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PREPARATION, CHARACTERISATION AND PHOTOCATALYTIC ACTIVITY OF TERNARY GRAPHENE-Fe_3O_4:TiO_2 NANOCOMPOSITES

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Ternary graphene-Fe_3O_4:TiO_2 nanocomposites (GF:TiO_2) were successfully prepared by a hydrothermal method. Characteristics of the nanocomposites were investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and UV-visible spectroscopy (UV-vis). Photocatalytic activity evaluated by degradation of methylene blue (MB) under UV and visible light determined the efficiency of GF:TiO_2 at a ratio of 1:4, reaching 88.11% and 90.52% in 90 min under UV and visible light respectively. Enhanced visible light photocatalytic activity for degradation of MB was mainly attributed to the two dimensional structure of graphene as a good electron acceptor and transporter.

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Keywords: Graphene, Fe_3O_4, TiO_2, Photocatalytic

1. Introduction

Titanium dioxide (TiO_2) is a commonly used as photocatalyst because it is highly stable, water soluble, acid resistance, non-toxic and inexpensive [1]. TiO_2 photocatalysts are used in wastewater treatment but have the disadvantage of an energy gap of 3.2 eV which can absorb only ultraviolet light with a wavelength of less than 380 nm, accounting for only about 3-4% of the solar spectrum. In addition, easy recombination of electron-hole pairs produced by light stimulation results in reduced photocatalytic efficiency [2]. Therefore, many researchers have attempted to achieve TiO_2 catalytic operation in visible light by reducing the recombination of electrons and holes through doping with substances such as gold [3], platinum [4], nickel [5] and other transition metals.

Graphene is a two-dimensional material with unique mechanical, electrical and optical properties [6]. When graphene is added, TiO_2 can be catalysed by visible light [7]. However, one of the main problems is the separation of catalysts from wastewater after treatment. Magnetite (Fe_3O_4) blends have been used as guiding principles to solve this issue.

Here, graphene-Fe_3O_4:TiO_2 (GF:TiO_2) was synthesised by a simple and environmentally friendly hydrothermal process. Prepared samples were characterised by X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and UV-visible spectrophotoscopy (UV-vis). Photocatalytic activity was evaluated by methylene blue (MB) photodegradation. The results can be used for academics and industrial agencies to develop novel visible light and reusable photocatalysts.

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2. Experimental

2.1 Materials and reagents

Natural graphite powder and titanium IV oxide (P25) were sourced from Sigma-Aldrich Co. Ltd., Germany. All other reagents including ferrous sulphate heptahydrate $FeSO_4{\cdot}7H_2O$, ferric chloride hexahydrate, $FeCl_3{\cdot}6H_2O$, potassium permanganate $KMnO_4$, hydrogen peroxide H_2O_2, methylene blue, concentrated hydrochloric acid (HCl) and sodium nitrate $NaNO_3$ were purchased from Loba Chemie Pvt. Ltd., India. All chemicals were used without further purification. Solution pH was adjusted with sodium hydroxide and sulphuric acid. Distilled water was used in all experiments.

2.2 Preparation of graphene oxide (GO)

Graphene oxide (GO) was prepared following Hummer's method as follows. 1 g of graphite and 0.5 g of $NaNO_3$ were added to 23 ml of H_2SO_4 under constant stirring in an ice bath. While stirring vigorously, 3 g of $KMnO_4$ was slowly added to the solution and the mixture was stirred continuously at 35 ^oC for about 30 min. Then, 46 ml of distilled water was added and stirred for 15 min at 98 ^oC. Subsequently, 140 ml of distilled water and 10 ml of H_2O_2 were added to the mixture and stirred for 2 h to stop the oxidation reaction and reduce excess $KMnO_4$. The mixture was filtered and washed with 4% HCl and distilled water until neutral and then dried in an oven at 110 ^oC for 12 h.

2.3 Preparation of graphene-Fe_3O_4 (GF)

20 mg of prepared graphene oxide (GO) was dissolved in a beaker containing 40 ml of distilled water and 4 ml of Fe_3O_4 solution (5 mg/ml) under vigorous stirring for 2 h. The solution was filtered and rinsed with distilled water 5 times, then dried at 110 ^oC for 12 h.

