Highly efficient magnetically separable TiO2–graphene oxide supported SrFe12O19 for direct sunlight-driven photoactivity

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HIGHLIGHTS

• Natural energy active recoverable TiO2/GO/SrFe12O19 photocatalyst was synthesized.
• Resulted in fine band gap (~1.8 eV), improved utilisation between 400–800 nm.
• Achieved ~98% mass recovery with dominant ferromagnetic susceptibility.
• Demonstrated superior solar photoactivity by degrading 2,4-DCP successfully.

ABSTRACT

A highly solar photoactive, magnetically separable, TiO2–graphene oxide supported SrFe12O19 (TiO2/GO/SrFe12O19) photocatalyst was synthesised via the solid reaction of silica (SiO2)-coated SrFe12O19 with TiO2 and GO, which were produced by a hydrothermal reaction and Hummer’s method, respectively. Several aspects of the material chemistry of the prepared photocatalyst were explored: its crystallite phase, particle size, surface morphology, inorganic elemental composition, adsorption–desorption hysteresis, BET surface area, organic functional group, chemical state of surface, magnetic hysteresis, coercivity (Hci), saturation magnetisation (Ms), remanence (Mr), thermal property and visible light absorption analysis. The synthesised TiO2/GO/SrFe12O19 exhibited greater ferromagnetic properties (Hci: 2103 Oe; Ms: 3.406E-3 - emu g⁻¹; Mr: 1.642E⁻3 emu g⁻¹), which further enhanced its re-usability. The incorporation of GO and SrFe12O19 resulted in a drastic reduction in the bandgap energy (1.80 eV). Moreover, this incorporation contributed for the higher visible light absorption. The photocactivity of TiO2/GO/SrFe12O19 was evaluated under direct sunlight for the degradation of 2,4-dichlorophenol (2,4-DCP). The degradation over a period of 5 h suggested excellent photoactivity.
The modification of TiO$_2$ by single atomic layer of sp$^2$ carbon atoms (graphene) can produce a novel electronic configuration system and a “dyad” 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 n–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 catalyst is vital for any catalytic process [23]. Previous researchers used hard and soft ferromagnetic materials. For example, magnetite (Fe$_3$O$_4$) core material, which is described as a soft ferromagnetic material, can straightforwardly be oxidised to maghemite ($\gamma$-Fe$_2$O$_3$) 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, zinc–nickel (Zn–Ni) 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 photocactivity 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$_4$H$_9$)$_4$), reagent grade 97%), nitric acid (HNO$_3$, ACS reagent >90%), 2-propanol ((CH$_3$)$_2$CHOH, >99.7%), graphite nanofiber (C, >95% trace metals), potassium permanganate (KMnO$_4$, 97%), hydrogen peroxide solution (H$_2$O$_2$, 30% w/w in H$_2$O), sodium nitrate (NaN$_3$, >99%), strontium hexaferrite nanopowder (SrFe$_{12}$O$_{19}$, 99.8% trace metals basis), sodium hexametaphosphate crystalline ([NaPO$_3$]$_6$, 96%), sodium silicate solution reagent grade (Na$_2$O$_n$(Na,OSiO$_3$)$_{1-x}$H$_2$O), sulfuric acid (H$_2$SO$_4$, 99.999%), hydrochloric acid ACS reagent (HCl, 36.5–38%) and 2,4-dichlorophenol (Cl$_2$C$_6$H$_4$OH, 99%) were purchased from Sigma Aldrich, Malaysia and used without further purification. Milli-Q water (\(>18.2\,\text{M} \Omega\text{-cm}\)) 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 alkyl 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 NaN$_3$ (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$_2$O: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$_2$SO$_4$ 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 Cu K$_\alpha$ emission of wavelength (λ) 1.5406 Å. The angular 2θ diffraction was fixed 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–Scherer 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$_2$H$_5$OH), dispersed by sonication (Starsonic, 35) for 15 min and fixed on the lacey formvar carbon-coated copper grid.

