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Visible light improved, photocatalytic activity of magnetically separable titania Nanocomposite

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Introduction

The titanium dioxide (TiO_2) semiconductor photocatalyst has been widely applied to various environmental applications including water, wastewater and air [1–3]. Various types of application specific photocatalytic reactor configurations have been proposed till date to degrade undesirable organics present in water and wastewater [2]. In general, immobilized reactor is preferred over slurry type reactor because the removal of nano-size titania particles requires an additional filtration adding up the treatment cost. Unfortunately, the immobilization leads to reduced reaction surface area per unit volume of the reactor [4–6].

In recent times, titania with magnetic property have been reported to ensure the recovery and reuse of the catalyst for the wastewater treatment [7]. Generally, photocatalytic reaction is conducted in a suspension of submicrometer-sized TiO_2 [8]. Removing such fine particles from huge volume is not economical. This presents a major drawback to the application of the photocatalyst for treating water and wastewaters. Hence TiO_2 photocatalyst with ferromagnetic property has evolved as a mean to resolve such difficulty of separation from the treated water, simply by applying an external magnetic field [9–14]. Till date few reports have been published. But most of them focused on soft ferromagnetic materials, like magnetite (Fe_3O_4) and maghemite (_-Fe_2O_3) [12,13,15–17]. Regrettably, the nano-sized core magnetic materials are easily oxidized and transform rapidly when the temperature is raised beyond 400 ◦C [9,18]. Therefore, it is intrinsically difficult to produce titania photocatalyst without losses of magnetic property.

Recently many extensive efforts have been made in the development of TiO_2 photocatalyst that can efficiently utilise visible light [19–22], since the conventional TiO_2 is photo active only under ultraviolet (UV) radiation and cannot excite under visible light spectrum [23]. In addition, a low quantum yield is also observed due to relatively high recombination rate of photo-generated electron–hole (e^-/h^+) pairs from TiO_2 itself [24,25]. Only a very few electrons (e^-) in the conduction band (CB) have high enough energy that can overcome the potential barrier to reach the surface [26]. The bulk property of TiO_2 resulted in increased recombination possibility of electron–hole (e^-/h^+) pairs during the photocatalytic reaction. To overcome both the issue, Wang et al. [27] suggested that doping can lower the energy below the conduction band (CB) of TiO_2. Thus the photo-generated electrons (e^-) in the conduction band (CB) can transfer to the surface via this doping energy level, without crossing over the potential barrier, and take part in photocatalytic process [27]. As a result, more photo-generated electrons (e^-) and holes (h^+) can contribute to the photocatalytic reaction, resulting in enhancement of photocatalytic activity of the catalyst under visible light [27].

Furthermore, numerous efforts have been made such as surface modification [28–31], doping TiO_2 with metal ions [6,32,33] and combining TiO_2 with other semiconductors [34–36]. Sikong et al. [6] in their work prepared Fe doped TiO_2/SnO_2 by sol–gel method and photoactivity was investigated for E. coli killing. The E. coli was completely killed within 90 min under UV radiation and almost 100% under visible light exposure [6]. Metal coating has proved to improve photocatalytic efficiency of a semiconductor under visible light spectrum. The deposition of noble metals (NM) like Pt, Au, Ag, Pd and Rh on photocatalyst surface will also improve the photocatalytic efficiency [37,38]. As the photo-generated holes (h^+) react with adsorbed species, the electrons (e^-) might be accumulated on the semiconductor particles, leading to an increase of the recombination process. Oxygen (O_2) is habitually used as electron scavenger and equal role could be fulfilled by metal deposits acting as electrons (e^-) trapping [39,40].

Hence the major objectives of the present work are to prepare visible light improved Titania nanocomposite photocatalyst with additional ferromagnetic property for reuse. The objectives were achieved by supporting a transition ferromagnetic oxide material namely nickel ferrite ($NiFe_2O_4$), by simple modified sol–gel technique along with hydro-thermal method. The photocatalytic activity of the prepared catalysts was investigated by degrading a bio-recalcitrant and toxic pesticide pollutant viz., 2,4-dichlorophenol (2,4-DCP) under bright and diffused sunlight irradiation condition.

2. Materials and methods

2.1. Synthesis of photocatalysts

All chemicals were of analytical grade. Milli-Q water (>18.2 M _ cm) was used for all experiments. Titanium tetrabutoxide

($Ti(OC_4H_9)_4$) (97%) was used as a precursor to synthesize TiO_2 sol by partial hydrolysis and poly-condensation with water (H_2O). Nitric acid (HNO_3) was used as catalyst and isopropyl alcohol (IPA) as a solvent. The titanium tetra-butoxide ($Ti(OC_4H_9)_4$): water (H_2O) in a mole ratio of 1:2 was prepared approximately. The mixture then was stirred vigorously with a magnetic stirrer for more than an hour. Finally, it resulted in a coloured transparent solution and calcined in atmospheric air for an hour at 500 ◦C.

