Facile Synthesis of Magnetic Reduced Graphene Oxide-ZnFe$_2$O$_4$ Composites with Enhanced Visible-Light Photocatalytic Activity

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Abstract: Magnetic ZnFe$_2$O$_4$-the reduced graphene (rGO) nanocomposites (ZnFe$_2$O$_4$-rGO NCs) have been successfully synthesized by a facile solvothermal method. The photocatalytic activities of the prepared photocatalysts were evaluated by degradation of methylene blue (MB) dyes under visible-light irradiation. In comparison with ZnFe$_2$O$_4$ nanoparticles (NPs) catalyst, the ZnFe$_2$O$_4$-rGO NCs can generate more hydroxyl radicals ($\bullet$OH) via photoelectron chemical decomposition of H$_2$O$_2$. Moreover, the as-prepared ZnFe$_2$O$_4$-rGO NCs can magnetically separable in a suspension system. Therefore, they can be conveniently applied to dispose toxic organic pollutants during water treatment.

1. Introduction

The environmental problem concerning organic waste has increased with the increase in industrial development in the past few decades, and waste accumulation is a danger to human health. Semiconductor photocatalysis has attracted a great deal of attentions due to their wide application to environmental remediation, especially for organic pollutants removal [1, 2]. Many semiconductor photocatalysts have been extensively researched in field of photocatalytic degradation of organic dyes, e.g. ZnO, TiO$_2$ and so on, but the wide band gap (3.0-3.8 eV) of these semiconductors limits their photocatalytic activity under visible-light irradiation [3-5]. Therefore, developing efficient visible-light responsive photocatalysts for wastewater remediation has been an active research area in recent years [6-8].

Among these photocatalysts, the spinel ZnFe$_2$O$_4$ has been attracted considerable attention due to its special properties, for example a visible-light response, low toxicity, good photochemical stability, and excellent ferromagnetic properties for magnetic separation from suspensions [9-12]. However, ZnFe$_2$O$_4$ is seldom used as a photocatalyst with high efficiency, which stems from its poor photoelectric conversion property and low valence band potential [13-15]. Inspiring, it is possible to improve the efficiency of the photo-induced charge separation in ZnFe$_2$O$_4$ by coupling it with another semiconductor.

Recently, graphene nanosheets have been considered as an ideal co-catalyst to satisfy the quick transfer of electrons and avoid the recombination of photo-induced electron-hole pairs, due to their
superior electrical conductivity. Meanwhile, the two-dimensional (2D) honeycomb structure of graphene is appropriate as a supporting material to adjust the growth of nanoparticles (NPs). Particularly, a few efforts have been made for coupling ZnFe$_2$O$_4$ with graphene to fabricate heterojunction photocatalysts with improved photocatalytic activity. Lu et al [16] synthesized ZnFe$_2$O$_4$-graphene composite via a one-pot solvothermal method. The results show that the composite serves a dual function as the catalyst for photoelectrochemical degradation of dyes and the generator of a strong oxidant hydroxyl radical ($\cdot$OH). Furthermore, Shen et al [17] prepared reduced graphene oxide-ZnFe$_2$O$_4$ composites through chemical co-precipitation method, authors studied their adsorption behavior and photocatalyst degradation on RhB. Fu et al [18] prepared the ZnFe$_2$O$_4$-graphene by hydrothermal method, and briefly studied the photocatalytic degradation on MB, photocatalytic mechanism, and magnetic property. Although the influence of graphene on the photocatalytic activity of ZnFe$_2$O$_4$-graphene under visible-light irradiation has been reported, the confined growth of ZnFe$_2$O$_4$ on graphene sheets is often not examined.

In this work, we have employed a one-pot solvothermal reaction method to prepare magnetic ZnFe$_2$O$_4$-graphene nanocomposites (ZnFe$_2$O$_4$-rGO NCs). The XDR and morphology results indicate that ZnFe$_2$O$_4$ is well crystallized and the graphene sheets are much thin. Moreover, we were able to understand the dependence behavior of photocatalytic activity on the morphological and structural characteristics of the ZnFe$_2$O$_4$-rGO NCs. Furthermore, the as-synthesized ZnFe$_2$O$_4$-rGO NCs have excellent adsorption and photocatalytic activity to methylene blue (MB) dyes. These magnetic composites can be easily recovered and reused as promising photocatalysts for remove organic pollutants during water treatment.

