Highly efficient magnetically separable TiO_2–graphene oxide supported $SrFe_{12}O_{19}$ for direct sunlight-driven photoactivity

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Introduction

The natural environment can be decontaminated from toxic chemicals by photocatalytic oxidation powered by solar light [1]. This process of heterogeneous photocatalysis was initially reported for the splitting of water with light energy for hydrogen (H_2) production [2–5]. Titanium dioxide (TiO_2), an n-type oxide semiconductor that has offered superior oxidation efficiency for many toxic contaminants, is chemically inert and stable in many environments [6]. However, this semiconductor can be photo-activated only by photons in the ultraviolet (UV) region of the solar radiation spectrum (approximately 3–5% of total sunlight) due to its large band gap (3.20 eV for anatase) [1,7,8].

The modification of TiO_2 by single atomic layer of sp_2 carbon atoms (graphene) can produce a novel electronic configuration system and a ''dyade'' structure, which favours the absorption of visible and infrared solar photons (420–800 nm) [9–12]. Furthermore, graphene constrains the recombination of electron–hole (e_-/h_+) pairs and can increase the charge-carrier transfer rate of e_- and the amount of surface-adsorbed species through p–p bond interactions [6,13,14]. Nevertheless, graphene is poorly soluble in water or polar organic solvents, which makes it difficult to deposit metal or metal oxide on its surface to synthesise graphene-based hybrid materials [15]. Unlike graphene, graphene oxide (GO) is hydrophilic due to the oxygen-containing functional groups on the sheet surface [16], which renders the GO a good candidate for supporting metal or metal oxide particles. Moreover, the surface modification of GO allows the individual GO to be suspended in both polar and non-polar solvents. GO has been identified as a suitable candidate for the charge-trapping layer of photoelectric devices. Due to the excellent mobility of charge carriers and charge trapping, both

GO and graphene are excellent e- acceptors.

The separation, recovery and reuse of the catalyst from the reactor after treatment can be enabled by incorporating the photocatalyst structure into alkaline earth hexaferrite with magnetic properties [17–19]. This material offers a potential approach for the recovery and reusability of the photocatalyst [20–22]. Preventing agglomeration and maintaining the durability conditions of the catalysts is vital for any catalytic process [23]. Previous researchers used hard and soft ferromagnetic materials. For example, magnetite (Fe_3O_4) core material, which is described as a soft ferromagnetic material, can straightforwardly be oxidised to maghemite (c-Fe_2O_3) and decrease the saturation magnetisation (M_s) by 12% after annealing treatment. Consequently, a solitary successful attempt has been published [24] that applied only the hard ferromagnetic material to prevent the core oxidation from adversely affecting the separation capability. As a result, zincAnickel (ZnANi) ferrite has been used with the intent of magnetic agitation [25] and magnetic recovery [26,27]. The principal use of a silica (SiO_2) interlayer in a magnetic photocatalyst was described by Chen and Zhao in 1999 [28] and shortly elaborated by Beydoun et al. in 2001 [29]. They indicated that the photoactivity of the magnetic photocatalyst could be increased by adding a SiO_2 interlayer deposited as a shell around the magnetic particles. The increase in the photocatalytic activity was attributed to the prevention of the e_-/h_+ recombination rate between ferrite–TiO_2 interfaces [28,29].

In this study, we reported the synthesis of a novel hybrid photocatalyst made of GO nanofibers supported with TiO_2 and strontium ferrite ($SrFe_{12}O_{19}$) magnetic particles. TiO_2/GO/$SrFe_{12}O_{19}$ is a mixture of TiO_2 crystals, SiO_2/$SrFe_{12}O_{19}$ prepared by liquid catalytic phase transformation and GO prepared by Hummer's method [9,30]. The photocatalyst can harvest solar photons in the UV and visible regions of the electromagnetic spectrum and can be magnetically recovered and reused from an aqueous suspension. The photocatalytic activity was investigated by degrading a bio-recalcitrant and toxic pesticide, 2,4-dichlorophenol (2,4-DCP) under transient sunlight irradiation.

2. Materials and methods

2.1. Materials

Tetrabutyl titanate ($Ti(OC_4H_9)_4$), reagent grade 97%), nitric acid (HNO_3, ACS reagentP90%), 2-propanol (($CH_3)_2CHOH$, P99.7%), graphite nanofiber (C, >95% trace metals), potassium permanganate ($KMnO_4$, 97%), hydrogen peroxide solution (H_2O_2, 30% (w/w) in H_2O), sodium nitrate ($NaNO_3$, P99%), strontium hexaferrite

nanopowder (SrFe$_{12}$O$_{19}$, 99.8% trace metals basis), sodium hexametaphosphate crystalline ((NaPO$_3$)$_6$, 96%), sodium silicate solution reagent grade (NaOH$_x$(Na$_2$OSiO$_3$)$_y$_zH$_2$O), sulphuric acid (H$_2$SO$_4$, 99.999%), hydrochloric acid ACS reagent (HCl, 36.5–38%) and 2,4-dichlorophenol (Cl$_2$C$_6$H$_3$OH, 99%) were purchased from Sigma Aldrich, Malaysia and used without further purification. Milli-Q water (P18.2 MX cm) was used in all experiments.

