



Synthesis of the high durability photocatalytic materials with tertiary components

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ABSTRACT

The high durability, re-collectable and low-cost materials with tertiary (reduced graphene-TiO₂-Fe₃O₄, denoted as GrTiFe) components for degradation of toxic organic compounds have been prepared from different precursors by coprecipitation and hydrothermal methods. By this procedure, TiO₂ and Fe₃O₄ nanoparticles have been growing on the reduced graphene oxide. The as-synthesized nanocomposites have been characterized with X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscope and magnetic hysteresis, and studied on the photo-degradation reaction of Moderacid Black (MDB). The result shows that the photocatalytic activity of as-synthesized composites is much higher than that of pure TiO₂ nanoparticles and the composites can be easily collected from water using a magnet for reusing. In addition, the GrTiFe is also able to degrade the organic compounds under modeling sunlight radiation.

Introduction

Nowadays, water pollution is a huge global problem, especially, in developing countries where textile industry uses a large number of dyes, is one of the most important fields. More than 3600 individual textile dyes are being manufactured by the industry and more than 8000 chemicals are used in different processes of textile manufacture including printing and dyeing [1]. It is reported that textile dyeing discharged about 15-20 percent of organic dyes to environment leading to a seriously adverse impact on the human health and living environment as it is one of the most chemically intensive industries on the earth and the number one polluter of cleaning water [2, 3]. Various methods have been developed to treat waste water containing dye pollutants including adsorption, biodegradation and photocatalytic degradation methods. Nevertheless, most of adsorption methods face with several drawbacks, such as low adsorption

capacity, complex operations for recycling or non-recyclability. The biodegradation methods revealed high potential application on treating dye-effluent, but these methods still remain several problems, such as the low efficiency in waste water containing toxic dyes. Compared with adsorption and biodegradation methods, the photocatalytic degradation is an outstanding method that can overcome problems mentioned above [4].

Amongst photocatalytic materials, titanium dioxide is an environmentally friendly and inexpensive material and has been used widely in many photocatalytic applications due to its highly chemical stability, non-toxicity and light-induced oxidation. In addition, the titanium dioxide can generate electron-hole pairs with high reductive and oxidative power under ultraviolet radiation producing corresponding highly reactive species which can reduce and oxidize organic pollutants, such as dyes, in solution. Though owing to

various advantages over many other materials, titanium dioxide itself has low photocatalytic efficiency due to recombination of generated electron-hole and is difficult to reuse in aqueous solution due to the complicated process to separate it [1-3]. In order to increase lifetime of generated electron-hole pairs and make it become reusable materials, it is necessary to develop titanium dioxide materials. Graphene, with two-dimensional honeycomb lattice and sp^2 -hybridized single layer sheet of carbon atoms, has received extensive attention since its discovery in 2004 due to its unique properties such as excellent mechanical, electronic, optical and thermal properties. Both generated electrons and holes can highly mobilize in pristine graphene sheet. Therefore, in principle, electrons and holes generated from titanium dioxide under suitable irradiation would be easily transferred to graphene leading to the low probability of electron-hole recombination and the high photocatalytic efficiency [4-6]. Therefore, the combination of titanium oxide and graphene would possess excellent photocatalytic performance to degrade dye pollutants.

In previous paper, we have reported the synthesis of graphene titanium composite as photocatalytic materials for degradation of dyes [4]. In this work, we developed a material composed of TiO_2 -wrapped Fe_3O_4 particles loaded on reduced graphene oxide nano sheets. Such composite (GrTiFe) would be a high stable and reusable photocatalyst for degradation of hazardous organic compounds in effluent. The GrTiFe can be a potential material for practical application in treating waste water containing hazardous organic compounds.

Experimental

Chemicals

$TiCl_4$ was purchased from Merck and used as received. The graphite powder (GP) has been purchased from Sigma Aldrich. All other chemicals were analytical grade reagents and used as received.

Preparation of graphene oxide (GO)

GO was synthesized from graphite powder according to a modified Hummer's method. In a typical procedure, 4.0 g of (GP) and 2.0 g of $NaNO_3$ were mixed with 100 mL concentrated H_2SO_4 (98%) in a 1000 mL beaker. The mixture was stirred for 3.0 hours at

room condition. During stirring, 5.0 g $KMnO_4$ was slowly added to the suspension and the temperature was maintained at room temperature. After addition of $KMnO_4$, the reaction mixture was then stirred for 7.0 hours at a constant temperature of $30^\circ C$. Then, 250 mL dilute H_2SO_4 (5%) was slowly added to the mixture with vigorous stirring. The diluted suspension was again stirred for 4.0 hours at a stable temperature of $90^\circ C$. Finally, the mixture was added by 50 mL 30% H_2O_2 , washed by centrifuging with 5% H_2SO_4 followed by plenty of distilled water and filtered to obtain gray GO.

