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Synthesis, characterization and catalytic activity of co-doped Ag–Au–ZnO for MB dye degradation under UV-A light

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The Ag loaded Au–ZnO was successfully synthesized by the precipitation–decomposition method. The catalyst was characterized by X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FE-SEM), Energy Dispersive Spectrum (EDS), Transmission Electron Microscopy (TEM), Diffuse Reflectance Spectra (DRS), Photoluminescence spectra (PL) and BET surface area measurements. The photocatalytic activity of Ag–Au–ZnO was investigated for the degradation of Methylene Blue (MB) in aqueous solution using UV-A light. Ag–Au–ZnO is found to be more efficient than Ag–ZnO, Au–ZnO, commercial ZnO, bare ZnO, TiO_2-P25 and TiO_2 (Aldrich) at pH 7 for the mineralization of Methylene Blue dye. The effects of operational parameters such as the amount of photocatalyst, dye concentration, initial pH on photo mineralization of MB dye have been analyzed. The mineralization of MB has been confirmed by Chemical Oxygen Demand (COD) measurements. A mechanism is proposed for the degradation of MB under UV-A light.

1. Introduction

Environmental pollution and energy shortage are the two major global challenges faced by human beings. Semiconductor photocatalysis is a “Green technology” that allows the utilization of UV–vis light for pollutants degradation, thus providing a potential route to solve both problems [1–3]. Photocatalysis, an effective technology that can completely mineralize most of the organic contaminants into small inorganic molecules without any selectivity, has attracted considerable attention in recent years. Remarkable progress has been made in the fabrication of various semiconductors including TiO_2, ZnO, CdS [4], and their composites [5,6] and in their applications as new photocatalysts to successfully decompose environmental pollutants [7]. To develop efficient photocatalytic systems, high-quality semiconductor based materials have been widely studied. Among a wide spectrum of semiconductors, TiO_2 and ZnO have attracted significant attention due to their cheap availability, nontoxicity, stability and photocatalytic activity.

Photocatalytic degradation of various types of dyes in water by UV light irradiated semiconductor oxides are considered as a valuable technique for purifying and reusing aqueous effluents [8,9]. But, the photocatalytic activity of ZnO is limited by fast charge carrier recombination and low interfacial charge transfer rate of photogenerated carriers. In order to separate the excited e^-/h^+ efficiently, transition metal ions were used as the dopant. Metal or non-metal doping enhances the photocatalytic efficiency by decreasing the recombination of electron–hole pairs and increase their photocatalytic activity [10–15].

Different noble metals including Ag [16], Au [17–20], Pt [21] and Pd [22], have been researched for doping and reported. Furthermore, coincident doping of two kinds of

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atoms (co-doping) into semiconductor materials has attracted significant interest, as it may possibly result in a superior photocatalytic activity and special characteristics contrasted with single element doping into semiconductor oxides. Bimetallic doping with Ag and V [23], Zr and Ag [24,25], Ce and Ag [26], W and Ag [27], and Ag^+ and La^{3+} [28] have been reported. Besides to this, transition metals are found to have good thermal stability, due to their 3d electron configuration. Especially "Ag" can trap the photogenerated electrons from the semiconductor and allow the holes to react with the surface-bound H_2O or OH^- to produce hydroxyl radicals ($^{\bullet}OH$) that result in the degradation reaction of organic species present [29]. In addition to this "Au" was used for the metal–ZnO formation because of high electron affinity behavior [30] and the highest Schottky barrier produced among the various metals [31]. A quite different kinds of approach to protect Ag is based on the creation of bimetallic Ag/Au layers taking advantage of the long-term stability of Au. The Au spread over the surface, being in contact with the solution, protects the Ag due to its high chemical stability [13,32–34]. In continuation of our ongoing research on environmental remediation [35–37], we designed a simple, efficient, and low-cost way to prepare Ag loaded Au–ZnO. The photocatalytic efficiency was evaluated by analyzing the degradation of Methylene Blue (MB) in aqueous solution under UV-A light.