2.2. Synthesis of TiO$_2$

Ti (OC$_4$H$_9$)$_4$ was used as a precursor to the synthesis of TiO$_2$ sol via partial hydrolysis and poly-condensation with H$_2$O. Ti (OC$_4$H$_9$)$_4$ was specifically chosen because it has the highest amount of alkoxy groups, which can prevent oligomerisation and increase the rate of hydrolysis and condensation. Approximately 3 mL of HNO$_3$ was added dropwise as a catalyst to enhance the hydrolysis process, and (CH$_3$)$_2$CHOH was used as the solvent. The Ti (OC$_4$H$_9$)$_4$:H$_2$O molar ratio was 1:2. The mixture then was stirred vigorously by a magnetic stirrer for over an hour. The resulting coloured solution was calcined at 500 _C for an hour in a muffle furnace [31].

2.3. Synthesis of GO by Hummer's method

Concentrated H$_2$SO$_4$ was added to a mixture of graphite nanofibers (1.0 g, 1 equiv wt) and NaNO$_3$ (0.75 g, 0.5 equiv wt). The mixture was cooled to 0 _C. KMnO$_4$, which acts as a strong oxidising agent (3.0 g, 3 equiv wt), was slowly added in portions to maintain the reaction temperature below 20 _C. The reaction was increased to 35 _C and stirred for 30 min, after which Milli-Q water (175 mL) was slowly added. This process produced a large exothermic reaction, which raised the temperature to 98 _C. External heating was introduced to maintain the reaction temperature at 98 _C for an additional 15 min. The mixture was then cooled in a water bath to ambient temperatures (_21 _C) for 10 min. An additional 1.5 mL of Milli-Q water and 1.5 ml of 30% H$_2$O$_2$ were added, which produced another increase in the temperature. After air-cooling, the mixture was filtered by centrifugation (2500 rpm, 1 h) and washed repeatedly with both 1 M HCl and Milli-Q water. Finally, the product was dried at 60 _C for 24 h to obtain GO.

2.4. Synthesis of TiO$_2$/GO

GO (3 wt%) was dissolved in Milli-Q water, and TiO$_2$ powder (1 wt%) was added to the GO solution. The mixture was sonicated for 1.5 h. The mixture was further stirred for 12 h at room temperature (without heating) to obtain a homogeneous solution. The product was centrifuged (2500 rpm, 1 h) and dried at 100 _C.

2.5. Synthesis of SiO$_2$/SrFe$_{12}$O$_{19}$ dispersion by liquid catalytic phase transformation

Approximately 100 ml of a (NaPO$_3$)$_6$ aqueous solution (5%) was added to 150 mL of a SrFe$_{12}$O$_{19}$ dispersion. Initially, 3.62 g

of $SrFe_{12}O_{19}$ was added to Milli-Q water and diluted to 150 mL
to obtain the $SrFe_{12}O_{19}$ dispersion. Subsequently, 33 mL of
$Na_2O\_3SiO_2$ solution (10%) were added to the mixed dispersion
to obtain a 200 wt% $SiO_2/SrFe_{12}O_{19}$ dispersion. The dispersion
was sonicated for 15 min in an ultrasonic water bath, followed
by heating to 90 _C on a magnetic stirrer provided with a heater.
The pH value of the dispersion was adjusted to ca. 10.0 by titrating
with a H_2SO_4 solution (5%) under vigorous stirring. Further
stirring was carried out at 90 _C to obtain a viscous dispersion.
A thin SiO_2 layer was deposited on the $SrFe_{12}O_{19}$ nanoparticles.
The SiO_2-coated $SrFe_{12}O_{19}$ nanoparticles were repeatedly washed
by centrifugation and re-dispersion in Milli-Q water to prevent
agglomeration [32].

2.6. Synthesis of $TiO_2/GO/SrFe_{12}O_{19}$

Approximately 6 mL of the SiO_2-coated $SrFe_{12}O_{19}$ dispersion
and 1 g of TiO_2/GO were mixed. A small portion of water was then
added to alter the mixture to a paste. The mixture was sonicated
for 15 min, dried, ground and annealed for 30 min at 400 _C to obtain
the sunlight-driven and magnetically separable $TiO_2/GO/$
$SrFe_{12}O_{19}$ composite photocatalyst.