The physical phenomenon (surface interaction) or so-called physisorption of the materials was investigated by Fourier transform infrared spectroscopy (FTIR). The spectra were recorded on a Thermo Scientific i510 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 40–7.5e$^{14}$ 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 spectroscopy (XPS) Ultra DLD. The binding energy (BE) of C1 s = 284.5 eV was used to internally calibrate the energy scale.

The magnetoochemistry and correlation between the magnetisation and applied magnetic field intensity (M–H loop) were recorded by a MicroMag alternating gradient force magnetometer (AGM).

The mass changes and transformation energies of materials were investigated by a MicroMag alternating gradient force magnetometer (AGM).

The XRD spectra of the prepared photocatalysts are shown in Fig. 1. The XRD spectra of TiO$_2$ in Fig. 1a revealed the mixture of the TiO$_2$ phases. The peaks appeared at 2θ = 25.3°, 48.0°, 62.1°, and 70.3° and were ascribed to the [101], [200], [213], [204] and [220] Bragg reflections of the body-centred tetragonal TiO$_2$ anatase phase with a fixed volume of 136.313 Å. The JCPDS card number is 89-4920. Conversely, the peaks that appeared at 35.8°, 38.3°, 41.2°, 44.9°, 53.9°, 55.7°, and 62.7°, and 70.3° were ascribed to 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 769.9 W m$^{-2}$ of sunlight. Run 2 was performed under 775.6 W m$^{-2}$ of sunlight intensity with the recovered photocatalyst. The final cycle was performed under 487.2 W m$^{-2}$ of sunlight intensity. The inconsistencies in the solar irradiation were due to its transient nature and local weather condition.

3. Results and discussion

3.1. Structural and morphological properties

The XRD spectra of the prepared photocatalysts are shown in Fig. 1. The XRD spectra of TiO$_2$ in Fig. 1a revealed the mixture of the TiO$_2$ phases. The peaks appeared at 2θ = 25.3°, 48.0°, 62.1°, and 70.3° and were ascribed to the [101], [200], [213], [204] and [220] Bragg reflections of the body-centred tetragonal TiO$_2$ anatase phase with a fixed volume of 136.313 Å. The JCPDS card number is 21-1272. Conversely, the peaks that appeared at 2θ = 27.5°, 36.2°, 41.3°, 44.1°, 54.4°, 56.8° and 69.2° were ascribed to the [110], [101], [111], [210], [211], [220] and [301] Bragg reflections of the primitive tetragonal TiO$_2$ rutile phase with a fixed volume of 62.0516 Å. The JCPDS card number is 89-4290. Primitive rhombohedral graphite (JCPDS card No. 75-2978; fixed volume, 17.4850 Å) was detected at an angle of 26.9° [002] and 43.3° [100], as shown in Fig. 1b. Fig. 1c shows the peaks that occurred in the TiO$_2$/GO sample. This figure again indicates the presence 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 300 mL capacity. The suspension was constantly magnetically stirred under direct sunlight at the University of Malaya, Kuala Lumpur (latitude 101° 39’ E and longitude 3° 7’ N) 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), 1000 W m$^{-2}$ 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 µm and analysed by Ultra Performance Liquid Chromatography (Waters Acquity UPLC H-Class; Acquity UPLC BEH C18 column, 100 mm x 2.1 mm, 1.7 µm particle size; 60% acetoneitrile (CH$_3$CN), 40% H$_2$O 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 769.9 W m$^{-2}$ of sunlight. Run 2 was performed under 775.6 W m$^{-2}$ of sunlight intensity with the recovered photocatalyst. The final cycle was performed under 487.2 W m$^{-2}$ of sunlight intensity. The inconsistencies in the solar irradiation were due to its transient nature and local weather condition.