2.4 Preparation of graphene-Fe_3O_4:TiO_2 (GF:TiO_2)

50 mg of GF was dispersed in 25 ml of distilled water for 1 h in an ultrasonic bath. Certain amounts of P-25 (TiO_2) were dissolved in the GF solution at weight ratios of GF:TiO_2 1:3, 1:4, 1:5, 1:6 and 1:7. The whole mixture was then transferred into a 50 ml Teflon-lined stainless steel autoclave and sealed, heated to 180 ^oC and then kept for 6 h. After cooling to room temperature naturally, the resulting solid was washed with water and dried at 110 ^oC in an oven.

2.5 Characterisation

Characteristics of the prepared nanocomposites were investigated using a scanning electron microscope (SEM, Jeol-JSM5410LV) with maximum acceleration voltage of 20 kV, a transmission electron microscope (TEM, Philips Tecnai 12) with a maximum acceleration voltage of 80 kV, an X-ray diffractometer (XRD, Bruker AXS-D8 ADVANCE) with Cu Kα radiation (λ= 0.15406 nm) and a UV-vis spectrophotometer (Thermo Scientific Evolution 600).

2.6 Photocatalytic activity

Photocatalytic activity was evaluated based on the degradation of MB (12.5 mg/l). 90 mg of as-prepared GF:TiO_2 was dispersed in 30 ml of MB solution. The suspension was stirred in the dark for 30 min and then irradiated for 60 min using UV and visible light. At specific time intervals, 2 ml of suspension was withdrawn, centrifuged and the supernatant analysed by a UV-vis spectrophotometer at a wavelength of 663 nm. Percentage degradation of MB was calculated using the equation:

$$\%\,\text{degradation} = \frac{C_0 - C_t}{C_0} \times 100 = \frac{A_0 - A_t}{A_0} \times 100 \qquad (1)$$

where C_0 and C_t are MB concentration at initial and anytime respectively and parameters A_0 and A_t are absorbance of the MB solutions in the 663 nm wavelength at initial and any time respectively.

3. Results and discussion

3.1 Characteristics of as-prepared GF:TiO_2 nanocomposites

Both SEM and TEM were used to investigate the morphology of as-prepared GF:TiO_2 nanocomposites. Fig. 1 shows the SEM images of as-prepared GF:TiO_2 nanocomposites. When the amount of TiO_2 increased, small particles were covered throughout the graphene sheets. Fig. 2 shows the TEM image of as-prepared GF:TiO_2 nanocomposites with a weight ratio of 1:5. GO is seen as transparent folds with Fe_3O_4 (black granules) and TiO_2 (grey granules) scattered on the surface.

