1 **Synthesis, Characterization and Photocatalytic Activity of Inexpensive and**
2 **Non-toxic Fe₂O₃–Fe₃O₄ Nano-composites Supported by Montmorillonite and**
3 **Modified by Graphene**

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Abstract: Inexpensive and non-toxic novel $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$ nano-composites supported by montmorillonite and modified by graphene were successfully synthesized using the liquid phase reduction hydrothermal method. The presence of montmorillonite reduced sizes of iron crystals, and the loading of graphene enhanced the separation efficiency and electron-conductivity of photo-induced electron-hole pairs. The methyl orange degradation experiment was made to investigate the photocatalysis performance of pure $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$, $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--Montmorillonite}$ and $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--Montmorillonite--Graphene}$ at the same condition. The absorption of nano-composites was a slight blue-shifted with a decreasing crystallite size of iron nano-particles, while it was clearly shifted toward longer wavelengths upon the modification using graphene. $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--Montmorillonite--Graphene}$ exhibited the excellent optical response and photocatalytic activity in visible region: the degradation rate of methyl orange reached 2.77 times faster than that of $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$ and 1.61 times faster than that of $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--Montmorillonite}$ within 30 mins irradiation. Results implied that applications of montmorillonite helped to prevent agglomeration of iron nano-particles, and graphene helped to reduce the charge recombination rate, further validated an enhanced photocatalytic performance of $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--Montmorillonite--Graphene}$ superiorly. The current study shed new light on synergetic effects of the inexpensive and non-toxic iron oxide nano-photocatalyst with visible-light responsible and magnetic-active compositions, agglomeration-preventive nano-structures by montmorillonite and enhanced electron separation by graphene.

Keywords: $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$; Montmorillonite; Graphene; Photocatalysis

1. Introduction

Recently semiconducting sub-micro/nano materials have attracted immense research interest

1 due to their optical, chemical, magnetic and electronic properties [1-5]. They can be utilized in the
2 field of catalysis [6], photoelectric devices [7-8], drug targeting, gas sensors [9], medical imaging
3 and magnetic materials [10], etc. Nanostructured catalysts like nanorods [11], nanobelts [12],
4 nanotubes [13], and nanofibers [14] have completely demonstrated excellent photocatalytic
5 activity to the oxidation of toxic organic contaminants. However, large scale application available
6 today is generally far from ideal due to the high cost of catalysts and toxicity potentials to
7 environment [15-16]. Besides, the photocatalytic activity has bearing on the dimension and the
8 surface area of crystal [17-18]. Moreover, many catalysts can only have responses to ultraviolet
9 light (wavelength $\lambda < 400$ nm) [19], which is a small portion of the solar spectrum, such as TiO_2 ,
10 ZnO and ZnS , etc [20-21]. In contrast to these catalysts, others like CdS , Fe_2O_3 , WO_3 , CaIn_2O_4 ,
11 BaBiO_3 , and Bi_2SbVO_7 with narrower band gap [19] can adsorb visible light, which is the
12 majority portion of solar spectrum. This will be more beneficial to the wastewater treatment in
13 practice in consideration of the energy utilization.

14 As a kind of semiconducting catalyst, Fe_2O_3 is deemed to be a promising visible-light-driven
15 photocatalyst because of its low cost, simple production, environmental friendliness, excellent
16 chemical stability and absorbing most of the visible light [22]. Many authors studied the
17 photocatalytic performance of nanoscale iron (hydr)oxides [20, 23, 24]. Recently, our group has
18 reported effectiveness of nanoscale zero-valent iron on heavy metal removals in wastewater, and
19 also confirmed the existence of Fe_2O_3 in partly oxidized nanoscale zero-valent iron [25-27]. In
20 light of the lower photocatalytic activity caused by the big size, the most beneficial photoelectric
21 characteristics of Fe_2O_3 can be enhanced by reducing the size of nanoparticles to increase the
22 active surface areas of the materials. An alternative approach is to support functional nanoparticles

1 with clay, such as montmorillonite, which functions as a carrier or stabilizer to reduce the
2 self-agglomeration of functional nanoparticles. However, it deteriorates the conductivity of the
3 material, which is especially critical in the photo-induced electron separation and transport.

