

Preparation, characterisation and solar photoactivity of titania supported strontium ferrite nanocomposite photocatalyst

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Introduction

In photocatalytic processes, organic pollutants in water are degraded in the presence of semiconductor photocatalysts (e.g. TiO₂ and ZnO), exciting light sources with band-gap energy and electron acceptors such as oxygen (O₂) [1]. The process gradually breaks down the contaminant molecule, thus zero residues of the original material remain and therefore no sludge requiring disposal to landfills is produced [2,3]. Titanium dioxide (TiO₂) is recognised as one of the best heterogeneous photocatalyst due to its powerful photo-oxidative activity, chemical constancy defiant against photo and chemical corrosion [4], commercial availability and safety. It occurs naturally in three crystallographic phases: rutile, anatase and brookite, with anatase the most commonly employed in photocatalytic applications [5–7]. Anatase is the polymorph of TiO₂, less thermodynamically stable, although from energy calculations this phase appears as the more likely phase when the grain size is ≤ 10 nm [8].

Solid semiconductors are characterised by the existence of a prohibited energy gap for free electrons between the valence band (VB) and the conduction band (CB). The process of photocatalysis is comparatively simple. It is initiated by the absorption of photons with energy equal to or greater than the band gap of the semiconductor (e.g. 3.2 eV for anatase TiO₂), producing electron-hole (e⁻/h⁺) pairs [9–13]. The wide band gap of anatase confines its application to ultraviolet (UV) light (≤ 387.5 nm) activation [13,14]. Since sunlight contains only 5–6% of UV radiation in its electromagnetic spectrum, an external UV source is often needed to maximise the photoactivity of such TiO₂ photocatalyst [13,14]. Although the thermodynamically stable rutile phase can absorb visible light (up to 412 nm), its activity is inadequate as a result of a typically low surface area, low redox potential and a faster e⁻/h⁺ recombination rate [15].

The development of photocatalysts that can be activated by visible light is necessary to effectively exploit a wider spectrum of radiation from sunlight or from artificial light sources [15] in photocatalytic processes. Hence, many attempts have been employed to improve the efficiency of TiO₂ photocatalyst in utilising solar light (daylight) as the irradiation source. One

such adaptation is made by coating/supporting the semiconductor photocatalyst with metals. Metal outside layer has been certified as an enhanced method to improve the photocatalytic efficiency of a semiconductor under the visible light spectrum. Deposition of noble metals (NM) such as Pt, Au, Ag, Pd and Rh on the semiconductor surface has been considered to improve the photocatalytic efficiency [16,17]. As the photo-generated holes ($h\nu$) react with adsorbed species, the electrons (e^-) might be accumulated on the semiconductor particles, leading to an increase of the recombination process. O_2 is normally used as an electron scavenger and equal role could be fulfilled by metal deposits acting as electron traps [18–21]. Moreover, exterior coating of nanoparticles with various functional materials to form core–shell morphologies resulted in the development of composite materials that can be used for the improvement of catalysts and optoelectronic devices [22–25].

Generally, a photocatalytic reaction is performed in a suspension of small size of TiO_2 which requires an extra separation step to remove the catalyst from the treated water [26]. This method yields faster pollutant removal rates compared with when the catalyst is supported on a fixed surface. However, removing the catalyst from large volumes of water involves extra cost and manpower. This presents a foremost drawback to the application of suspensions of photocatalysts for treating water and wastewaters. Hence, TiO_2 photocatalysts with added magnetic properties have been proposed to resolve the separation of the suspended catalyst from the treated water, merely by the application of an exterior magnetic field [25,27–32]. Most of these studies primarily focus on TiO_2 supported on soft ferromagnetic materials [30,31,33–35]. However, the nano-sized core magnetic materials are readily oxidised and altered above an annealing treatment temperature of 400_C [27,36]. Therefore, it is very difficult to produce titania-coated particles with high visible light photoactivity without a loss of the magnetic property.

In this study, we have addressed the above limitations by producing, via hydrolysis and polycondensation methods, a ferromagnetic catalyst made of TiO_2 supported on strontium ferrite ($SrFe_{12}O_{19}$) which shows sturdy magnetic properties. The catalyst can be easily recovered and reused. Furthermore, the catalyst enhances the absorption of visible light which makes the catalyst more active under irradiation with sunlight. The photocatalytic activity was evaluated by degrading a bio-recalcitrant and toxic pesticide pollutant, namely 2,4-dichlorophenol (2,4-DCP) under two dissimilar irradiation conditions. This study provides further evidence on the activity, characterisation and stability of magnetic TiO_2 supported on strontium ferrite ($SrFe_{12}O_{19}$) as previously shown by Aziz et al. [37] in their study of nitrogen-doped titania supported $SrFe_{12}O_{19}$.

