigaku Miniflex 600 diffractometer (CuKα radiation) equipped with a rotating anode. SEM-JSM 848 instrument was used for analyzing the morphology of the prepared systems. Fourier transform infra-red (FTIR) spectra were recorded in JASCO 4100 model instrument by the KBr disk method over the range 400–4000 cm^{-1}. The BET surface areas of the catalyst samples were measured by N_2 adsorption at -197 °C using Micromeritics Gemini surface area analyser. UV–visible absorption spectra of the samples were recorded in the wavelength range of 200–800 nm using Jasco V-550 spectrophotometer in diffuse reflectance mode using $BaSO_4$ as reference.

2.4. Photocatalytic activity measurement

The photocatalytic activity of the zinc oxide catalysts was evaluated by monitoring the photo decomposition of aqueous rhodamine B solution under UV irradiation. The reactions were carried out at room temperature. 50 mg of the catalyst was added to 50 mL of 10 mg/L rhodamine B aqueous solution. The pH of the dye solution was adjusted to 11. The mixture was stirred in dark up to 30 min to reach the adsorption desorption equilibrium by noting the concentrations