4 Another restriction on the photocatalytic activity of Fe_2O_3 arises from the re-combination of
5 separated photo-induced electron-hole pairs [28]. The bonding between graphene and Fe_2O_3 has
6 been proved to be effective to improve the separation efficiency of photo-induced electron-hole
7 pairs [29]. Graphene is a monolayer of carbon atoms stripped from graphite [30] with many
8 outstanding advantages such as low resistivity, high mobility of charge carriers, and some new
9 quantum effects [31]. The electron in graphene can migrated much more efficiently than
10 traditional semiconductor or conductor, such as silicon and copper [32]. The classical method to
11 produce functionalized graphene-based materials is hydrothermal method by using graphene oxide
12 as precursor [33], which was creatively developed by Zhang et al. in 2010. It has been reported
13 that many materials modified by graphene exhibits good biocompatibility, outstanding electronic
14 properties and unique optical properties [29, 34-35]. It is interesting to explore more
15 photocatalytic properties of different graphene-iron oxide composites. However, there is still a
16 problem of the agglomeration of nanoparticles. There is no evidence to suggest that layer of
17 graphene can facilitate the dispersity of nanoparticles. Meanwhile, graphene itself incurs the
18 serious agglomeration.

19 In this work, we synthesized and characterized graphene-modified
20 montmorillonite-supported $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4$ nanoparticles composites ($\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4\text{-M-GP}$), and
21 reported its photocatalytic functionalities to the degradation of methyl orange dye. We expected
22 that the iron photocatalyst composites, containing montmorillonite and grapHEME, can function

together to better facilitate a combined effect on the dispersity of nanoparticles and the separation efficiency of photo-induced electron-hole pairs. The existence of Fe_3O_4 in the synthesized composite facilitated an easy separation and recycle via in a magnetic field. The aims of the current study are to (i) synthesize and characterize ($\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M--GP}$), (ii) compare the properties of pure $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$, $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M}$ and $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M--GP}$, (iii) evaluate combined effect of different component (montmorillonite, other iron (hydr)oxides, graphene) on the photocatalytic process, and confirm the feasibility of the combination of the high conductivity of graphene and the dispersive effect of montmorillonite on nanoparticles, the excellent photo-effectiveness of $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M--GP}$ nanoparticles to enhance its practical applications.

2. Material and methods

2.1 Synthesis of $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$ and $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M}$

$\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$ and $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M}$ were prepared in atmosphere by the liquid-phase reduction according to the previously published method [36]. First, 20.43 g $\text{Fe}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$ was added to 100 mL deionized water with/without 2 g uniformly distributed montmorillonite. The mixture was magnetically stirred for 12 h to form the stable iron solution. The sodium borohydride (NaBH_4) solution was prepared by dissolving 10.84 g solid NaBH_4 in a 100mL deionized water, maintaining a specific B/Fe ratio of 4:1. Prior to dipping the NaBH_4 solution into the iron solution for the reduction, the triple-narrow-blade propeller agitator was adopted to prevent the effect of magnetism on nanoparticles. The NaBH_4 solution was dropwise feed to the iron solution under consistent stirring to disperse the reaction mixture homogeneously. The obtained material was centrifuged at 5000 rpm/min for 20 min, followed by a thorough rinse in 50 vol% ethanol solution and acetone via centrifugation at 8000 rpm/min, and then dried overnight in oven at 45°C . The

1 obtained composite iron material was stored in the refrigerator.

2 **2.2 Synthesis of GO**

3 GO was synthesized from graphite powder by a modified Hummers' method [37], in which
4 pre-oxidation of graphite was followed by oxidation. The detail operation followed the experiment
5 procedure described by Li et al. [29]: The graphite powder (4.0 g) was added with stirring into the
6 concentrated H₂SO₄ (40 mL) solution in which K₂S₂O₈ (2.0 g) and P₂O₅ (2.0 g) were completely
7 dissolved at 80 °C. The mixture, in a beaker, was kept at 80 °C for 4.5 h using an oil bath. Then, the
8 mixture was cooled down and was diluted with 1 L of distilled deionized water. The pretreated product
9 was filtered and washed until the pH of filtrate water became neutral. The shiny, dark-gray,
10 pre-oxidized graphite was dried in air overnight. Then, it was dispersed by stirring into chilled H₂SO₄
11 (92 mL) in a flask in an ice bath. KMnO₄ (12 g) was added slowly with stirring to keep the temperature
12 of reaction mixture below 20 °C. The resulting thick, dark green paste was allowed to react at 35 °C
13 for 3 h followed by addition of H₂O (184 mL) to give a dark brown solution. After additional stirring
14 for 2 h, the dark brownish solution was further diluted with distilled water (560 mL) and then H₂O₂
15 (30 %, 40 mL) was added slowly and the color of the mixture turned into brilliant yellow. The mixture
16 was allowed to settle overnight and the supernatant was decanted. The remaining product was washed
17 with 10 % HCl solution with stirring and the brownish solution was allowed to settle overnight. The
18 supernatant was decanted and the remaining product was centrifuged and washed with deionized water.
19 The washing process was repeated until the pH of the solution became neutral. After filtration and
20 drying under vacuum, GO was obtained as a gray powder.