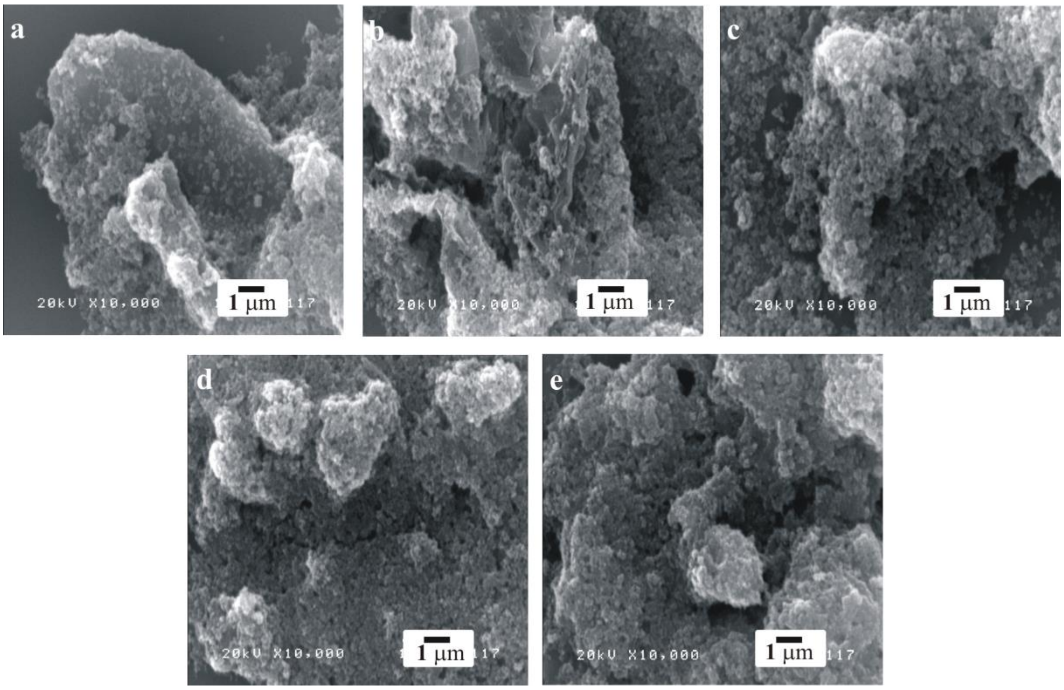

Fig. 1. SEM images of as-prepared GF:TiO_2 nanocomposites with weight ratio (a) 1:3, (b) 1:4, (c) 1:5, (d) 1:6 and (e) 1:7.

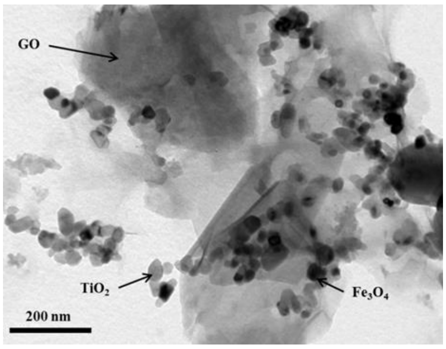

Fig. 2. TEM image of as-prepared GF:TiO_2 nanocomposites with weight ratio 1:5.

The XRD patterns of GO, Fe_3O_4 and TiO_2 are shown in Fig. 3. GO gave a sharp peak at 11.5^o with 0.769 nm d-spacing, indicating 2-3 layers compared with the d-spacing of graphite (0.332 nm) [8. For Fe_3O4, diffraction peaks were observed at 30.2^o, 35.7^o, 43.4^o, 53.7^o, 57.4^o, 62.9^o and 74.7^o attributed to the (111), (220), (400), (422), (333), (440) and (622) planes of Fe_3O_4. The pattern matched JCPDS no. 821533. The series of characteristic peaks shown by TiO_2 at around 2θ of 25.2°, 38.0°, 48.1°, 53.8°, 55.0°, 62.7°, 69.0°, 70.7° and 75.2° related to reflection of (101), (004), (200), (105), (211), (204), (116), (220) and (215) planes of the anatase phase of TiO_2 (JCPDS no. 894921). Fig. 4 shows XRD patterns of as-prepared GF:TiO_2 nanocomposites. The major phase of anatase was represented by small amounts of GO and Fe_3O_4 phases suggesting that GO and Fe_3O_4 were mainly coated with a TiO_2 layer. Peaks were also observed at positions 27.3° and 41.0° as the rutile phase in as-prepared GF:TiO_2 nanocomposites.

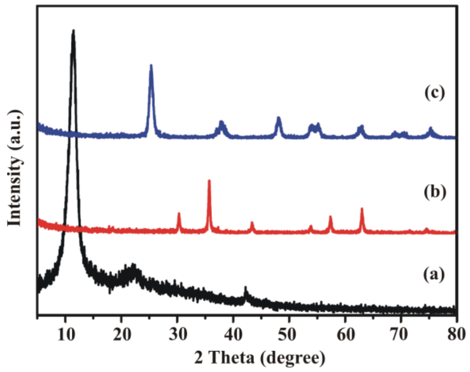

Fig. 3. XRD patterns of (a) GO, (b) Fe_3O_4 and (c) TiO_2.

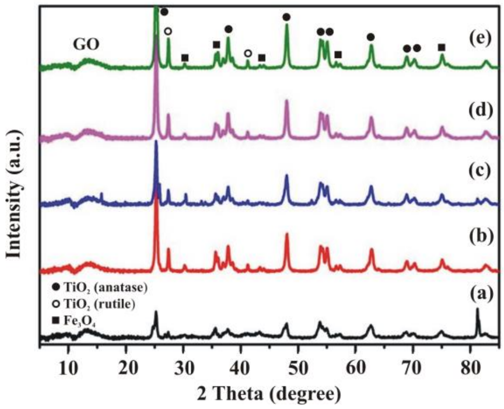

Fig. 4. XRD patterns as-prepared GF:TiO_2 nanocomposites with weight ratio of (a) 1:3; (b) 1:4; (c) 1:5; (d) 1:6 and (e) 1:7.