2. Experimental procedure

2.1. Raw materials

All chemicals were of analytic grade and used as received without further purification, unless otherwise stated. Zinc nitrate hexahydrate (Zn(NO$_3$)$_2$•6H$_2$O, AR), iron nitrate nonahydrate (Fe(NO$_3$)$_3$•9H$_2$O, AR), and methylene blue (MB) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Sodium hydroxide (NaOH, AR) were obtained from Xilong Chemical Co., Ltd (Shantou, China). Anhydrous ethylene glycol and deionized water were used in this experiment. Commercially available graphene suspension (thickness of 3-10nm, size of 5-10 $\mu$m) with a concentration of 1mg/mL was purchased from XFNANO Materials Tech Co. Ltd (Nanjing, China).

2.2. Fabrication of ZnO nanoparticles

The ZnFe$_2$O$_4$-graphene nanocomposite photocatalysts were synthesized via a solvothermal method. In a typical synthesis, 0.05 mol/L Zn(NO$_3$)$_2$ ethanol solution and 0.10 mol/L Fe(NO$_3$)$_3$•9H$_2$O ethanol solution mixed together in equal volume under constant stirring, the mixed solution labeled as Ms. Secondly, different volume of graphene suspension (Gs) (Ms/ Gs volume ratio= 0.5) were added slowly with constant stirring until a homogeneous solution was achieved. Then, 4M NaOH aqueous solution was added to make the above homogeneous solution pH about 13 (without any surfactant or chelating agent). The resulting mixture was transferred into the Teflon liner stainless-steel autoclaves with effective volumes of 100ml. The autoclaves were filled with 80ml of above solution, seal and then kept in an oven at 180°C for 20 h. After cooling to room temperature, the precipitate was washed repeatedly with deionized water and ethanol before being dried at 65°C for 12h. The products were labeled as ZnFe$_2$O$_4$-rGO NCs. For comparison, the same method was used to synthesize pure ZnFe$_2$O$_4$ without graphene.

2.3. Characterization

The crystal phase was studied with powder X-ray diffraction analysis (XRD, D/Max-2550 V, Rigaku, Japan; CuK, $\lambda$=0.15406 nm) in the wide angle region from 10° to 80° with a scanning speed of 2°/min. The structure and morphology of products were examined with field emission scanning electron
microscopy (FESEM, S-4800, Hitachi, Japan) equipped with an energy dispersive spectrometer (EDS, INCA Energy, Oxford, UK). UV-visible absorbance spectra were obtained for the dry-pressed disk samples with a UV-visible spectrophotometer (Lambda750, Perkin Elmer, USA). BaSO₄ was used as a reflectance standard in a UV-visible diffuse reflectance experiment. The sample specific surface area was measured by low-temperature (77.4K) nitrogen adsorption on the basis of the Brunauer-Emmett-Teller (BET) equation with a surface area analyzer (Autosorb- iQ2, Quantachrome, USA). The room-temperature hysteresis loop (M-H curve) of the pure ZnFe₂O₄ or ZnFe₂O₄-rGO NCs was measured using a physical property measure system (Quantum Design PPMS-9, USA ). The zeta potential as a function of pH were performed using a zeta potential analyzer (Zetaplus, Chenhua, JS94K2 Powereach, China). The as-received suspension containing 0.2g/L pure ZnFe₂O₄ or ZnFe₂O₄-rGO NCs were diluted to using deionized water.

2.4. Evaluation of photocatalytic performance
The photocatalytic properties of as-obtained samples were evaluated by measuring the degradation of methylene blue (MB) under visible-light irradiation. A 500-W xenon lamp with 420 nm filter was used as visible-light irradiation. The distance between the liquid surface of the suspension and the light source was set to about 11cm. The photodegradation experiments were performed with the sample powder (58mg) suspended in solutions of the pollutants (58ml; MB 10mg/L) with constant stirring. Prior to irradiation, the suspensions were stirred in dark for 1.0h to ensure adsorption/desorption equilibrium between the dye and the catalyst. After that, 1.0 mL of 30% H₂O₂ was added to the above each reaction mixture, the lamp was turned on. At certain time intervals, 3ml solution was drawn out each time and centrifuged at 5000rpm for 5min to get clear liquid. The quantitative determination of MB was performed by measuring its intensity of the absorption peak (MB at 664 nm) with a UV-vis spectrophotometer (Lambda35, Perkin Elmer, USA).