Hydrothermal preparation of GrTiFe

The GrTiFe sample was prepared with different mass percent of Fe_3O_4 ranging from 1.5 to 15.0%, a fixed mass percent of 20% TiO_2 and the rest is reduced graphene oxide. In a typical process, a certain amount of $FeCl_3 \cdot 6H_2O$ and $FeCl_2 \cdot 4H_2O$ with molar ratio of 2 : 1 was dissolved in water to form 25 mL solution. The 30% ammonia solution is then added to Fe_3+/Fe_2+ solution under stirring condition to adjust the pH to 10. The red brown suspension was formed. To this suspension, 25 mL of alcohol containing suitable $TiCl_4$ is slowly added under magnetic stirring condition, following by a calculated amount of GO. The stirring was kept for 2 hours to form dark brown suspension. The suspension was then transferred to Teflon-lined steel autoclave maintained at to $200^\circ C$ for 12 hour. The final product was filtered, washed with plenty of distilled water and dried at $80^\circ C$ for 24 hours. The samples were denoted as GrTiFe-X (X is mass percent of Fe_3O_4).

Characterization

Scanning electron microscope (SEM) was performed by a Hitachi S-4800 field emission scanning electron microscope at 5 kV. X-ray diffraction (XRD) patterns of the samples were measured on a Bruker-D5005 powder X-ray diffractometer using copper $K\alpha$ -radiation with $\lambda = 1.5406 \text{ \AA}$. Thermogravimetric analysis (TGA) was carried out on a Shimadzu DTG-60H instrument at a heating rate of $10^\circ/min$ under air flow. The FR-IR was performed on NEXUS-670, Nicolet, USA equipment and solid UV-Vis spectra were measured with Jasco V670 spectrophotometer. The magnetic hysteresis curves were recorded room temperature by a vibrating sample magnetometer.

Results and discussion

Characterization

XRD patterns

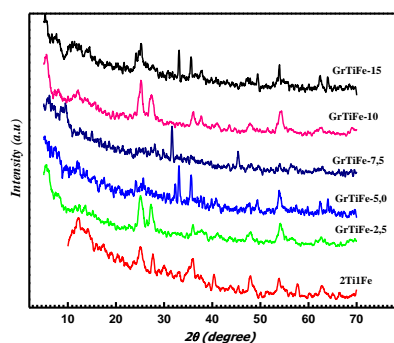


Figure 1: X-ray diffraction patterns of GrTiFe-X samples

Figure 1 presents XRD patterns of powder GrTiFe-X ($X = 2.5; 5.0; 7.5; 10.0; 15.0$) samples. The diffraction peaks in figure 1 can be found at 25.3° , 37.8° , 48.1° , 54.7° and 68.8° , which corresponding to the (101), (200), (211) and (116) reflection planes of TiO_2 [7], respectively. These diffraction peaks are consistent with those of anatase form of TiO_2 . Another phase of Fe_3O_4 occurs with diffraction peaks at 27.5° , 35.1° , 43.9° , 53.5° , 56.5° and 63.2° , which assign to (200), (311), (400), (422), (511) and (400) reflection planes [7]. The characteristic diffraction peaks of graphene do not appear clearly in these XRD patterns. This may be due to the low intensity of these peaks or the merging of these peaks with adjacent peaks characteristic for Fe_3O_4 or TiO_2 phase. As can be seen from fig. 1, there is diffraction peaks characteristic for a new phase. This reveals that the Fe_3O_4 and TiO_2 remain thermodynamically stable in the range of studied temperature.

FT-IR analysis

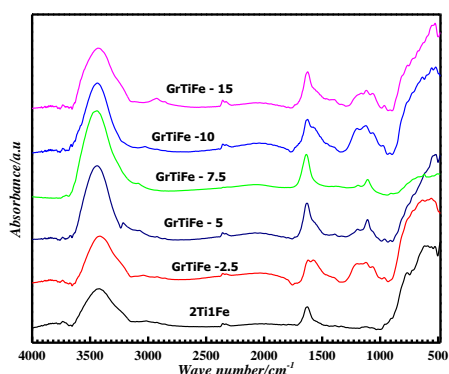


Figure 2: FT-IR spectra of GrTiFe-X samples

The FT-IR study has been used to understand interaction of components present in the sample. As shown in Fig. 2, FTIR spectra of synthesized GrTiFe-X

samples are quite similar. The broad peak between $3460\text{--}3500\text{ cm}^{-1}$ is due to stretching of O-H group, which may belong to water molecules adsorbed on the surface of samples [8, 9]. The weak absorption peaks in the range from $520\text{ to }556\text{ cm}^{-1}$ are characteristic peak of Fe-O bond [1], while the sharp absorption peak at about 1630 cm^{-1} is designated as the stretching of Ti-O bond. The intensity peaks assigned to Fe_3O_4 increase as the content of Fe_3O_4 increases. The absorption peak, which appears as a shoulder at around 1580 cm^{-1} , is characteristic for C=C stretching vibration of graphene. It is concluded that, from FT-IR information, graphene oxide has been reduced well without clear peak of surface functional groups on surface graphene sheet.