21 **2.3 Synthesis of Fe₂O₃–Fe₃O₄–M-GP**

22 The loading of graphene onto Fe₂O₃–Fe₃O₄–M nanoparticles was performed using the

1 hydrothermal method. GO was dispersed into deionized water with specific ratio (0.1 g: 100 mL) and
2 was deal with ultrasonication for 24 h. This was followed by adding 0.25 g $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$ nanoparticles
3 into 30 ml of the above solution, and the mixture was vigorously stirred for 24 h. The mixture was
4 transferred into a 200 mL Teflon-lined stainless steel autoclave, which was tightly sealed. The
5 autoclave was put into a muffle furnace where temperature was maintained to be 120°C for 24 hours.
6 Afterwards, the autoclave was cooled to an ambient temperature naturally, and the resulted product was
7 separated by centrifugalization, dried at 60°C in oven, and grinded for the future characterizations and
8 tests.

9 **2.4 Materials and Characterization**

10 The reagents used in this study were analytical grade and purchased from different
11 commercial corporations. Ferric sulfate polyhydrate, sodium borohydride, hydrogen peroxide
12 (H_2O_2 , 30%, w/w), graphite powder, potassium peroxodisulfate, potassium permanganate,
13 phosphorus pentoxide, sulfuric acid and sodium hydroxide were used as primary reagents.
14 Characterizations of obtained samples were performed using XRD with Cu $K\alpha$ radiation (ARL
15 X'TRA Powder Diffractometer, Japan), SEM (Model JSM-6510LV, JEOL Ltd., Tokyo, Japan)
16 connecting with the EDX, TEM (HRTEM; Model JEM-1400Plus, JOEL Ltd., Tokyo, Japan), DSC
17 combined with TGA (TA Instrument, 2960 Simultaneous DSC-TGA), FTIR spectrometer
18 (PerkinElmer, Spectrum Two), UV–vis absorption spectra (Cary, 100 Bio).

19 **2.5 Photocatalytic Activity Measurement**

20 Methyl orange is one of major cationic dyes and not biodegradable in wastewater. The
21 obtained iron composite was subject to the photo-catalytic degradation of Methyl orange. 10 mg
22 of photocatalysts ($\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$, $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M}$ or $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--GP}$) were added into 20 mL of
23 methyl orange solution (20 mg L^{-1} , Alfa Aesar, CAS# 81-88-9). Then the mixture was stirred for 5

min and sonicated for 10 min to reach a complete adsorption-desorption equilibrium in dark, and then transferred into a quartz photo-reactor, which was exposed to a visible light irradiation by a 300 W xenon lamp, maintained by a distance of 10 cm. The photo-reactor is a cylindrical quartz container with a length of 10 cm and a radius of 1 cm. Light went through the circular surface along its length. The photocatalytic activity of loaded photocatalysts for the degradation of methyl orange was frequently measured by the absorbance of the supernatant during different intervals in kinetic tests. The concentrations of methyl orange were monitored by checking the absorbance of residual supernatant solution at 464 nm. All photocatalysis experiments were performed at 20°C.

2.6 Magnetic tests of $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4\text{-M-GP}$ and its recycling

Magnet field were applied to the bottom of beakers of mixtures to collect or recovery the $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4\text{-M-GP}$. Four orientations of magnet were organized, including a big magnet (15 cm×2 cm×2 cm), a small magnet (4 cm×1 cm×1 cm), two shunt-wound magnets (4 cm×1 cm×1 cm) and two series-wound magnets (4 cm×1 cm×1 cm). After 5 mins of the magnetic separation, the residual iron particles was filtrated and rinsed ultrasonically for three times using 30 ml of distilled water. Each ultrasonic rinsing was preferred for 30 min. Then recovered iron particles were further washed by anhydrous ethanol for once, and dried to a constant weight at 45 °C in a vacuum to obtain a regenerative $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4\text{-M-GP}$. The sample was weighed to calculate the recovery rate.