![Figure 1. XRD of samples: (a) ZnFe₂O₄ nanoparticles(NPs), (b) ZnFe₂O₄-rGO nanocomposites (NCs).](image)

3. Results and discussion

3.1. Composition and morphology
The XRD diffraction patterns of the as-prepared ZnFe₂O₄-graphene nanocomposite and pure ZnFe₂O₄ are shown in Figure 1. It can be seen that almost all the diffraction peaks of ZnFe₂O₄-graphene may be assigned to spinel-type ZnFe₂O₄ (JCPDS 22-1012). However, no typical diffraction peak of graphite (002) is observable in the XRD pattern for ZnFe₂O₄-graphene. This may be ascribed to the reduced
GO sheets were decorated by ZnFe$_2$O$_4$ nanocrystals. On the other hand, as reported previously, graphene oxide sheets can be reduced under hydrothermal conditions in the presence of alcohols, and the reduced graphene oxide sheets show no visible sign of the (002) peak [18].

![Figure 2](image)

**Figure 2.** Typical FESEM images of samples: (a) ZnFe$_2$O$_4$ nanoparticles (NPs), (b) ZnFe$_2$O$_4$-rGO nanocomposites (NCs). Inset of figure represents the corresponding EDS spectrum for pure ZnFe$_2$O$_4$.

The general morphologies of as-obtained ZnFe$_2$O$_4$ and ZnFe$_2$O$_4$-rGO nanocomposites were analyzed by FESEM. It is evidently seen that ZnFe$_2$O$_4$ NPs with diameters in the range of 10-15 nm present the spherical morphology, they display a slight agglomeration due to their own magnetism. To examine the elemental composition, the ZnFe$_2$O$_4$ NPs was evaluated by EDS. Inset of Figure 2(a) represent the typical EDS spectra along with elemental compositions of ZnFe$_2$O$_4$ NPs. Except Zn, Fe, and O, no other peak related with any impurity in the spectrum, which confirmed that the ZnFe$_2$O$_4$ NPs without any impurity. After hybrid with rGO sheets, the ZnFe$_2$O$_4$ NPs are attached on the interlayer of graphene sheets, and the agglomeration among ZnFe$_2$O$_4$ NPs becomes alleviated (as shown in Fig. 2(b)). The strong interaction may be attributed to the formation of Fe-O-C bonds between graphene and ZnFe$_2$O$_4$ NPs.

![Figure 3](image)

**Figure 3.** N$_2$ adsorption-desorption isotherms of samples: (a) ZnFe$_2$O$_4$ nanoparticles (NPs), (b) ZnFe$_2$O$_4$-rGO nanocomposites (NCs).

3.2. **Specific surface area and optical property**

N$_2$ sorption isotherms of the products were measured to gain the information about the specific surface area. As shown in Figure 3, the nitrogen adsorption-desorption isotherm belongs to type IV, revealing
the existence of abundant meso-porous structures in the ZnFe$_2$O$_4$ nanoparticles and ZnFe$_2$O$_4$-rGO nanocomposites. The specific surface area for ZnFe$_2$O$_4$ nanoparticles and ZnFe$_2$O$_4$-rGO nanocomposites are, 63.63 and 90.23 m$^2$/g, respectively. The much larger specific surface area of ZnFe$_2$O$_4$-rGO NCs, is may be due to the smaller grain size and the more interfacial boundaries among graphene. A single-modal size pore size distribution was formed in ZnFe$_2$O$_4$ NPs, and strong pore peak at about 11.12 nm. While, bimodal size pore size distribution was formed in ZnFe$_2$O$_4$-rGO NCs. Obviously, this ZnFe$_2$O$_4$-rGO NCs with high specific surface area, relative to ZnFe$_2$O$_4$ nanoparticles, will favorable to improve the adsorption and photocatalytic activity.

Figure 4. Typical UV-visible spectra for samples: (a) ZnFe$_2$O$_4$ nanoparticles (NPs), (b) ZnFe$_2$O$_4$-rGO nanocomposites (NCs).

Figure 4 exhibits the typical UV-visible spectra for ZnFe$_2$O$_4$ nanoparticles and ZnFe$_2$O$_4$-rGO nanocomposites. It can be seen that pure ZnFe$_2$O$_4$ nanoparticles exhibited strong photo-absorption from the UV to visible light region shorter than 664.7nm. The incorporation of graphene sheets into ZnFe$_2$O$_4$ matrix has a significant effect on the optical property of the composite. Additionally, the presence of the reduced graphene (rGO) sheets induced a continuous absorption band in the range of 640-800 nm, which is caused mainly by the background absorption of rGO.