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
rhombohedral graphite, anatase and rutile TiO\textsubscript{2} at specific peaks. The XRD spectra of SiO\textsubscript{2}/SrFe\textsubscript{12}O\textsubscript{19} (Fig. 1d) show a wide wave peak between 17° and 30° of amorphous SiO\textsubscript{2}, which was intercalated in the hybrid to avert the direct flow of the magnetic field created by SrFe\textsubscript{12}O\textsubscript{19} into the TiO\textsubscript{2}. TiO\textsubscript{2}/GO/SrFe\textsubscript{12}O\textsubscript{19} (Fig. 1e) showed a mixture of anatase and rutile TiO\textsubscript{2}, as well as SrFe\textsubscript{12}O\textsubscript{19}. The peaks appeared at 2θ = 32.4°, 34.2°, 37.1°, 42.5° and 63.1° and were ascribed to the [107], [114], [203], [206] and [220] Bragg reflections of hexagonal SrFe\textsubscript{12}O\textsubscript{19}. The JCPDS card No. was 33-1340. The anatase phase of TiO\textsubscript{2} is well known to be more stable than the rutile phase due to its higher enthalpy of formation [32]. Moreover, this form has been found to result in higher photocatalytic processes.

![Image](https://example.com/image.png)
However, the rutile phase of TiO$_2$ formed from the reduced stability of the semiconductor anatase phase in this study due to the annealing treatment at 500 °C [31]. This process can contribute to the photocatalysis system where the bulk-generated charge-carrier prevails because only the holes ($h^+$) sufficiently close to the surface will migrate before the recombination [7,34]. The presence of SrFe$_{12}$O$_{19}$ magnetic particles, on the other hand, is beneficial for easing the catalyst recovery. Furthermore, the lack of additional peaks for the TiO$_2$/GO/SrFe$_{12}$O$_{19}$ suggests that impurities were not formed in the synthesised photocatalyst. The crystallite grain size of TiO$_2$ was 25.4 nm. This value was calculated by employing the Debye–Scherer equation to the full width at the half maximum (FWHM) of the reflections for rutile TiO$_2$ (27.5°). The nanosized TiO$_2$ photocatalyst resulted in a quantum effect. The electronic properties of solids changed as the crystal size was reduced. In general, the quantum effect will dominate and the physical properties will change when the photocatalyst particles are smaller than 100 nm. Likewise, the absorption spectra shift to a higher photon energy and develop a discrete character as the size of the particles decreases [32].

The FESEM (Fig. 2a) and STEM bright and dark field micrographs of TiO$_2$/GO/SrFe$_{12}$O$_{19}$ (Fig. 2b and c) reveal that TiO$_2$, GO and SrFe$_{12}$O$_{19}$ were well hybridised. The bright field micrograph of TiO$_2$/GO/SrFe$_{12}$O$_{19}$ (Fig. 2b) shows a densely packed structure composed of an aggregation of discoidal TiO$_2$ together with the SrFe$_{12}$O$_{19}$ crystals, which were deposited on the GO nanofiber. The difference in the energy scattering ability, which depends on the atomic number (Z) for each element, was demonstrated by the dark field micrographs (Fig. 2c). The lighter element, carbon (C) (Z=6) contributed by the GO, was colourless in comparison to the elements contributed by SrFe$_{12}$O$_{19}$ and TiO$_2$. This finding proved that Sr (Z=38), Fe (Z=26) and Ti (Z=22) have different energy scattering abilities that depend on Z. A previous study by Aziz et al., 2012 indicated a positive correlation between the values of Z and the energy scattering ability [32]. HRTEM micrograph from Fig. 2d indicates that the GO nanofiber had an internal diameter (I.D.) of approximately 10 nm and an outer diameter (O.D.) of approximately 100 nm. Additionally, the visible lattice fringes and their corresponding FFT images (Fig. 2e) indicate a (001) TiO$_2$ facet with a lattice spacing of 0.236 nm. Conversely, a lattice spacing of 0.335 nm indicates the lattice fringes of anatase TiO$_2$. The selected area electron diffraction (SAED) ring patterns shown in Fig. 2f indicate that the TiO$_2$/GO/SrFe$_{12}$O$_{19}$ was somewhat crystalline. In addition, the SAED ring patterns show that the TiO$_2$/GO/SrFe$_{12}$O$_{19}$ consisted of a mixture of anatase TiO$_2$ reflected by the (101) lattice plane and rutile TiO$_2$ reflected by the (110) and (211) lattice planes.