Nickel ferrite ($NiFe_2O_4$) nanoparticle was synthesized by mixing iron (III) nitrate nanohydrate ($Fe(NO_3)_3{\cdot}9H_2O$) solution (3 M, 60 mL) and nickel (II) nitrate hexahydrate ($Ni\ (NO_3)_2{\cdot}6H_2O$) solution (1.25 M, 60 mL) in 1:2 (mole) for Ni^{2+}/Fe^{3+}. Potassium hydroxide (KOH) solution (6–7 M) was added slowly into the mixture solution until pH 9.5–10, followed by ferrous (II) chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$) solution (1.25 M) under vigorous stirring. The pH value of it was adjusted to ca. 10.0 by the drop wise addition of prepared KOH solution. Then it was kept boiling and refluxing for 2 h under vigorous stirring. Finally, the synthesized $NiFe_2O_4$ nanoparticles dispersion was repeatedly washed by centrifugation to prevent agglomeration of the nanoparticle.

Silica (SiO_2) coating was provided to $NiFe_2O_4$ in order to avoid the influence of magnetization onto the photocatalytic property and vice versa. This was achieved by adding aqueous sodium polyphosphate ($(NaPO_3)_6$) solution (5%) using 5 g $(NaPO_3)_6$ and 100 g of Milli-Q water. The aqueous solution was then added into 150 mL of $NiFe_2O_4$ dispersion. As to get the mixed dispersion with 16 wt.% $(NaPO_3)_6$ for $NiFe_2O_4$, 3.62 g of $NiFe_2O_4$ was added into distilled water and made up to 150 mL dispersion. It was followed by the addition of 35 mL of sodium trisilicate ($Na_2O{\cdot}3SiO_2$) solution into the dispersion. The dispersion was sonicated for 15–20 min in ultrasonic water bath and followed by heating at 90–100 ◦C on a magnetic stirrer provided with heater. The pH value of the dispersion was adjusted to ca. 10.0 by titrating sulphuric acid (H_2SO_4) solution (5%) under vigorous stirring. Further stirring was carried out at 90–100 ◦C to obtain a viscous dispersion. A thin silica layer was deposited on the $NiFe_2O_4$ nanoparticles dispersion. The silica-coated $NiFe_2O_4$ dispersion was washed by centrifugation and redispersed repeatedly with distilled water to prevent them from agglomeration.

Finally TiO_2 supported $NiFe_2O_4$ magnetic nanoparticle was synthesized by dispersing 0.15 g of $NiFe_2O_4$ dispersion into 1.0 g of TiO_2 in Milli-Q water. The mixture was sonicated for 20 min, dried, grinded and calcined for 30 min at 500 ◦C.

2.2. Characterization of synthesized photocatalysts

The X-ray diffraction (XRD) analysis was performed with Bruker D8 Advance diffractometer using Cuκ_ (_ = 1.5406A˚) radiation, to study the crystal structure and crystallinity of the photocatalyst. The average crystallite size was obtained using the Scherrer's equation (D = k_/˘ cos _). A transmission electron microscope (TEM) (Philips CM-12) was employed to obtain catalyst size and structure at the nanoscale. The samples in ethanol were dispersed using an ultrasonicator (Starsonic, 35) for 15 min and fixed on carbon-coated copper grid. Samples were analysed with FESEM and energy dispersive X-ray spectroscopy (EDS) (Zeiss Auriga®) to detect the surface morphology and characteristic X-ray excited by incident electrons. Brunauer–Emmett–Teller (BET) surface area, pore volume, and Barret–Joyner–Halenda (BJH) pore size distribution (based on nitrogen adsorption and desorption isotherms) were determined by Quantachrome Autosorb Automated Gas Sorption. Prior to determination the samples were degassed for 5 h at 150 ◦C with nitrogen. The fine elemental composition and electronic structure was determined with an X-ray photoelectron spectroscope (KRATOS XPS, Axis Ultra DLD). The binding energies were calibrated with respect to C_{1s} core level peak at 284.6 eV. The magnetization with applied magnetic field was measured by vibrating sample magnetometer (VSM, Lakeshore 7410) at room temperature. It reveals the magnetic properties like coercivity, saturation magnetization and remanence of the synthesized supported photocatalyst. The visible light absorption spectrum (350–800 nm) was obtained with a UV-Vis spectrophotometer (Merck, Spectroquant Pharo 100) and quartz cell (10 mm path length). The prepared catalysts were dispersed in distilled water, and their spectral were examined. The band gap energy (E) was calculated as per the literature report [41] using the following equation:

Full text is available at :

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