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Synthesis of supported silver nano-spheres on zinc oxide nanorods for visible light photocatalytic applications

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ABSTRACT

We report the synthesis of silver (Ag) nano-spheres (NS) supported on zinc oxide (ZnO) nanorods through two step mechanism, using open vessel microwave reactor. Direct reduction of ZnO from zinc nitrates was followed by deposition precipitation of the silver on the ZnO nanorods. The supported Ag/ZnO nanoparticles were then characterized by electron microscopy, X-ray diffraction, FTIR, photoluminescence and UV–vis spectroscopy. The visible light photocatalytic activity of Ag/ZnO system was investigated using a test contaminant, methylene blue (MB). Almost complete removal of MB in about 60 min for doses higher than 0.5 g/L of the Ag/ZnO photocatalyst was achieved. This significant improvement in the photocatalytic efficiency of Ag/ZnO photocatalyst under visible light irradiation can be attributed to the presence of Ag nanoparticles on the ZnO nanoparticles which greatly enhances absorption in the visible range of solar spectrum enabled by surface plasmon resonance effect from Ag nanoparticles.

1. Introduction

Nanomaterials have gained much attention in the field of catalysis in recent years due to their unique physical and chemical properties, large surface area, and strong interaction with other materials [1,2]. Nano-crystalline titanium dioxide (TiO_2) and zinc oxide (ZnO) semiconductors are well known for their novel photocatalytic activity, easy availability, chemical stability, strong oxidative capacity, and lower cost [3,4], which make them attractive solution for waste water treatment. ZnO nanostructures are technologically important material and are used in a wide range of applications such as catalysis, photocatalysis, gas sensors and other industrial applications [5–9]. ZnO nanoparticles show excellent photocatalytic activity to reduce contaminants in the environment. ZnO is an n-type II–VI semiconductor with a relatively large band gap of ~3.3 eV and high excitation binding energy (~60 meV) at room temperature [10], and it has a stable hexagonal wurtzite structure [11]. ZnO is considered more efficient photocatalyst than TiO_2 under visible light irradiation due to its higher quantum efficiency and lower cost of production [12–17].

The photocatalytic activity of ZnO nanoparticle can be enhanced by allowing absorption in the visible range with the help of modification of ZnO through cationic or anionic doping or adding metals or non-metals [18–20]. Doping ZnO with noble metals such as silver (Ag) or gold (Au) has been reported to enhance the photocatalytic activity of the composite due to improved charge separation, and reduction in electron–hole recombination in ZnO [21]. The creation of a localized electric field and the optical vibration of surface plasmons in metal nanoparticles allow absorption in the visible region and hence enhance the photocatalytic activity of these metal-semiconductor composites under visible light [22]. Ag nanoparticles have been studied and investigated by many researchers for their important role in visible light absorption [23] and electronic applications [24]. Numerous studies reported the synthesis of heterogeneous Ag/ZnO nanocomposites using various synthetic routes for different applications such as waste water treatment and disinfection [25–33]. Application of Ag/ZnO nanostructures for photocatalytic degradation of organic materials in water has been reported previously, where majority of them are based on photocatalysis using ultra-violet (UV) light irradiation [34,35]. In

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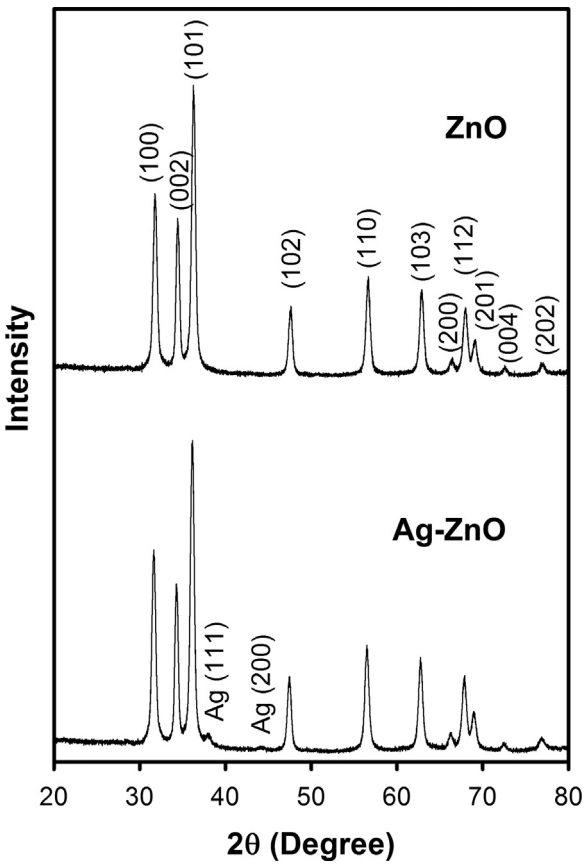

Fig. 1. XRD patterns of ZnO and Ag/ZnO nanoparticles.

contrast, Fageria et al. [36] has recently reported Ag/ZnO nanostructures as an efficient visible light photocatalyst for the degradation of methylene blue (MB) in water.