The EDX spectra of the TiO$_2$/GO/SrFe$_{12}$O$_{19}$ photocatalyst are illustrated in Fig. 2g. The TiO$_2$/GO/SrFe$_{12}$O$_{19}$ consisted of Ti, C, O, Sr, Si and Fe. Each peak was particular to an element, and they were distributed due to the heating at high temperatures during the preparation. The peak intensity indicates the concentration level of the element in the photocatalyst. The electronic properties of solids changed as the crystal size was reduced. In general, the quantum effect will dominate and the physical properties will change when the photocatalyst particles are smaller than 100 nm. Likewise, the absorption spectra shift to a higher photon energy and develop a discrete character as the size of the particles decreases [32].

3.2. BET surface area analysis

Fig. 3 shows the adsorption–desorption isotherms of TiO$_2$, TiO$_2$/GO and TiO$_2$/GO/SrFe$_{12}$O$_{19}$. The figures indicate that the
synthesised photocatalysts are categorised as Type IV, commonly associated with the presence of mesoporosity. The lower pressure region of graph is quite similar to Type II, which shows a rounded knee and explains the formation of a monolayer. After the knee, the micropores cease to contribute to the adsorption process. The low slope region in the middle of isotherm indicates the first few multilayers on the external surface, including meso- and macroporous layers, before the onset of capillary condensation. The saturation level was reached at a pressure below the saturation vapour pressure. The hysteresis indicates capillary condensation in the meso- and macroporous state [32]. The H1 type hysteresis of the synthesised photocatalysts indicates a cylindrical pore geometry of uniform size. The average pore size was found to be 19.45 nm with a surface area of 35.40 m² g⁻¹ for TiO₂. TiO₂/GO had an average pore size of 1.043 nm with a surface area of 27.29 m² g⁻¹. TiO₂/GO/SrFe₁₂O₁₉ had an average pore size of 15.25 nm with a surface area of 70.87 m² g⁻¹. The small crystallite size might have increased the BET surface area of the TiO₂/GO/SrFe₁₂O₁₉. This relationship indicates that the number of TiO₂/GO/SrFe₁₂O₁₉ pores in the solid negatively correlates with the pore size and positively correlates with the surface area and adsorption capacity. A high surface area provides more active adsorption sites for the photodegradation reaction but will enlarge the amount of substrate that comes in contact with TiO₂/GO/SrFe₁₂O₁₉ by means of adsorption. Furthermore, the most active oxidant (·OH) generated by the photocatalyst, does not migrate very far from the active centres of the TiO₂/GO/SrFe₁₂O₁₉. Therefore, degradation will virtually take place on the surface of the photocatalyst.

3.3. ESR, FTIR, Raman and XPS analysis

Fig. 4 shows the ESR spectra of the synthesised TiO₂ recorded at room temperature. A strong ESR signal recorded at g = 1.979 indicates the presence of bulk Ti³⁺. Generally, the commercial TiO₂ fails to have a strong signal at g = 1.979. The presence of Ti³⁺ on the TiO₂ surface can trap photogenerated electrons (e⁻) and leave unpaired charges behind to promote the photoactivity. Hence, Ti³⁺ promotes the effective segregation of the e⁻ and cavity and interface charge transfer. It also lowered the probability of compounding the cavity, but it increased the photocatalytic performance. In addition, one minor peak for the g-value at 2.004 corresponds to the presence of O²⁻. The ESR spectra resulted in a complex pattern because the synthesised TiO₂ contained anatase and rutile phases.