Morphology analysis

In order to get further information of materials, the synthesized GrTiFe-X samples were characterized using scanning electronic microscope (SEM).

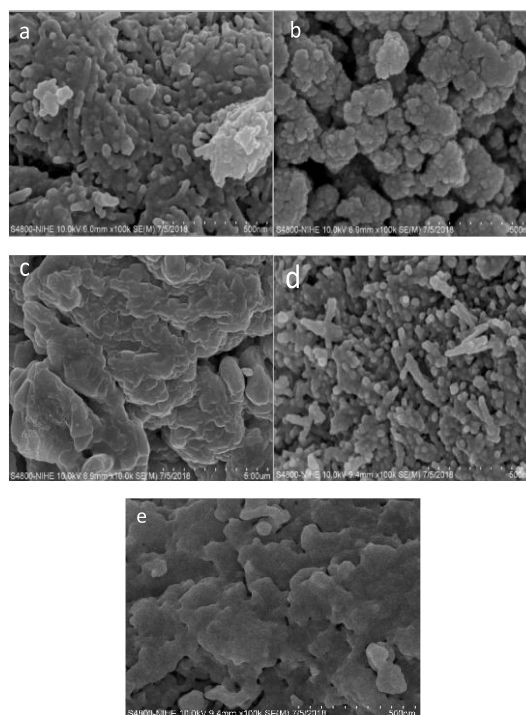


Figure 3: SEM images of Synthesized samples: (a) GrTiFe-2.5, (b) GrTiFe-5, (c) GrTiFe-7.5, (d) GrTiFe-10 and (e) GrTiFe-15

The results are depicted in fig. 3. As shown in fig. 3, SEM images reveals clearly that Fe_3O_4 wrapped TiO_2 particles are dispersed well on surface of graphene sheet with the average size of around 30 nm. However, there is a little difference in samples as the Fe_3O_4 content changes and sample GrTiFe-10 shows the most

uniform dispersion. The dispersion of Fe₃O₄-wrapped TiO₂ may affect on the photocatalytic activity of the samples, and therefore on the degradation efficiency of organic compounds.

Magnetic hysteresis measurements

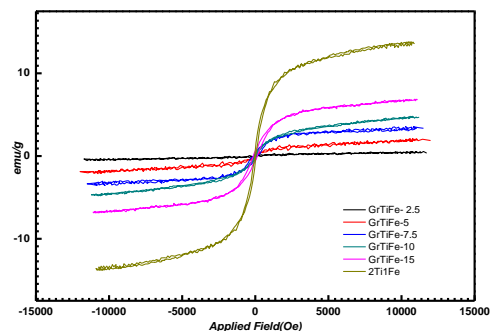


Figure 4: Hysteresis curves of GrTiFe-X samples

The magnetic hysteresis curves for synthesized GrTiFe-X materials were measured by a vibrating sample magnetometer shown in fig. 4. As can be seen from curves, the hysteresis loops in the *M-H* curves reveal the ferromagnetic behavior of synthesized materials. The saturation magnetization (*M_s*) and retentivity (*M_r*) increase as the Fe₃O₄ content increases. The *M_s* of the bulk materials is in the range from 46.7 to 82.5 emu/g [10, 11]. However, the values of *M_s* are relatively low (7.0 emu/g for GrTiFe-15). This can be explained due to the low content of Fe₃O₄ present in the samples and Fe₃O₄ particles are wrapped by TiO₂. In principle, ferromagnetic materials, such as GrTiFe-X, are easily aggregated with a magnetic field [12]. In addition, the Fe₃O₄-wrapped TiO₂ particles are uniformly dispersed on graphene sheets in the GrTiFe-X samples as shown in figure 3. This reveals that the aggregation of studied materials would be highly efficient.

Photocatalytic activity of GrTiFe-X

Effect of Fe₃O₄ content on degradation efficiency

In previous study, we found that GrTiO₂ with 20% wt. of TiO₂ has the highest photocatalytic activity. In this work, Fe₃O₃ particles are added for recycling the materials. Therefore, effect of Fe₃O₄ content must be studied. The photocatalytic activity of materials was studied with a number of experiments carrying out on the degradation of MDB under modelled sunlight irradiation. In each experiment, 2.0 mg of GrTiFe-X material was mixed thoroughly with 10 mL of 20 mg

MDB/L. The pH of the mixture was established itself by nature of MDB compound without any adjustment. The mixture was then illuminated for 180 min at room temperature and separated using a permanent magnet. The results are shown in fig. 5.

