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The influence of noble metals on photocatalytic activity of ZnO for Congo red degradation

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ABSTRACT

The most suitable method to improve the photocatalytic activity of semiconductors is doping of noble metallic nanoparticles on them. In this research, Au, Ag and Pd noble metals were separately doped on ZnO nano photocatalysts by borohydride reduction method. The as-prepared doped on ZnO nano photocatalysts were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), energy dispersive spectroscopy (EDS), inductively coupled plasma optical emission spectroscopy (ICP-OES), ferromagnetic resonance (FMR) and UV–Vis diffuse reflectance/absorbance spectroscopy (DRS). The photocatalytic activities of nano photocatalysts were evaluated by the degradation of Congo red (CR) dye under UV irradiation. It was found that noble metals doped ZnO nano photocatalysts could significantly increase the photocatalytic activity of ZnO. When we compared the enhancing effects of Au, Ag and Pd, it was found that Pd was more effective than others. The differences in activities of various noble metals doped ZnO may be related differences in the amount of reducing noble metals, in their work functions and in their heights of Schottky barriers. The results of these studies demonstrate that doping of noble metals on ZnO can delay significantly the recombination process of the electron–hole pairs generated by the photon absorption and consequently improve the photocatalytic activity of the ZnO.

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Introduction

The dyestuffs from the textile and dye industries are the major sources of environmental pollution [1]. The presence of these pollutants in water is highly toxic and hazardous for the environment and living organisms. Many different techniques have been applied for water treatment such as coagulation, flocculation, membrane filtration, adsorption and specially the photocatalysis [2].

Among these techniques, photocatalysis is an effective and applicable method to degrade the organic contaminants dyes in wastewater. Therefore, nano-sized metal oxide semiconductors have shown good photocatalytic activity for water purification under irradiation due to their special optical and electrical properties [3]. ZnO is one of the technologically important semiconductors and has been widely used as a photocatalyst because of its large area-to-volume ratio, direct wide band gap (3.37 eV), high photosensitivity, low cost and

high chemical stability [4,5]. One of the major disadvantages of ZnO as a photocatalyst is the rapid electron/hole recombination, which is faster than the surface redox reactions and limits the photodegradation reaction under normal conditions [5–7]. Many studies have been reported to prevent recombination of electron/hole pairs and improve photocatalytic activity of ZnO, such as using ZnO with noble metals (e.g., Au, Ag, Pt, or Pd) [8–11], metals (Fe, Mg, Ca and Al) [12], metal oxide [13,14] and carbon materials (graphene and graphene oxide) [15]. As a principle, doping ZnO nanomaterials by noble metals prevents the recombination of photoinduced electrons and holes, broadens the absorption spectrum and facilitates some specific reactions on the surface of catalysts. The noble metals such as palladium and gold were used for the ZnO–metal formation because they have high electron affinity behavior [16,17] and produce the highest Schottky barrier when between metal and semiconductor. Fermi levels of Au (E_F,Au), Ag (E_F,Ag) and Pd (E_F,Pd) are lower than the conduction band edge of ZnO (4.2 eV), so Au, Ag and Pd accumulate photogenerated electrons during photoexcitation of ZnO and lead to increase the photocatalytic efficiency [18–20].

Herein, ZnO nanoplates were successfully fabricated by microwave-hydrothermal method. The Ag, Au and Pd noble metals were separately doped on ZnO nano photocatalysts by borohydride reduction method. We have compared effect of Au, Ag, and Pd doped ZnO photocatalysts on the photocatalytic degradation of Congo red (CR) in the presence of UV irradiation. Congo red ($C_{32}H_{22}N_6Na_2S_2O_6$) is a benzidine-based anionic diazo dye prepared by coupling tetrazotised benzidine with two molecules of naphthionic acid [21]. Benzidine is a toxic metabolite of CR, a known human carcinogen. Therefore, the CR removal from wastewater is crucial important to prevent its toxicity for aquatic life. Improved photocatalytic activity of ZnO by doping noble metals may be attributed to dispersion of high metal nanoparticles on ZnO surfaces or incorporation in ZnO lattice, enhancement of light absorption of ZnO and the differences of work functions of noble metals-ZnO systems.