3 Results and discussion

3.1 Characterization

3.1.1 Morphology and EDX analysis

The SEM images in [Figure 1](#) showed the morphology of the pure $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4$,

1 $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M}$, and $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M--GP}$ sample. The morphologies of pure $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$ were
2 showed in Figure 1a and 1b. Figure 1b indicated the presence of some larger floc clumps (2 μm),
3 suggesting that pure $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$ sample was either poorly dispersed or more easily reunited.
4 Images c and d in Figure 1 showed the typical SEM morphology of $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M}$ composite. A
5 lower magnified TEM image (Figure 1 c) revealed that the surface of montmorillonite was
6 covered by catenulate $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$ nanoparticles in $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M}$ composite. In contrast to
7 the poor dispersion of $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$ sample, the $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$ particles immobilized on
8 montmorillonite were clearly distinguished in $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M}$ composite (Figure 2b). The
9 $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$ particles in $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M}$ composite exhibited a better dispersity with a wider
10 size range of 10-80 nm. Therefore, we confirmed that $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M}$ composite were
11 successfully prepared. $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$ particles showed better homogeneity and reduced sizes after
12 loading onto montmorillonite. Consequently $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M}$ composite was chosen to further
13 load graphene to improve the electron transfer and separation efficiency of photo-induced
14 electron-hole pairs. As shown in the Figure 1e and 1f, $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M--GP}$ composite still
15 presented a typical nanoparticles structure: with thin silk fabrics closely coated on the surface of
16 $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$ particles. The $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$ particles with an average size from 20 nm to 50 nm
17 were uniformly anchored onto graphene nanosheets in $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M--GP}$ composite.
18 $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M--GP}$ composite was successfully synthesized, this result was also confirmed by
19 the XRD analysis. As images at low magnification (Figure 1a), we can see that there was still
20 some ferric sulfate which was not reduced. The composition of $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M--GP}$ composite
21 was further confirmed by the EDX analysis. The composition in different points of
22 $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M--GP}$ composite was a little different (Figure 1e) and it was mainly composed of

1 Fe and O elements in point 1 with the molar ratio (Fe to O) of about 1: 1.14 (Figure 2a). The peaks
2 of Al and Si were the characteristic signals of montmorillonite; Signal of C was considered to be
3 from graphene. It is mainly composed of Fe and O elements in point 2 with the molar ratio (Fe to
4 O) of about 1: 2.5 (Figure 2b). The theoretical value expected between Fe and O in pure
5 Fe_2O_3 – Fe_3O_4 was 1: 1.4, presenting the ratio of Fe_2O_3 to Fe_3O_4 is 1:1. As showed by the signal
6 intensity of C, there may be slightly difference in the loading quantity of graphene at different
7 point. It showed that it was complex for iron species in the synthesized materials that including
8 unoxidized zero valent iron, Fe_2O_3 , Fe_3O_4 , FeOOH , montmorillonite and graphene. But the major
9 components are Fe_2O_3 , FeOOH and Fe_3O_4 .

10 The microstructure and morphology of Fe_2O_3 – Fe_3O_4 –M–GP composite were further
11 investigated by TEM (Figure 3). The internal structure of Fe_2O_3 – Fe_3O_4 –M–GP composite
12 indicated that how different types of parts (Fe_2O_3 – Fe_3O_4 nanoparticles, montmorillonite and
13 graphene) were able to be integrated to form Fe_2O_3 – Fe_3O_4 –M–GP composite. There are two
14 phases of graphene in Fe_2O_3 – Fe_3O_4 –M–GP composite depend on the quantitative distribution of
15 Fe_2O_3 – Fe_3O_4 nanoparticles on montmorillonite. It was observed that some graphene existed as
16 curled nano-surfaces and adhered on the surfaces of montmorillonite, which contact a few
17 Fe_2O_3 – Fe_3O_4 nanoparticles sometimes (Figure 3a). However, most of graphene covered on the
18 surfaces of Fe_2O_3 – Fe_3O_4 nanoparticles or a few small montmorillonite particles, resulting in the
19 morphology of a thin smooth layer (Figure 3b). A further magnified TEM images (Figure 3c, d)
20 clearly revealed an outer layer of coating resulted from graphene: it acted as an electronic
21 transmission blanket on montmorillonite and Fe_2O_3 – Fe_3O_4 nanoparticles that dispersed on the
22 surface of montmorillonite were also crosslinked by this covering, which was well consistent with

that in the SEM images (Figure 1e, f).