Fig. 5. (A) Functional group analysis of prepared photocatalysts, and (B) Raman spectra of GO.
The FTIR spectra of GO in Fig. 5A showed characteristic bands between 900 and 4000 cm\(^{-1}\). The broad band between 3000 and 3500 cm\(^{-1}\) is the stretching vibration of the O–H bond. The C–O stretching vibration at 1076 cm\(^{-1}\) and vibration of the peroxide group at 950 cm\(^{-1}\) were also observed. A less intense band at 1271 cm\(^{-1}\) was attributed to the breathing vibration of the epoxy group. The peak at 1577 cm\(^{-1}\) was attributed to the stretching vibration of the C=C in the GO. Each group that was present in the GO was also present in the TiO\(_2\)/GO/SrFe\(_{12}\)O\(_{19}\). However, the amounts were marginal.

A Raman G band at 1425 cm\(^{-1}\) and a typical D band at 1332.8 cm\(^{-1}\) were observed for the GO sample (Fig. 5B). The G band is characteristic of pristine graphite. It was assigned to the \(E_{2g}\) phonon of the C sp\(^2\) atoms. The D band was attributed to the breathing mode of the \(\kappa\)-point phonons of \(A_{1g}\) symmetry, which arose from local defects and disorders, particularly the defects
located at the edges or in samples. The presence of the D band indicates that GO is highly disordered with a high density of defects. We observed that G band of the prepared GO shifted towards a lower wavenumber and that the D band was more intense. This change might be due to amount of oxidising agent used to prepare the GO. Furthermore, this oxidation degree of graphite signifies the structure of the prepared carbon material [35,36]. However, this oxidation degree does not significantly influence the photocatalytic activity of the composite.

The fully scanned XPS spectra indicate that the elements Ti, C, Si, Sr and Fe were present in the TiO$_2$/GO/SrFe$_{12}$O$_{19}$. The XPS of the Ti 2p, C 1s, Si 2p, Sr 3d and Fe 2p core levels were present in the following forms: (1) Ti 2p region (450–470 eV); (2) C 1s region (280–293 eV); (3) Si 2p region (98–105 eV); (4) Sr 3d region (129–137 eV) and (5) Fe 2p region (708–732 eV). The peaks were fitted to the spectra using a Gaussian–Lorentzian peak shape after the background was subtracted. As shown in Fig. 6a, the peaks observed at 459 eV (Ti 2p$_{3/2}$) and 465.1 eV (Ti 2p$_{1/2}$) corresponded to Ti$^{4+}$. This finding indicates an active compound for the enhancement of visible light photocatalytic activity. The BE peak at 284.6 eV in Fig. 6b can be attributed to the graphitic carbon C–C, C=C and C–H bonds. Furthermore, the BE peak observed at 98.7 eV and 103.2 eV for the Si 2p (Fig. 6c) corresponds to the elemental Si and SiO$_2$. Fig. 6d and e show the presence of elemental Sr at BE values of 134.2 eV for Sr 3d. Fe$_2$O$_3$ was detected at a BE value of 711.7 eV for the Fe 2p$_{3/2}$. The magnetic properties of Sr and Fe$_2$O$_3$ help to separate and recover the TiO$_2$/GO/SrFe$_{12}$O$_{19}$ after use.