In this work, we report microwave assisted deposition–precipitation (MAD) synthesis and characterization of a heterogeneous Ag/ZnO photocatalyst, with 1 wt.% Ag (NPs) grown on the surface of the ZnO nanorods (NRs). A two-step synthesis method was used, starting with direct reduction of zinc nitrates to ZnO in open vessel microwave reactor followed by deposition–precipitation of Ag on the ZnO nanorods. The as obtained product did not show any core/shell nanocomposite formation as reported earlier by Yin et al. [27] The photocatalytic activities of the samples towards methylene blue (MB) degradation under visible light irradiation were then monitored and it was found that presence of Ag nanoparticles greatly improves the photocatalytic activity of the Ag/ZnO photocatalyst by making them visible light active.

2. Materials and methods

All chemicals, such as zinc nitrate ($Zn(NO_3)_2$; Alfa Aesar), silver nitrate ($AgNO_3$; Sigma–Aldrich), sodium hydroxide (NaOH; Alfa Aesar) and Glucose ($C_6H_{12}O_6$; natural) were used as received without further purification. Unless mentioned, distilled water was used as solvent in all the preparations.

2.1. Synthesis of ZnO nanorods

In a typical synthesis process of ZnO nanorods, the precursor solution of zinc was prepared by dissolving 5 g of $Zn(NO_3)_2$ in 100 mL of ethanol in a 250 mL reaction flask. The solution was kept stirring while 1 M NaOH was being added drop wise to the solution until pH of the resulting solution reaches 10. The solution was subsequently placed in a microwave chemical reactor (MCR-3) where the microwave power was adjusted to 1/3 of full 800 W power rating. The solution was exposed to microwave irradiation for approximately 10–15 min and was removed upon onset of boiling. The resulting solution was then left to cool down in the atmosphere. The precipitated particles were then filtered and collected after washing thoroughly several times with distilled water and ethanol.

2.2. Syntheses of Ag/ZnO nanoparticles

In order to deposit 1 wt.% Ag nanoparticles on the surface of the ZnO NRs, we used deposition precipitation (DP) method as reported by Haruta et al. [37] In a typical synthesis process, 4 g of the as prepared ZnO nanoparticles was dispersed in 100 mL aqueous solution containing 2 wt.% of reducing agent (glucose). The solution was vigorously stirred for 10 min. Silver nitrate solution was then added to the stirring solution drop wise until a pH value of seven was obtained. Finally, the solution was placed in a microwave oven and irradiated for 10 min and was removed before onset of boiling. The solution was left to cool down in the atmosphere, centrifuged at 5000 rpm for 5 min and the particles were collected and washed thoroughly with distilled water and ethanol.

2.3. Characterization

The ZnO and Ag/ZnO samples were characterized by using X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM), Fourier transform infrared (FTIR), photoluminescence (PL), specific surface area (SSA) and UV/vis spectroscopy. X-ray diffraction (XRD) of the samples were recorded by using a Rigaku MiniFlex600 (CuKα radiation, wavelength = 1.54 Å) X-ray diffractometer. HRTEM (model: JEOL JEM-2100F) was used for the morphological and crystallographic characterization of the nanoparticles. FTIR (PerkinElmer Spectrum one spectrometer) was used to explore the chemical bonding between ZnO and Ag nanoparticles. UV/vis absorption spectra of the nanoparticles were collected by using PerkinElmer Lambda25 spectrometer and photoluminescence (PL) spectra of ZnO and Ag/ZnO nanoparticles were obtained using a PerkinElmer LS55 fluorescence spectrometer. The specific surface area (SSA) of the nanoparticles was measured using Acorn Area–Particle Surface Area Analyzer from XiGo Nanotools, which works based on nuclear magnetic resonance (NMR) technique. Uniform pastes of the nanoparticle samples were prepared in ethanol with solid to liquid ratio of 0.06% by weight for the surface area measurements.

2.4. Photocatalytic Activity Ag/ZnO

Photocatalytic activity of the Ag/ZnO photocatalysts was studied by degrading an aqueous solution of 5 mg/L methylene blue (MB) solution under visible light as representative dye indicator. Bare ZnO and Ag/ZnO samples were mixed with the as prepared MB solution, where the concentration of the photocatalysts was varied from 0.1 g/L to 1 g/L. For the visible light photocatalysis simulated solar light (AM 1.5G) with 1000 W/m^2 incident power was used as light source. The distance between the light source and MB solution was kept constant at 30 cm in all cases. Prior to the light irradiation, the MB solution containing different amount of photocatalysts were kept in dark for 1 h in order to reach to an adsorption–desorption equilibrium between the MB molecules and catalyst surface. The photocatalytic degradation of MB was then carried out for 2 h and the photocatalytic reduction of MB concentration with time was recorded by measuring the optical absorption of the MB solution