3.1.2 XRD analysis

The crystalline phases of $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$, $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M}$, and $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M--GP}$ were studied as presented in Figure 4. Diffraction peaks in XRD pattern of $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$ was sharp and intense, suggesting higher degree of crystallinity. It showed that the loading of montmorillonite can effectively reduce the growth of crystalline grain. Sharp diffraction peaks possessed by $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M--GP}$ and $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$ at 2θ values of 33.23° , 35.67° , 49.45° , 54.11° , 57.38° , 62.70° and 64.16° which could be indexed to the (104), (110), (024), (116), (018), (214) and (300) planes of hematite with rhombohedral structure belonging to the space group of D_{6h}^{3d} crystal space group (JCPDS 84-0311) [38, 39]. $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M--GP}$ composite was successfully synthesized because no obvious peaks respectively to graphite and graphene oxide were discovered in the XRD patterns of the synthesized $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M--GP}$. In addition, there was no significant difference in terms of the intensity of diffraction peaks between bare $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$ and $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M--GP}$ composite. However, the synthesis of $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M--GP}$ may have a certain effect on the transversely displacement of the XRD patterns of $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$ and $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M}$. Reflection peaks for montmorillonite were presented at 2θ values of 7.78° , 12.13° , 14.95° and 28.05° in the XRD pattern of $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M}$, indicating that $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$ nanoparticles were loaded onto montmorillonite successfully. Clearly, the addition of montmorillonite or graphene into composites likely affects the components of synthetic composite materials. $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$ particles were primarily composed of maghemite (Fe_2O_3), lepidocrocite (FeOOH), goethite ($\text{Fe}(\text{OOH})_3$), magnetite (Fe_3O_4) and little Fe^0 . $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M}$ composite was primarily composed of montmorillonite, lepidocrocite (FeOOH), magnetite (Fe_3O_4) and

1 maghemite (Fe_2O_3). $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4\text{-M-GP}$ composite primarily contained maghemite (Fe_2O_3).
2 Based on XRD data and estimated by the Scherer's formula, the average crystallite sizes were
3 20.58 nm for $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4$, 16.95 nm for $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4\text{-M}$ and 24.28 nm for $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4\text{-M-GP}$,
4 respectively. It showed that the loading of graphene will initiate a slight polymerization of
5 $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4\text{-M}$. Although it has abuses and is not as effective as montmorillonite in this aspect,
6 it could make a big enhancement of the aim of decreasing re-combination of separated
7 photo-induced electron-hole pairs and improving the conductivity of $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4\text{-M}$ with a little
8 change by itself.

9 **3.1.3 FTIR spectra analysis**

10 **Figure 5** recorded the FTIR spectra of pure $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4$, $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4\text{-M}$, and
11 $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4\text{-M-GP}$. As what can be seen from the diagram, the FTIR spectra of
12 $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4\text{-M}$ and $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4\text{-M-GP}$ composite were similar, possessing all the absorption
13 peaks in the FTIR spectra of pure $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4$ even though it was not very obvious sometimes.
14 The intensity of main absorption peaks at 1085, 1640 and 3310 cm^{-1} in the FTIR spectrum of
15 $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4\text{-M}$, and $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4\text{-M-GP}$ composite was smaller than that in the spectra of the
16 pure $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4$, because the effective quantity of photocatalysts has been diluted by
17 montmorillonite and graphene. Another similarity between $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4\text{-M}$ and
18 $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4\text{-M-GP}$ composite was the presence of infrared absorption characteristic peaks at
19 1024 cm^{-1} for $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4\text{-M}$, and at 1564 cm^{-1} for $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4\text{-M-GP}$ respectively, which most
20 likely resulted from Si-O stretching vibrations band [40] in montmorillonite and -C=C- bending and
21 stretching vibrations band [41] of graphene layers. Adsorbed peaks associated with iron oxides
22 were located at 470, 547 cm^{-1} in the FT-IR spectrum of pure $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4$, which was assigned to