3.4. AGM analysis

The magnetochemistry of the photocatalyst showed a clear hysteresis behaviour in response to an applied magnetic field, which is shown in Fig. 7. Pure SrFe$_{12}$O$_{19}$ (Fig. 7A(a)) showed a wide hysteresis in the M–H loop with an Oe coercivity ($H_{ci}$) of 3637, which is significantly higher compared to other ferrite nanoparticles. As a consequence, a high $H_{ci}$, remanence ($M_r$) and saturation magnetisation ($M_s$) are retained in the material. Generally, ferrite materials with a high $H_{ci}$ value are called...
“hard ferromagnetic” materials. This material shows good magnetic properties that are very stable against magnetic property losses [32]. The intercalation of SiO2 into the SrFe12O19 (Fig. 7A(b)) widened the hysteresis in the M–H loop and increased its magnetic properties (Hc = 3889 Oe, Mr = 8.567E–3 emu g–1 and Ms = 0.01481 emu g–1). However, the Hc, Mr, and Ms of the TiO2/GO/SrFe12O19 were lower (Hc = 2103 Oe, Mr = 1.642E–3 emu g–1 and Ms = 3.406E–3 emu g–1) and the hysteresis in the M–H loop narrowed (Fig. 7A(c)) due to the deposition of paramagnetic TiO2 and GO. TiO2 has a very small magnetic susceptibility because the e– have unpaired spins, which decreases the interparticle interactions and increases the particle separation. Such detrimental effects, which are caused by the dipole–dipole interactions between the nanoparticles, contribute to the magnetic anisotropy of the TiO2 material (mixture of antiferromagnetism and ferromagnetic interaction) [37]. Nevertheless, the relatively high Hc of the TiO2/GO/SrFe12O19 implies that the particles lacked superparamagnetic properties. The photocatalyst can therefore be easily recovered from a suspension by applying an external magnetic field, as shown in Fig. 7B [38]. Moreover, it can be almost completely recovered with a minimum loss for many cycles without diminishing both the magnetic property and photoactivity. The properties of this material are highly desirable for the treatment of contaminated waters.

3.5. Thermal property

Fig. 8a shows a mass loss of ~1% between 80 and 120 °C of TiO2 due to the removal of physisorbed water molecules, which resulted in an endothermic effect. At 240 °C, an initial stage or pre-pyrolysis of the oxygen (O2) that contacted functional groups was observed, while the structural water molecule (O–H) was removed at 400 °C. A negligible exothermic effect was observed between 600 and 800 °C with an enthalpy of ~27.1 J g–1, which was clearly attributable to the phase transition of TiO2 from anatase to rutile. Beyond 800 °C until 1000 °C, the carbon-containing functional groups were covered either as CO or CO2, and these functional groups were dominated by the pyrolysis reaction above 1000 °C. The finding was similar for other composites, but the temperatures were slightly shifted due to the influence of the materials employed as a composite. The TGA/DSC curve of TiO2/GO is depicted in Fig. 8b and shows a weight loss between 700 and 1300 °C. The weight loss was also observed below 700 °C, but the loss was minor. Fig. 8c shows two overlapping endothermic effects (total enthalpy of 153 J g–1) with peak temperatures at 934 and 984 °C. A third endothermic peak was observed at 1263 °C. Similarly to other composites, the low temperature range was associated with a weight loss due to the release of moisture; higher temperatures were associated with pre-pyrolysis, structural water removal, the removal of carbon-associated functional groups and pyrolysis in the respective temperature zone. At higher temperatures, the thermal effects and weight loss were attributed to the release of oxygen (O2) and hydroxides (O–H) from the GO. These losses were caused by the release of moisture and organic impurities at lower temperatures and the release of the hydroxyl group from the GO at temperatures above 800 °C. The endothermic effects were observed for all the samples from lower (~100 °C) to higher temperatures (~1263 °C) with varied enthalpies, as shown in Fig. 8a–c.

3.6. UV–vis absorption spectra and band gap energy

The UV–vis absorption spectra of the synthesised photocatalysts were compared and are depicted in Fig. 9A. The synthesised TiO2 (Fig. 9A(a)) shows a sharp edge at approximately 425 nm, whereas TiO2/GO (Fig. 9A(c)) and TiO2/GO/SrFe12O19 (Fig. 9A(d)) display an obvious red shift of approximately 275 nm at the absorption edge. SiO2/SrFe12O19 (Fig. 9A(b)) enhances the visible light absorption by shifting the edge to approximately 375 nm at the absorption edge. This shift indicates that the presence of GO and the dispersion of SrFe12O19 particles in the TiO2 matrix enhanced the excitation of TiO2/GO/SrFe12O19 in the visible light region. We ascribed the enhanced photocatalytic performance of TiO2/GO/SrFe12O19 under a visible light source (sunlight) to the band gap narrowing of the photocatalyst. Fig. 9B shows plots of the Kubelka–Munk remission function (i.e. relationship of [zhv]1/2 with the photon energy) corresponding to each spectrum. These plots indicate that the band gap of the synthesised TiO2 was 2.90 eV (Fig. 9B(a)). The band gap of TiO2/GO/SrFe12O19 in the spectrum was significantly reduced to 1.80 eV (Fig. 9B(d)). This phenomenon should occur due to the direct interaction between the C and Ti atoms on the TiO2/GO/SrFe12O19 surface. This interaction revealed that the synthesised TiO2/GO/SrFe12O19 had lowered the band gap energy between the conduction (CB) and the valence band (VB), which means that the excitation occurred at a much lower energy obtained from the visible spectrum of electromagnetic radiation [32].

