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Original Research Paper

Photocatalytic properties of Au/Fe_2O_3 nano-composites prepared by co-precipitation

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ABSTRACT

Nano-composites of Au/Fe_2O_3 with different Au concentrations were prepared by a co-precipitation method. The microstructure and phase analysis of the nano-composites were carried out by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The compositions of the powders were confirmed by energy dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS). Band gaps of the powders were analyzed by UV–Vis spectroscopy. The photocatalytic property of the nano-composites was analyzed for methylene blue (MB) degradation and the powders with 0.5 mol of Au show the best photocatalytic degradation efficiency toward methylene blue dye. Evaluation of the reaction conditions for Au(0.5)/Fe_2O_3 was also carried out at different process conditions such as reaction temperature, light intensity, and pH.

1. Introduction

Limited availability of nonrenewable energy sources has directed the focus of researchers toward photocatalytic materials, materials that use solar radiation. Photocatalytic materials have applications in various fields such as water splitting for hydrogen production [1–3], removal of organic and inorganic pollutants from water [4–6] as well as from air [7–9], deactivation of microorganisms from water [10,11] and artificial photosynthesis [12,13], self cleaning applications [14,15] and solar cells [16,17].

An ideal photocatalyst should have good photoactivity, should be able to absorb near ultraviolet (UV) or visible (Vis) wavelengths of light, must be biologically and chemically inert, inexpensive and non-toxic and must resist photo corrosion.

There are many semiconductors that are photocatalytic such as CdS, ZnS, TiO_2, ZnO, SnO_2 and WO_3. Most of these oxides have an absorption edge only in the UV region which limits the range of the solar spectrum in which they are useful. Although sulfides and nitrides have a lower band gap than oxides, the stability of these materials in an aqueous medium is a major disadvantage. Compared to other photocatalytic materials, Fe_2O_3 has a lower band gap (~2.0 eV), which allows ~40% of solar radiation to be utilized. Due to its lower band gap, it has a band edge in the visible range. Fe_2O_3 is stable in most aqueous solutions (pH > 3), and is one of the least expensive semiconductor materials available. The valence band (VB) edge of Fe_2O_3 is lower than the water oxidation potential, which makes Fe_2O_3 a potential candidate material for water splitting applications to produce hydrogen (H_2). Disadvantages of Fe_2O_3 include a high recombination rate and low hole diffusion length (2–4 nm) [18,19]. The basic mechanism behind the photocatalytic properties of Fe_2O_3 is as follows [20].

$$Fe_2O_3 \rightarrow Fe_2O_3\ (e^- + h^+)$$
$$h^+ + H_2O \rightarrow HO^{\cdot} + H^+$$
$$O_2 + e \rightarrow O^{2-}$$
$$O^{2-} + 2H^+ + e^- \rightarrow H_2O_2$$
$$HO^{\cdot} + H_2O_2 \rightarrow HOO^{\cdot} + H_2O$$
$$HOO^{\cdot} + Fe^{3+} \rightarrow Fe^{2+} + H^+ + O_2$$
$$Fe^{2+} + H_2O_2 \rightarrow HO^{\cdot} + OH^-$$
$$HO^{\cdot} + Dye \rightarrow Dye_{oxd}$$

Many methods have been adapted to improve photocatalytic properties, including synthesizing materials in different morphological nano-structure forms [21–24], doping with different materials [25,26], forming composites [27–29] and preparing hetero structures [30–33]. All these techniques help to improve the photocatalytic properties of the photocatalyst by increasing the surface area and lowering the recombination effect of electrons (e^-) and holes (h^+). Addition of noble metals is one useful technique to improve the photocatalytic properties of materials. Adding metals

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to a photocatalyst reduces the recombination effect by trapping the e^- which is generated during the photo-excitation process. Other experimental parameters that affect the photocatalytic property include the pH of the reaction medium, reaction temperature, light intensity and presence of oxidizing agents, because they affect the photocatalytic reaction process [34]. Additions of Au [35–39], Ag [40–42], Pt [37,43–45] and Pd [46–49] to TiO_2, ZnO and Fe_2O_3, have improved photocatalysis.

The present manuscript describes the synthesis of Fe_2O_3 and Au/Fe_2O_3 nano-powders by a co-precipitation technique. The powders were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR) and an UV–Vis technique. The photocatalytic property analysis of the powders was carried out by observing the degradation of methylene blue (MB) dye in the presence of light.

2. Experimental procedure

2.1. Nano-composite preparation

Fe_2O_3 and Au/Fe_2O_3 nano-powders were synthesized by a co-precipitation method from iron nitrate nonahydrate ($Fe(NO_3)_3{\cdot}9\ H_2O$), sodium carbonate (Na_2CO_3) and chloroauric acid ($HAuCl_4$) as starting materials [50]. Aqueous solutions of Fe $(NO_3)_3{\cdot}9\ H_2O$ (1 M) and $HAuCl_4$ (0.1 M) were mixed together to create Fe:Au molar ratios of 50:0, 50:0.05, 50:0.5, 50:1, 50:2.5 and 50:4. The mixed solution was stirred with a magnetic stirrer and heated to 80 °C followed by dropwise addition of Na_2CO_3 (1 M) aqueous solution (~50 ml) till complete precipitation occurred. The final pH of the solution was noted to be ~11. After the precipitates were formed, the solution was cooled to room temperature and left to age overnight. The precipitates were washed with deionized water to remove the Sodium (Na^+) and Chlorine (Cl^-) ions followed by drying at 100 °C. After drying the powders were calcined at 400 °C for 4 h.