1 Fe–O–Fe bending and stretching vibration mode [42-44] respectively. Broad adsorbed bands
 2 associated with iron hydroxides displayed at 2980–3706 cm^{-1} , which was ascribed to the vibrational
 3 modes of hydroxyl group (O–H), including stretching vibrational modes of hydroxyl group (O–H)
 4 from M–OH in the region of 3400–3600 cm^{-1} [45], the bending and stretching vibrations of O–H
 5 groups [18, 45-47] from bound water and constituent water combined with M–OH at 3310 and 3354
 6 cm^{-1} [45-47]. Some absorption peaks in the FT-IR spectrum show that there were some impurities left
 7 during the preparation, such as the O=C–C bending modes and C–OH stretching modes at 613 and
 8 689 cm^{-1} [48] for ethanol, the C–OH vibration modes at 1363 cm^{-1} [49] for borate species, the S=O
 9 or S–O vibration modes in the region of 800–1300 cm^{-1} [20, 45, 50] for sulfate groups, the O=C=O
 10 stretching vibration modes at 1481 cm^{-1} for carbon dioxide [18, 51] and the epoxy group vibration
 11 modes at 1178 cm^{-1} for graphite oxide [52]. The study of FTIR spectra verifies the results of XRD
 12 analysis, and further pointed out that there is still some graphene oxygen contained in
 13 $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M--GP}$ composites.

14 **3.1.4 DSC-TGA analysis**

15 [Figure 6-7](#) presented DSC-TGA curves for pure $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$, $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M}$ and
 16 $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M--GP}$ samples. The pure $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$ generated a complex DSC curve below
 17 318°C ([Figure 6](#)) with endothermic peaks in addition to two slight exothermic peaks at 75°C and
 18 125°C. The first peak at 75°C represented the oxidation of FeO, which existed in the DSC curve
 19 of $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M}$ and $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M--GP}$. The second peak at 125 °C that absent for
 20 $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M}$ and $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M--GP}$ should be attributed to the oxidation of Fe^0 , combined
 21 with XRD analysis results in [Figures 1](#). These two signals were not clear to be showed in [Figure 7](#),
 22 due to a serious weight loss caused by the evaporation or desorption of water in samples. Another

1 similarity was the presence of obvious exothermic signals started at 318°C, 309°C and 300°C,
 2 respectively, that most likely resulted from the transformation from magnetite (Fe_3O_4) to
 3 maghemite (Fe_2O_3), higher than that previously reported rough range of 170°C to 290°C [53-55].
 4 In addition to the decreasing of evaporation or desorption of water, it should be responsible for the
 5 flat portions in TGA curves of Fe_2O_3 - Fe_3O_4 and Fe_2O_3 - Fe_3O_4 -M. However, another endothermic
 6 event, which began at approximately 400°C for Fe_2O_3 - Fe_3O_4 -M-GP, was most likely due to the
 7 decomposition of graphene [56], and the loss of bound water maintained in goethite (α - FeOOH)
 8 and further decomposition of goethite (α - FeOOH) to hematite (α - Fe_2O_3) or magnetite (Fe_3O_4)
 9 [57]. Subsequently, the curve exhibited two obvious exothermic signal (Figure 6) at 492°C and
 10 547 °C , which was due to the newly formed magnetite (Fe_3O_4) to maghemite (Fe_2O_3)
 11 transformation. The multi-step process was finished at about 575°C with a gradual change of
 12 different-sized particles. The dehydroxylation process of montmorillonite appeared at 668°C with a
 13 slight exothermic signal. Afterwards, the temperature of the phase transformation from maghemite
 14 to hematite was at 738 °C (756 °C for Fe_2O_3 - Fe_3O_4 and Fe_2O_3 - Fe_3O_4 -M-GP), which was
 15 consistent with the previously reported phase-transformation temperature range of maghemite [53,
 16 55]. It was worth noting that DSC curves for Fe_2O_3 - Fe_3O_4 -M and Fe_2O_3 - Fe_3O_4 -M-GP exhibited
 17 an exothermic signal between 810 °C and 830 °C that was related to the liquation of
 18 ferrimontmorillonite [58, 59]. When the temperature reached from 318°C to 575°C (Figure 7),
 19 the relative percentage of weight loss of pure Fe_2O_3 - Fe_3O_4 , Fe_2O_3 - Fe_3O_4 -M and
 20 Fe_2O_3 - Fe_3O_4 -M-GP increased by 0.97%, 0.29% and 5.56%, respectively. Combined with the
 21 results of EDX and DSC-TGA analysis, the estimated effective dose in Fe_2O_3 - Fe_3O_4 -M and
 22 Fe_2O_3 - Fe_3O_4 -M-GP was about 25.5% and 21.73 % per unit mass.