2. Experimental

2.1. Synthesis of TiO₂ nanophotocatalyst

All chemicals were of analytical grade. Milli-Q water (418.2M_{cm}) was used in each experiment. Titanium (IV) butoxide, (Ti(OC₄H₉)₄) (97%) was used as a precursor to the synthesis of TiO₂ sol via partial hydrolysis and poly-condensation with water (H₂O). Ti(OC₄H₉)₄ was specifically chosen as it has the largest alkoxy groups, which can prevent oligomerisation and increase the rate of hydrolysis and condensation. Nitric acid (HNO₃) was used as the catalyst to enhance hydrolysis and isopropyl alcohol (IPA) was the solvent. The Ti(OC₄H₉)₄:H₂O mole ratio was 1:2. The mixture was then stirred vigorously by a magnetic stirrer exceeding an hour. The resulting coloured transparent solution was calcined at 673.15K for 1 h in a muffle furnace.

2.2. Synthesis of SiO₂-coated SrFe₁₂O₁₉ nanoparticles

Sodium polyphosphate (NaPO₃)₆ aqueous solution (5%) was prepared using 5 g (NaPO₃)₆ and 95 g of Milli-Q water. It was then added into 150mL of SrFe₁₂O₁₉ nanoparticles dispersion. A quantity of 3.62 g of SrFe₁₂O₁₉ nanoparticles powder (99.5%) were added into Milli-Q water and made up to 150mL dispersion in order to get the mixed dispersion with 16wt% (NaPO₃)₆ for SrFe₁₂O₁₉. This was followed by the addition of 33mL of sodium silicate (Na₂O(SiO₂)₃·H₂O) solution (10%) into the dispersion to get 200wt% SiO₂-coated SrFe₁₂O₁₉ nanoparticles dispersion. The formation of 200wt% ensures the proper and uniform coating of SiO₂ onto SrFe₁₂O₁₉ nanoparticles. The dispersion was sonicated at 303.15K for 15 min in an ultrasonic water bath and followed by vigorous stirring with heating at 363.15K on magnetic stirrer. The pH value of the dispersion was modified to pH 10.0 by dropping sulphuric acid (H₂SO₄) solution (5%) upon stirring. Continuous stirring was carried out to obtain a gelatinous dispersion. The SiO₂-coated SrFe₁₂O₁₉ nanoparticles were finally washed by centrifugation and redispersed numerous times with Milli-Q water to avoid agglomeration.

2.3. Synthesis of TiO₂ supported SrFe₁₂O₁₉ nanocomposite photocatalyst

About 6mL of SiO₂-coated SrFe₁₂O₁₉ dispersion (0.15 g) and 1.0 g of TiO₂ were mixed. Then a small portion of H₂O was added to alter the mixture to be a paste. The mixture was sonicated at 303.15K for 15 min, dried, grinded and calcined for 30 min at 673.15 K. Finally, the magnetically separable TiO₂ supported SrFe₁₂O₁₉ nanocomposite photocatalyst was obtained.

2.4. Characterisation of synthesised photocatalysts

The crystal structure and crystallinity of the photocatalyst was investigated by X-Ray diffraction (XRD) measurement performed in a Bruker D8 Advance diffractometer using CuKα

(1.5406 \AA) radiation. The angular 2θ diffraction was varied between 20° and 80° . The data were collected at an angular step of 0.02° at 1 s per step and sample rotation. The average crystallite size was obtained using Scherrer's equation ($D = \frac{k\lambda}{\cos \theta}$). The morphology of the catalysts were investigated by scanning transmission electron microscope (STEM) (Hitachi SU-8000) and transmission electron microscope (TEM) (Philips CM-12) analyses. The nanoparticles were dispersed in ethanol using an ultrasonicator (Starsonic, 35) for 15 min and fixed on lacey formvar and carbon-coated copper grid, respectively to obtain the structure of the synthesised nanocomposite photocatalysts at nanoscale. The inorganic compositions of the prepared photocatalysts were analysed by energy dispersive X-ray spectroscopy (EDS) of Zeiss Auriga FESEM. Brunauer–Emmett–Teller (BET) surface measurements using nitrogen (N_2) as adsorption molecule was carried out with Quantachrome 6B Autosorb Automated Gas Sorption System. The degassing of the sample was carried out for 5 h at 423.15 K. The pore-size distribution (PSD) curve was obtained from the analysis of the desorption portion of the isotherm via BJH (Barrett–Joyner–Halenda) method. X-ray photoelectron spectra (XPS) were acquired from Axis Ultra DLD instrument of KRATOS using monochromatic Al-K α radiation (225 W, 15 mA, 15 kV). The binding energy, (BE) of adventitious C1s (284.9 eV) was used as reference. The functional group transmittance between 500 and 4000 cm^{-1} was performed with Thermo Nicolet iS10 Fourier Transform Infrared Spectroscopy (FT-IR). The vibrational bands were characterised by the frequency (energy), intensity (polarisability) and band shape (environment of bonds). The magnetic properties such as coercivity (H_{ci}), saturation magnetisation (M_s) and remanence (M_r) of the synthesised nanocomposites were measured by a vibrating sample magnetometer (VSM, Lakeshore 7410) at room temperature. The absorption spectra of the as-prepared catalysts were analysed with UV-visible spectrophotometer (Merck, Spectroquant Pharo 100) at ambient temperatures over a wavelength ranging between 350 and 800 nm. Particles were dispersed with distilled water in a quartz cell (10mm path length) and their spectra were examined. The band gap energy (E) was calculated as per the literature report [38] using Equation (1):

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