2.2. Characterization of the powders

The microstructure and phase identification of the nano-composites were carried out with a Rigaku X-ray diffractometer with Cu $K\alpha_1$ (1.5406 Å) radiation in the 2θ range of 10–90°. The exact 2θ and full width at half maximum (FWHM) values were determined by Gaussian fitting of the peaks. From the FWHM and 2θ values, the crystallite sizes (C) were calculated using the Scherrer formula (Eq. (1)).

$$C = K\lambda/\beta \mathrm{Cos}\,\theta \tag{1}$$

where $\beta = \sqrt{B^2 - b^2}$, is the full width at half maximum (FWHM) after subtracting the instrumental broadening, θ is the diffraction angle, B is the experimental FWHM of the peaks, b is the instrumental broadening for the standard Si powder, K is the Scherrer constant, (~ 0.9), and λ is the wavelength of the X-rays used.

A JSM 6500F thermal field emission scanning electron microscope (FESEM) was used for the micro-structural and the compositional analysis of the powders. The chemical composition, electronic state and chemical state of the elements present in the nano-composites were analyzed using a Thermo Scientific K_α XPS spectrometer. The nano-composites were analyzed by a Thermo Scientific Nicolet 380 FTIR Spectrometer to determine if any chemical changes occurred in the nano-composites after the photocatalytic reaction. The optical properties such as absorption edge and band gap of the powders were analyzed by a Mecasys optizen pop UV–Vis spectrophotometer in the range of 200–800 nm.

2.3. Photocatalytic property analysis

Photocatalytic properties of the nano-composite powders were analyzed with respect to MB dye degradation in the presence of a 100 W white bulb as a light source. Catalyst (0.05 g) was added to 100 ml of MB solution (5 ppm) and stirred for 30 min using a hot plate and magnetic stirrer. The catalyst and MB solution mixture was exposed to light for 12 h. The schematic of the photocatalytic reaction system is shown in Fig. 1. After 12 h, 10 ml of the sample was withdrawn using a pipette and the catalyst powders were separated from the MB solution using a centrifuge. Absorbance of the supernatant liquid was recorded in the range of 200–800 nm using a Mecasys optizen pop UV–Vis spectrophotometer. The absorbance value at 665 nm is used for calculating the % degradation (D) of MB dye after a 12 h photocatalytic reaction (Eq. (2))

$$D = [(A_0 - A)/A_0] * 100 \tag{2}$$

where A_0 is the absorbance of the initial MB dye solution and A is the absorbance of the MB dye solution after 12 h of exposure to light. The photo catalytic properties of the nano-composites were analyzed for different Au concentrations, pH values of reaction media, light intensities, amounts of catalyst and reaction temperatures. The photocatalytic reactions were repeated four times using the same powders after washing, to analyze the reusability of the powders.

3. Results and discussion

The Au/Fe_2O_3 nano-composites that were prepared by a co-precipitation method were characterized by many techniques followed by photocatalytic property analysis that involved degrading the MB dye.

3.1. Characterization

3.1.1. X-ray diffraction analysis (XRD)

Fig. 2 shows the XRD pattern of the Fe_2O_3 and Au/Fe_2O_3 nano-powders with different Au concentrations. The XRD pattern shows the presence of poly-crystalline α-Fe_2O_3 (DB card number #01-076-4579) with reflections from (012), (104), (110), (113), (024), (116), (122), (214), (300), (1010), (217) and (134). The absence of any other peaks implies that the powder contains a phase with pure α-Fe_2O_3 and there are no other impurities in the samples. The XRD patterns also confirm the presence of elemental Au and shows peaks from the cubic phase of Au (DB card number # 03-065-8601) with reflections from the (111), (200) and (220) planes. The XRD pattern of the nano-composites with 0.05 and

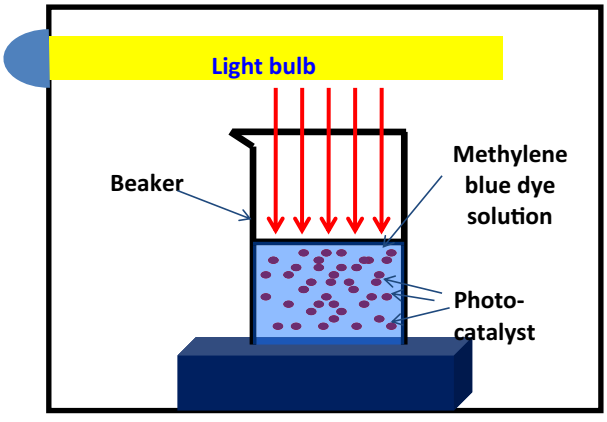

Fig. 1. Schematic of the photocatalytic property analysis reaction set-up.