2. Experimental

2.1. Materials

The commercial Methylene Blue dye, obtained (molecular formula $=C_{16}H_{18}N_3SCl$; molecular weight 319.86 and dye content 80%) from Aldrich was used as such. The structure of the dye, UV–vis spectrum and its absorption maxima are given in Fig. 1. Oxalic acid dihydrate (99%) and zinc nitrate hexahydrate (99%) were obtained from Himedia chemicals. $AgNO_3$ and $AuCl_3$ were obtained from Sigma-Aldrich. ZnO (Himedia) and TiO_2 (Merck) were used as received. A gift sample of Degussa TiO_2-P25 was obtained from Evonik (Germany). It is a 80:20 mixture of anatase and rutile. It has a particle size of 30 nm and BET surface area 50 $m^2\,g^{-1}$. AnalaR grade H_2O_2 (30 w/w%), oxone, KIO_4, and $KBrO_3$ (Qualigens). $K_2Cr_2O_7$ (s.d. fine), Ag_2SO_4 (s.d. fine), $HgSO_4$ and $FeSO_4 \cdot 7H_2O$ (Qualigens) were used as received. The double distilled water was used to prepare experimental solutions. The pH of the solutions before irradiation was adjusted using H_2SO_4 or NaOH.

2.2. Preparation of Ag loaded Au–ZnO

Ag loaded Au–ZnO was prepared by the precipitation–decomposition method (see Supplementary Scheme S1). Aqueous solutions of 100 mL of 0.4 M zinc nitrate hexahydrate and 100 mL of 0.6 M oxalic acid in deionized water were brought to their boiling points separately. About 0.041 g of $AuCl_3$ in 5 ml of water was added to zinc nitrate solution. Solution of zinc nitrate and $AuCl_3$ were mixed with oxalic acid solution. Precipitation of zinc oxalate with Au occurred (1 wt% Au related to ZnO). To this 0.127 g of $AgNO_3$ in 5 ml of water was added and stirred for 3 h. The suspension was stirred continuously to attain room temperature. The mixed precipitate of Ag with Au–zinc oxalate was rather fine and uniform in dimension. Ag–Au–zinc oxalate crystals were washed several times with distilled water, air-dried overnight and dried at 100 °C for 5 h. It was calcined in the muffle furnace at the rate of 20 °C min^{-1} to reach the decomposition temperature of zinc oxalate (450 °C). After 12 h, the furnace was allowed to cool down to room temperature. The Ag loaded Au–ZnO catalyst was collected and used for further analysis. This catalyst contained 3 wt% of Ag (related to ZnO). Catalysts with 1, 2, 4 and 5 wt% of Ag were prepared with this procedure. The bare ZnO was prepared without addition of $AuCl_3$ and $AgNO_3$. Ag–ZnO and Au–ZnO were prepared by the same procedure with respective precursors.

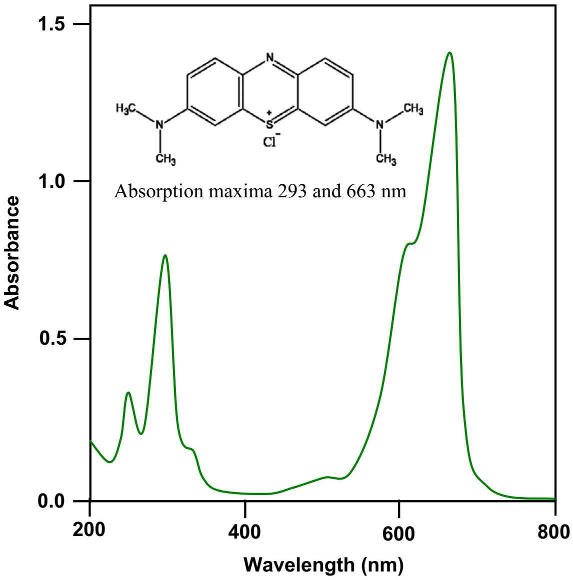

Fig. 1. The structure and UV–vis spectrum of MB.

2.3. Analytical methods

Powder X-ray diffraction patterns were obtained using X'Per PRO diffractometer equipped with a CuKα radiation (wavelength 1.5406 Å) at 2.2 kW Max. Peak positions were compared with the standard files to identity the crystalline phase. The transmission electron microscopic (TEM) observation was carried out on a Hitachi H-7000, Japan, with an acceleration voltage of 100 kV. The specimens were prepared by depositing a drop of the suspension of sample powder, which was ultrasonically dispersed in acetone for 10 min, on a carbon-coated copper grid, followed by drying at room temperature. On observation with a JEOL JSM-6500F cold field emission scanning electron microscope (FE-SEM), the samples were mounted on a gold platform placed in chamber. Energy dispersive X-ray spectrum (EDS) was examined using a JEOL-JSM 5610 LV. Diffuse reflectance spectra (DRS) were recorded using Shimadzu UV-2450. Photoluminescence (PL) spectra at