3.2 Photocatalytic Properties.

The UV-Vis absorption spectra of pure $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4$, $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4\text{-M}$ and $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4\text{-M-GP}$ samples were given in Figure 8a. A significant increase of absorption will appear when wavelengths shorter than 600 nm, other researchers have noted that which was due to the electron transitions from the valence band to conduction band of Fe_2O_3 ($\text{O}_{2p} \rightarrow \text{Fe}_{3d}$) [60]. It was observed that the absorption of $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4\text{-M-GP}$ composites in visible light region has been greatly increased when graphene was added in $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4\text{-M}$ composites, but the loading of only montmorillonite seemed detrimental to the absorption of pure $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4$ in the visible light region. $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4\text{-M}$ composites absorbed the light more effectively than pure $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4$ and $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4\text{-M-GP}$ composites near 470 nm. The undermentioned explanation offered the reference. With the loading of montmorillonite, the absorption of $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4\text{-M}$ composites was a slight blue-shifted. Other researchers [61-63] argued that the transition is caused by the decreasing crystallite size and the strengthening quantum confinement of charge carriers at smaller $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4$ particles on montmorillonite. However, the absorption of $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4\text{-M-GP}$ was clearly shifted toward longer wavelengths with the adding of graphene, suggesting a decrease in the bandgap energy of $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4\text{-M}$. The Kubelka-Munk equation for calculating the bandgap of photocatalysts is expressed as [64, 65]:

$$\alpha = B_d(h\nu - E_g)^{1/2} / h\nu \quad (13)$$

Where B_d is the absorption constant for direct transition. The direct bandgap energies of samples can be estimated by the plot of $(\alpha h\nu)^2$ versus $(h\nu)$. α can be determined from the scattering and reflectance spectra. The estimated band gap of $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4\text{-M}$ and $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4\text{-M-GP}$ sample (Figure 8b) were found to be 2.85 eV and 1.77 eV separately.

1 Compared with the band gap values of pure $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$ (2.14 eV), the absorption edge of
2 $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M--GP}$ was red-shifted and $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M}$ was blue-shifted, in agreement with
3 previous analysis results based on the [Figure 8a](#).

4 A series of experiments were performed to investigate the kinetics of methyl orange
5 degradation, based on the same dose of pure $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$ (10 mg) and $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M}$ (15.2
6 mg), and the same effective dose of $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M--GP}$ (23.5 mg) as comparative
7 photocatalysts. The temporal UV-vis spectral changes of methyl orange solutions in the process of
8 photodegradation were displayed in the [Figure 9](#). With the increasing photo exposure time, the
9 main absorbance at 462 nm, corresponding to the adsorption peak and concentrations of methyl
10 orange, decreased gradually. To compare the reactivity of the pure $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$, $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M}$
11 and $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M--GP}$ quantitatively, the degradation percentages of methyl orange at the same
12 time were calculated and after 30 min prolonged irradiation, the degradation rate of methyl orange
13 reached 2.77 times faster than $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$ and 1.61 times faster than
14 $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--Montmorillonite}$, respectively. The equilibrium times for photocatalytic degradation
15 of methyl orange by the pure $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$ and $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M}$ are much longer than 240 min of
16 $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M--GP}$. For different samples, the photocatalytic degradation efficiency of the three
17 samples in the initial stage decreased as follows ([Figure 10](#)): $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M--GP} >$
18 $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M} >$ pure $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$, $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M--GP}$ possessed a superior photocatalytic
19 performance of the methyl orange degradation. It showed that the loading of graphene or
20 montmorillonite have a few influences on the percentage of iron-bearing minerals in composites,
21 especially for FeOOH . Nevertheless, FeOOH has a very close intrinsic band gaps (2.2 eV) [66] to
22 Fe_2O_3 (2.1-2.2 eV) [67], and the percentage of FeOOH in different samples which didn't cause

1 much difference in the photocatalytic performance of different samples. As shown in [Figure 11](#),
2 once the electrons in the VB of Fe_2O_3 and FeOOH are excited under irradiation, the photo-induced
3 electrons will transfer to the CB of Fe_2O_3 and FeOOH with the same amount of positively charged
4 holes left. Afterwards, parts of electrons can be transferred to the surface of graphene, which make
5 the photogenerated electron-hole pairs to be separated more easily at the interface. Moreover,
6 graphene have huge mobility. Thus, the photogenerated electrons and holes could migrate more
7 effectively to the surfaces of photocatalysts. Subsequently, electrons will meet absorbed or
8 dissolved O_2 to produce superoxide anion radical ($\cdot\text{O}_2^-$), while holes could react with
9 surface-bound H_2O and OH^- to form the hydroxyl radicals ($\cdot\text{OH}$) which could decompose the
10 methyl orange as a powerful oxidant [[68](#), [69](#)].