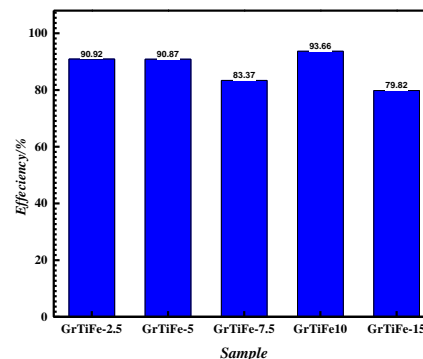


Figure 5: Degradation of MDB on GrTiFe-X materials

As the results, all samples show a relatively high degradation-efficiency after 180 min illuminating with efficiency value of more than 70%. The GrTiFe-10 shows the highest efficiency of 93.66% in comparison to others. As mention above, Fe₃O₄-wrapped TiO₂ particles in GrTiFe-10 sample are the most uniformly dispersed on surface of graphene sheets. This may be the reason for the highest degradation efficiency of GrTiFe-10 sample. For this reason, GrTiFe-10 will be used for further study.

Effect of GrTiFe-10 content on degradation efficiency

In order to study effect of GrTiFe-10 content on degradation efficiency, different amounts of GrTiFe-10 sample were used to mix with 10 mL of 20 mg/L MDB and illuminated for 180 min. The obtained results are present in figure 6. As the results shown, the degradation-efficiency increases as the mass of GrTiFe-10 used increases and reaches 93.66% for 2.0 mg and 99.49% for 5.0 mg of GrTiFe-10. For economic aspect, 2 mg of GrTiFe-10 was chosen for the following studies.

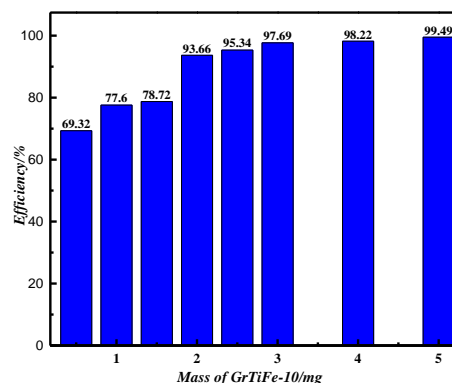


Figure 6: Effect of the mass of GrTiFe- 10 used

Effect of exposure time and concentration of MDB

Effects of exposure time and MDB concentration on degradation efficiency were studied in order to find the optimized condition for degradation of MDB compound. All experiments were carried out using 2.0 mg of GrTiFe-10, 10 mL MDB solution under 180 min illuminating. For exposure-time test, the MDB concentration of 10 mg/L was kept unchanged, but for concentration-effect test the concentration of MDB was varied. The obtained data were represented in form of chart shown in figure 7.

As the exposure time increases, the degradation efficiency increases as a linear function of exposure-time with the correlation coefficient of 0.982, and reaches value of 93.66% at the time interval of 180 min. The degradation efficiency also depends on the concentration of MDB. It reaches almost 100% for the concentration lower than 20 g/L, 93.66% for concentration of 20 mg/L after exposure-time of 180 min and start reducing rapidly as the concentration increases. The decrease of efficiency at high concentration may be explained as following: at high concentration, radiation is hindered and could not reach to the photocatalytic material hundred percent. The fewer radiation reaches to the material, the fewer generated electron-holes are produced. Therefore, less MDB is degraded, i.e., the degradation efficiency is low.

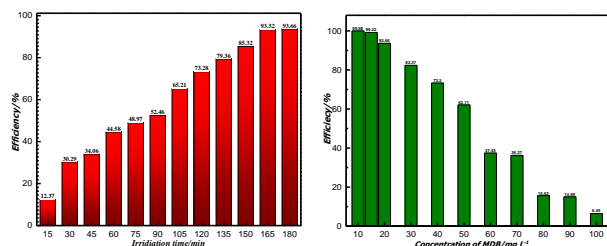


Figure 7. Effects of exposure time and concentration of MDB

Conclusion

GrTiFe-X materials have been fabricated by precipitation and hydrothermal procedures. The Fe₃O₄-wrapped TiO₂ particles with the average size of around

30 nm were the most uniformly dispersed on the graphene sheets in the GrTiFe-10 sample. The synthesized GrTiFe-10 behaviors as ferromagnetic materials and be collected with a magnetic field. The study on the photocatalytic activity shows that the optimized exposure-time, MDB concentration for the degradation of MDB on GrTiFe-10 under sunlight radiation are 180 min and 20 mg/L, respectively.

Acknowledgments

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