3.7. Photocatalytic evaluation

The photoactivity was evaluated for the photodegradation of 2,4-DCP under sunlight with pristine catalysts as well as after
and TiO$_2$ [39–41]. Although the conductivity of the prepared under nanorods interlayer inhibited the diffusion of Sr ions into the dyade structure photocatalyst can harvest visible spectrum light single crystals as efficient visible-light photocatalysts, photocatalyst could also limited the electronic interac- tion: porous assemblies of CdS nanoparticles was completely degraded from acting as an e$^-$/h$^+$ recombination centre. Furthermore, the narrowed band gap energy could effec- tively reduce the recombination of photogenerated charge carriers and enhance the photocatalytic activity. The photogenerated e$^-$ from CB was transferred to the trapping sites in the presence of sunlight irradiation. This transfer of e$^-$ to lattice trapping sites resulted from the dual effect of the presence of an anionic carbonaceous material, the GO and the higher surface area of the TiO$_2$/ GO/SrFe$_{12}$O$_{19}$ [39–41]. Although the conductivity of the prepared GO was quite low (based on Raman spectra observed, Fig. 5B), it nevertheless played a role as an electron acceptor that marginally contributed to the interfacial electron-transfer process from TiO$_2$, thus hindering the recombination of charge-carriers [42,43]. In addition, the GO is predicted to enhance the adsorption of reacting species due to the presence of abundant functional groups at the edge or on the surface of GO.

The SiO$_2$ interlayer inhibited the diffusion of Sr ions into the TiO$_2$, thereby preventing detrimental effects on the performance of the photocatalyst. The SiO$_2$ also limited the electronic interactions between the TiO$_2$ and SrFe$_{12}$O$_{19}$ heterojunction while preventing the SrFe$_{12}$O$_{19}$ from acting as an e$^-$/h$^+$ recombination centre. Furthermore, the narrowed band gap energy could effectively reduce the recombination of photogenerated charge carriers and enhance the photocatalytic activity. The photogenerated e$^-$ from CB was transferred to the trapping sites in the presence of sunlight irradiation. This transfer of e$^-$ to lattice trapping sites helps to effectively separate the charge carriers. These trapping sites also benefit by mostly preventing the recombination and facilitating the charge separation, which activates the catalyst. The trial runs were carried out by separating the catalyst under a strong magnetic field. A mass recovery of $\sim$98% was achieved with a minor loss. This loss was expected due to the nanoparticle size. Overall, the present study revealed the outstanding photoactivity for a sustainable development.

4. Conclusions

The above results demonstrate that the prepared novel TiO$_2$/ GO/SrFe$_{12}$O$_{19}$ photocatalyst can harvest visible spectrum light and sunlight for the photodegradation of organic species while exhibiting enhanced catalyst recovery properties. The degradation of 2,4-DCP concentration was maximized under both bright and diffused sunlight for both photocatalysts. The results of the present prepared photocatalyst laid a pathway for a green and sustainable catalyst design. Thus, the TiO$_2$/GO/SrFe$_{12}$O$_{19}$ photocatalyst could serve as a new generation of photocatalyst for the complete, economical and productive treatment of toxic wastewater.

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