2.7. Characterisation

Structural/physical properties were characterised by X-ray diffraction
(XRD) in terms of the crystal system and lattice. The crystallography
was identified using a Bruker diffractometer (D8) with
a $CuK\alpha$ emission of wavelength (k) 1.5406 Å. The angular $2h$ diffraction
was varied between 10_ and 80_, and the data collection
was completed using a step size of 0.02_ with a step time of 1 s.
The XRD patterns were compared with the Joint Committee on
Powder Diffraction Standards (JCPDS). The crystallite sizes were
calculated using the Debye–Scherrer equation.
To determine the morphology, orientation of materials and
inorganic elemental compositions, field emission scanning electron
microscopy (FESEM), scanning transmission electron microscopy
(STEM) (Hitachi SU8000) equipped with an energy dispersive
X-ray (EDX) silicon drift detector (SDD) and high resolution
transmission electron microscopy (HRTEM) (Carl Zeiss Libra 200
FE) analyses were performed. Prior to HRTEM analysis, each
sample was suspended in ethanol (C_2H_6O), dispersed by sonication
(Starsonic, 35) for 15 min and fixed on the lacey formvar carboncoated
copper grid.
The physical phenomenon (surface interaction) or so-called
physisorption of the materials was investigated by a Brunauer–
Emmet–Teller (BET) analysis. BET was performed using a Quantachrome
Autosorb 6B. The sample was degassed for 5 h at 150 _C.

The paramagnetism and unpaired electron behaviour of TiO_2 was evaluated by electron spin resonance (ESR) using a Bruker EMX plus at room temperature.

The organic compound content in the materials was determined by Fourier transform infrared spectroscopy (FTIR). The spectra were recorded on a Thermo Scientific iS10 from 500 to 3500 cm_{-1}. Raman scattering is a useful non-destructive tool to characterise carbonaceous materials, particularly for studying ordered and disordered carbon structures. Raman scattering was performed using a Perkin Elmer Raman Micro-200 at a frequency of radiation of $4.0–7.5E_{14}$ Hz and wavelength range between 500 and 2500 nm. The elemental analysis and quantification of elements were carried out using a Kratos X-ray photoelectron spectroscope (XPS) Ultra DLD. The binding energy (BE) of C1 s = 284.5 eV was used to internally calibrate the energy scale.

The magnetochemistry and correlation between the magnetisation and applied magnetic field intensity (MAHloop) were recorded by a MicroMag alternating gradient force magnetometer (AGM). The mass changes and transformation energies of materials were investigated by a thermo-gravimetric analysis and differential scanning calorimetry (TGA/DSC) using STA 449 F3Jupiter_. The optical absorption, especially the shift of the absorption edge, was evaluated using a UV–Vis (Shimadzu UV-2600) equipped with a diffuse $BaSO_4$ reflectance integrating sphere (DRS) at ambient temperatures between 200 and 800 nm. The reflectance data were converted to the absorption coefficient F (R_1) values according to the Kubelka–Munk function to calculate the band gap energy.

2.8. Photoactivity evaluation

A stock solution of 1000 mg L_{-1} of 2,4-DCP was prepared. Approximately 250 ml of a working solution (50 mg L_{-1}) of 2,4-DCP was prepared from the stock solution (1000 mg L_{-1}). Typically, 1 g of prepared photocatalyst was mixed in a batch quartz cylindrical reactor of 500 mL capacity. The suspension was constantly magnetically stirred under direct sunlight at the University of Malaya, Kuala Lumpur (latitude 101_39_0E and longitude 3_7_0N) from 0900 to 1400 h in June, 2012. The solar luminance was measured using a LT Lutron LX-101 Light Meter, and the average luminance over the duration of each run was calculated. The conversion of photon flux (lx) to power (W m_{-2}) depends on the spectrum of the lamp. For sunlight (AM 1.5), $1000Wm_{-2}$ corresponds to _120 000 lx [33]. Two millilitres of the suspension were withdrawn at given intervals, centrifuged at 10,000 rpm, filtered through a Millipore 0.25 Im and analysed by Ultra Performance Liquid Chromatography (Waters Acquity UPLC H-Class; Acquity UPLC BEH C_{18}

column, 100 mm $\times$ 2.1 mm, 1.7 İm particle size; 60% acetonitrile
(CH_3CN), 40% H_2O eluent). The TiO_2/GO/$SrFe_{12}O_{19}$ photocatalyst
was recycled for another two runs. The first run was carried out
with a prepared virgin photocatalyst under 769.9Wm$_2$ of sunlight.
Run 2 was performed under 775.6Wm$_2$ of sunlight intensity
with the recovered photocatalyst. The final cycle was
performed under 487.2Wm$_2$ of sunlight intensity. The inconsistencies
in the solar irradiation were due to its transient nature
and local weather condition.

Full text is available at :