11 **3.3 Magnetic recovery**

12 [Figure 12](#) presented most of used $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4\text{-M-GP}$, above 98.8% efficiency, was able to
13 be recovered from the aqueous environment by the magnetic separation approach. And the
14 recovery rate increased versus a increased magnetic intensity via different magnet orientations and
15 selection of magnetic intensities. The weak magnetic particles, such as $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4\text{-M-GP}$ in
16 this study, were confirmed to be effectively recovered even in the weak magnetic fields.
17 Uncertainty regarding 100 percent efficiency of the sample recovery was likely derived from that
18 part of montmorillonite or graphene was not combined with $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4$ nanoparticles or shed
19 off in solution environment.

20 **4 Conclusions**

21 In summary, novel $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4$ nanoparticles supported by montmorillonite and graphene
22 were successfully synthesized using liquid phase reduction method combined with hydrothermal

1 method. $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--Montmorillonite}$ composites exhibited the excellent optical response and
2 photocatalytic activity in visible region. The photocatalytic efficiency of photocatalysts decreased
3 as follows: $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--Montmorillonite--Graphene} > \text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--Montmorillonite} > \text{pure}$
4 $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$. The loading of graphene onto $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--Montmorillonite}$ composites has
5 clearly enhanced its photocatalytic activity, suggesting the increase separation efficiency of
6 photo-induced electron-hole pairs facilitated by graphene, and the enhanced photo-responsible
7 ability of $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--Montmorillonite}$ in the visible region of solar radiation. The results from
8 current study shed new light on synergetic effects of visible-light responsible compositions,
9 reduced size of nanoparticles by montmorillonite and enhanced electron separation by graphene
10 on photocatalysis under the variation of mechanical structure by inexpensive and non-toxic iron
11 oxide particles. Besides, our findings will render the environmental application of many other
12 important semiconducting metal oxides more potential, while allowing large linear dynamic
13 ranges in short response time.

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Figure Captions:

Figure 1, SEM images of $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$ (a and b), $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M}$ (c and d) and $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M--GP}$ (e and f).

Figure 2, EDX spectrum of $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M--GP}$.

Figure 3. TEM images of $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M--GP}$.

Figure 4, XRD patterns of $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$, $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M}$ and $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M--GP}$.

Figure 5, FTIR spectra of $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$, $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M}$ and $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M--GP}$.

Figure 6, DSC curves of $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$, $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M}$ and $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M--GP}$.

Figure 7, TGA curves of $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$, $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M}$ and $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M--GP}$.

Figure 8, The UV–Vis absorption spectra (a) and $(\alpha h\nu)^2$ vs. $(h\nu)$ curve (b) of $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$, $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M}$ and $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M--GP}$.

Figure 9, Absorption spectra of the solution of methyl orange exposed to irradiation for different time in the presence of $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$, $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M}$ and $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M--GP}$.

Figure 10. Photocatalytic performances of different samples under visible light irradiation: $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$ (10 mg), $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M}$ (15.2 mg) and $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M--GP}$ (23.5 mg).

Figure 11. Schematic illustration of the mechanism of high photocatalytic activity at interface of $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M--GP}$ nanocomposites under visible light.

Figure 12. The magnetic performance of $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4\text{--M--GP}$ and its recycling from aqueous solution by magnetic separation.

(a)

(b)

(c)

(d)

(e)

(f)

Figure 1. SEM images of $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4$ (a and b), $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4\text{-M}$ (c and d) and $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4\text{-M-GP}$ (e and f).

(a) point 1 in **Figure 1e**

(b) point 2 in **Figure 1e**

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Figure 12. The magnetic performance of Fe₂O₃-Fe₃O₄-M-GP and its recycling from aqueous solution by magnetic separation.

Graphic Abstract

Novel $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4$ was supported on montmorillonite and modified by graphene. Montmorillonite functions as a stabilizer to maintain sizes of nanoparticles and prevent graphene agglomeration. Graphene functions as an electron-conductive enhancer to improve the separation efficiency of photo-induced electron-hole pairs. This hetero-structure nano-composite exhibited an excellent optical response and photocatalytic activity in visible light region.