Materials and methods

Materials

Zinc chloride ($ZnCl_2$, Merck), sodium hydroxide (NaOH, Merck), palladium chloride ($PdCl_2$, Alfa-Aesar), Au solution ($HAuCl_4$, Merck), silver nitrate ($AgNO_3$, Carlo Erba), sodium borohydride ($NaBH_4$, Merck), CR (commercial grade), and ethanol (Merck) were purchased and used without further purification. All compounds except CR were of reagent grade. Deionized water was used throughout the entire experiments.

Preparation of photocatalysts

The ZnO powder was prepared by microwave-assisted hydrothermal process. The preparation method of undoped ZnO powders is as follows: 0.50 g of $ZnCl_2$ was dissolved in 10 mL of distilled water and then 10 mL 0.80 g of NaOH solution was added dropwise into the solution and stirred for 1 h to obtain a milky solution. The resulting solutions were transferred to

and sealed in a 100 mL Teflon-lined autoclave, placed into a reactor, and then heated to160 °C in a microwave oven (CEM Mars 5 model) with a controlled power of 700 W for 5 min and then cooled at room temperature naturally. The precipitate was centrifuged at 8000 rpm for 5 min, washed with distilled water and absolute ethanol several times, and then dried in an oven at 60 °C for 24 h.

Noble metal-doped photocatalysts were prepared by borohydride reduction method. Required amount of the salt solution of the metal for doping was added to 100 mg of ZnO and dispersed in 40 mL of distilled water. The weight ratio of Au, Ag and Pd to ZnO in this representative reaction was 5%.Then 0.0175 M 20 mL sodium borohydride solution as a reducing agent was added dropwise to the mixture and stirred for 1 h at room temperature to reduce adsorbed metals ions to metallic nanoparticles onto ZnO surface. The precipitate was collected by centrifugation at 8000 rpm for 5 min and washed distilled water and absolute ethanol several times, and then dried in an oven at 60 °C for 24 h.

Characterization of photocatalysts

The obtained samples were confirmed by powder X-ray diffraction (XRD, RIGAKU D max 2200 X-ray diffractometer with Cu KR (λ) 0.154 nm radiation) in the 2θ angles ranging from 10 to 90. The morphologies of Au/ZnO, Ag/ZnO, Pd/ZnO and undoped ZnO nano photocatalysts were characterized by using a field emission scanning electron microscopy (FESEM, FEI QUANTA FEG 450). The surface compositions of the samples were identified by energy dispersive spectroscopy (EDS). The Au, Ag and Pd contents of the photocatalysts were determined by an inductively coupled plasma-optical emission spectrometer (ICP-OES, Spectro Analytical Instruments, Kleve, Germany). FMR measurements have been carried out at room temperature using a commercial EMX X-Band (9.51 GHz) spectrometer, which is equipped with pole-cap providing a dc magnetic field up to the 22 kG magnetic field. The UV–Vis absorption spectra of the CR solution and photocatalysts were obtained by using a UV–visible spectrophotometer (UV–Vis, Shimadzu UV-2600PC). The diffuse reflectance of the photocatalysts was measured by using a UV–visible spectrophotometer fitted with a diffuse reflectance attachment. The band gap energies of the nano photocatalysts were determined by the Kubelka–Munk function, F(R) and by extrapolating the $[F(R)h\nu]^{1/2}$ versus photon energy ($h\nu$).

Photocatalytic testing

Photocatalytic activities of as-prepared photocatalysts were evaluated by degradation of CR in water under UV irradiation of a 100 W UV light (the strongest emission at 365 nm). For each experiment, 50 mg of photocatalyst was dispersed in 100 mL of 16 mg/L of the CR aqueous solution. Prior to UV irradiation, the suspensions were stirred magnetically for 30 min in the dark conditions to ensure establishment of adsorption/desorption equilibrium of CR on surfaces of the photocatalysts in the aqueous solutions. 5 mL of the aliquots were sampled at predetermined time intervals, centrifuged and analyzed by recording variations in the absorption band