3.3. Photocatalytic activity and magnetic property

The photocatalytic performance of the prepared photocatalysts were evaluated by degradation of methylene blue (MB) as model contaminant. From the Figure 5a, ZnFe$_2$O$_4$ NPs and ZnFe$_2$O$_4$-rGO NCs presented the high adsorption capacity for the methylene blue. The adsorption efficiency of MB solution over ZnFe$_2$O$_4$ NPs was about 91.5% in 1.0h. The adsorption efficiency of MB solution over ZnFe$_2$O$_4$-rGO NCs was about 86.56% in 1.0h. Figure 5b shows the effect of pH on the zeta potential of ZnFe$_2$O$_4$ NPs and ZnFe$_2$O$_4$-rGO NCs. The isoelectric point of ZnFe$_2$O$_4$ NPs and ZnFe$_2$O$_4$-rGO NCs are about 5.14 and 4.36 respectively. In the suspension containing photocatalysts remained negative, while methylene blue is a cationic dye. Therefore, ZnFe$_2$O$_4$ NPs and ZnFe$_2$O$_4$-rGO NCs presented the high adsorption capacity due to positive and negative charges attract. The photocatalytic degradation of MB follows the order: ZnFe$_2$O$_4$-rGO NCs (4.0h, 92.43%) > ZnFe$_2$O$_4$ NPs (4.0h, 85.54%). This observation implied that ZnFe$_2$O$_4$-rGO NCs manifested the higher degradation efficiency.

The magnetic property of the ZnFe$_2$O$_4$ nanoparticles (NPs) and ZnFe$_2$O$_4$-rGO nanocomposites (NCs) were investigated using a vibrating sample magnetometer at 300K in an applied magnetic field up to 15000 Oe (as shown in Figure 6). The ZnFe$_2$O$_4$-rGO NCs photocatalyst shows ferromagnetic
property with a saturation magnetization (Ms) of 24.0 emu/g, which is quite qualified for the magnetic separation and recycling of photocatalysts. Clearly, the saturation magnetization (Ms) of ZnFe$_2$O$_4$-rGO NCs is less than that of ZnFe$_2$O$_4$, which originates in that rGO is the nonmagnetic component. Even so, the considerable Ms value of ZnFe$_2$O$_4$-rGO NCs can still make it to separate rapidly from solution under an external magnetic field, the photograph of magnetic separation is shown in the inset of Figure 6.

![Figure 5](image1.png)

**Figure 5.** (a) Photocatalytic activity and (b) zeta potential of the synthesized ZnFe$_2$O$_4$ nanoparticles (NPs) and ZnFe$_2$O$_4$-rGO nanocomposites (NCs).

![Figure 6](image2.png)

**Figure 6.** The magnetic hysteresis loops of the synthesized ZnFe$_2$O$_4$ nanoparticles (NPs) and ZnFe$_2$O$_4$-rGO nanocomposites (NCs).

4. Conclusions

In summary, we have successfully synthesized Magnetic ZnFe$_2$O$_4$-the reduced graphene (rGO) nanocomposites (ZnFe$_2$O$_4$-rGO NCs) through facile solvothermal method. It is evidently seen that ZnFe$_2$O$_4$ NPs with diameters in the range of 10-15 nm present the spherical morphology, they display a slight agglomeration due to their own magnetism. After hybrid with rGO sheets, the ZnFe$_2$O$_4$ NPs are attached on the interlayer of graphene sheets, and the agglomeration among ZnFe$_2$O$_4$ NPs becomes alleviated. This ZnFe$_2$O$_4$-rGO NCs with high specific surface area, relative to ZnFe$_2$O$_4$ nanoparticles, will favorable to improve the adsorption and photocatalytic activity. Moreover, ZnFe$_2$O$_4$ NPs and
ZnFe$_2$O$_4$-rGO NCs presented the high adsorption capacity due to positive and negative charges attract. The photocatalytic degradation of MB follows the order: ZnFe$_2$O$_4$-rGO NCs (4.0h, 92.43%) > ZnFe$_2$O$_4$ NPs (4.0h, 85.54%). Meanwhile, the as-prepared ZnFe$_2$O$_4$-rGO NCs can magnetically separable in a suspension system. Therefore, they can be conveniently applied to dispose toxic organic pollutants during water treatment.

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