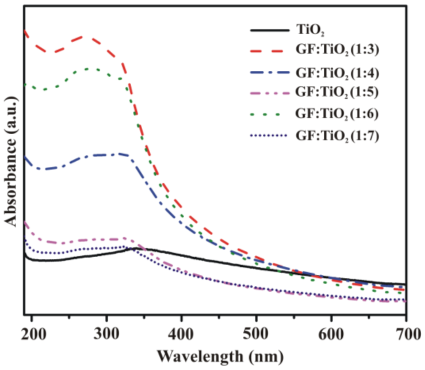

Fig. 5. UV-vis spectra of TiO_2 and as-prepared GF:TiO_2 nanocomposites with weight ratio of 1:3, 1:4, 1:5, 1:6 and 1:7.

The UV-vis spectra of TiO_2 and as-prepared GF:TiO_2 nanocomposites in the range of 200-700 nm are shown in Fig. 5. As-prepared GF:TiO_2 with weight ratios of 1:3, 1:4 and 1:6 displayed higher absorption in both UV and visible regions compared with TiO_2.

3.2. Photocatalytic degradation of MB

Fig. 6 shows the degradation of MB by TiO_2 and GF:TiO_2 with weight ratios of 1: 3, 1: 4, 1: 5, 1: 6 and 1: 7 under UV light. The TiO_2 demonstrated efficiency to degrade MB at up to 97.61%, while as-prepared GF:TiO_2 with weight ratios of 1: 3, 1: 4, 1: 5, 1: 6 and 1: 7 degraded MB by 71.52, 88.11, 79.99, 85.33 and 79.55% respectively. Fig. 7 shows the photocatalysis under visible light. As-prepared GF:TiO_2 with a weight ratio of 1: 4 gave the highest MB degradation efficiency at up to 90.52%.

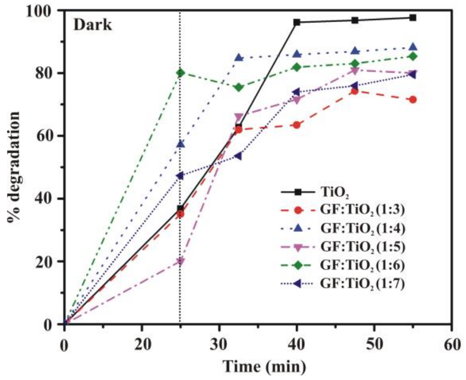

Fig. 6. Photocatalytic degradation efficiency of MB under UV light utilising TiO_2 and as-prepared GF:TiO_2 nanocomposites.

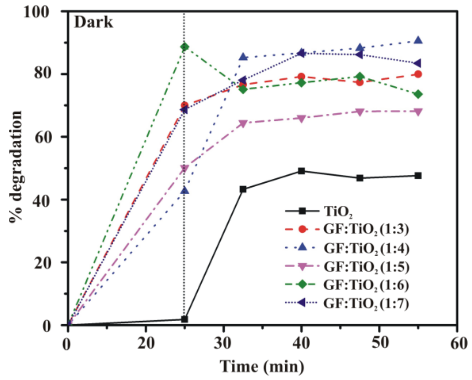

Fig. 7. Photocatalytic degradation efficiency of MB under visible light utilising TiO_2 and as-prepared GF:TiO_2 nanocomposites.

4. Conclusions

As-prepared GF:TiO_2 nanocomposites were successfully prepared by a hydrothermal process and demonstrated ability to absorb light in both the UV and visible ranges. The GF-TiO_2 nanocomposites exhibited higher photocatalytic activity with increased degradation of MB under visible light compared to TiO_2.

As-prepared GF:TiO_2 with a weight ratio of 1:4 proved the most effective in degrading MB. Results can be used as preliminary data for the development of photocatalysts that work under visible light. Further study is required regarding the magnetic separation of photocatalysts from MB solution as the magnetism of Fe_3O_4 decreases when covered with TiO_2 nanoparticles.

Acknowledgements

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