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ARTICLE

Magnetic g-C₃N₄/NiFe₂O₄ hybrids with enhanced photocatalytic activity

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Composite photocatalysts have attracted much attention in exploring both high efficient and low cost materials. In this study, novel magnetic g-C₃N₄/NiFe₂O₄ photocatalysts were fabricated by a facile chemisorption method. X-ray diffraction (XRD), transmission electron microscopy (TEM), IR spectra (IR), UV-vis diffuse reflectance spectra (DRS) and X-ray photoelectron spectroscopy (XPS) were utilized to analyze the structure and property of samples, which indicated that NiFe₂O₄ had been integrated into the surface of g-C₃N₄ successfully. The as-prepared 7.5% g-C₃N₄/NiFe₂O₄ with best photocatalytic activity can keep high photocatalytic activity and stability after five runs in the presence of hydrogen peroxide under visible light irradiation. During the catalytic reaction, the synergistic effect between g-C₃N₄ and NiFe₂O₄ can accelerate photogenerated charges separation and facilitate the photo-Fenton process to get an enhanced photocatalytic activity. Moreover, the collection and recycle of photocatalyst had become readily owing to the distinctive magnetism of g-C₃N₄/NiFe₂O₄.

Keywords: g-C₃N₄/NiFe₂O₄, photocatalytic degradation, magnetism

Introduction,

In the last decades, the term “photocatalyst” has become prevalent like “nano” in the field of environmental chemistry due to photocatalytic materials’ conspicuous functions. Degradation of contaminants, redox of organic chemicals and production of hydrogen, even molecule or ion detection can be achieved by photocatalysts under UV-visible light irradiation.¹⁻⁴ Nevertheless, most of photocatalysts are faced with one problem: difficult recycling process and constantly secondary pollution on the environment. Recently, the development of magnetic photocatalyst has interested a multitude of researchers, especially for MFe₂O₄ (M=divalent metal ion, e.g. Zn, Ni, Co, Cu, etc.) materials due to their easily recycling. Nanocrystalline ferrites, typical representatives of magnetic materials with high magnetic permeability and electrical resistivity have several distinctive applications for material science such as drug carrier, medical diagnostics, information storage, position sensing, spintronic devices.^{5,6} Nickel ferrite is one kind of inverse spinel with the chemical formula AB₂O₄ in which equal number of Ni²⁺ and Fe³⁺ reside on octahedral sites and remaining Fe³⁺ reside on tetrahedral sites. The band gap energy of NiFe₂O₄ is ~2.19 eV,⁷ however, there is still a standing controversy on it regardless of experimental data or computational results.⁸⁻¹⁰ Unfortunately, pure NiFe₂O₄ always shows weak photocatalytic activity even though in Fenton reaction, so some contributions have been made to improve the photocatalysis. Combination with other semiconductor materials and doping with lanthanide elements have been verified meaningful to solve the problem. Rana synthesized the anatase TiO₂-coated NiFe₂O₄ through reverse micelle and hydrolysis to degrade methyl-orange dye and inactivate bacteria.¹¹ When Ni ferrite was substituted by

neodymium, absorption edge red shifted and band gap narrowed, which induced significantly enhanced photoactivity.¹² In recent years, Wang and Fu synthesized NiFe₂O₄/MWCNT to degrade phenol, p-nitrophenol (PNP) with C/C₀ reaching 90% in 400 min under UV light.¹³ Later, they prepared NiFe₂O₄-graphene hybrids with outstanding photodegradation behaviour which may benefit from the well electroconductivity of graphene prolonging the life of photoinduced carriers.¹⁴ Therefore, fabricating a composite photocatalyst to enhance the photocatalytic activity of NiFe₂O₄ can be a feasible and efficient approach.

As a class of novel organic semiconductor, graphitic carbon nitride (g-C₃N₄) has prominent optical and photoelectrochemical properties with band gap ~2.7 eV.¹⁵ It has been reported that g-C₃N₄ can split water for hydrogen production and degrade organic pollutants under visible light irradiation.¹⁶⁻¹⁷ Besides, a great deal of research has confirmed that coupling g-C₃N₄ with noble metal, composite oxide, metal oxide and metal-free material could achieve exceptionally high photocatalytic capability. Normally the enhanced photocatalytic activity of semiconductor composite are attributed to the synergistic effect of heterojunction structure, like the combination of g-C₃N₄ and Bi₂WO₆,¹⁸ WO₃,^{19,20} ZnO,²¹ BiPO₄,²² BiVO₄,²³ CdS²⁴ and BiOX (X=Cl, Br, and I) etc.^{25,26} The matching energy level between g-C₃N₄ and another semiconductor can improve the separation and immigration rate of photoinduced electron-hole pairs. Lately, g-C₃N₄/ZnFe₂O₄ exhibiting superior photocatalytic activity has been reported for hydrogen generation and aqueous organic pollutants degradation.²⁷⁻²⁹ But g-C₃N₄/NiFe₂O₄ has not been studied till now, so we concentrate on the work hoping to construct one typical easily recycled material and meanwhile improve the photocatalytic performance of NiFe₂O₄.

Herein, we fabricated $g\text{-C}_3\text{N}_4/\text{NiFe}_2\text{O}_4$ hybrid material to build a semiconductor-semiconductor heterojunction via a convenient chemisorption method which has many advantages: availability of instruments, simplicity of operation and safety of procedure.³⁰ The crystal structure, surface characteristic, optical and magnetic property of $g\text{-C}_3\text{N}_4/\text{NiFe}_2\text{O}_4$ products had been characterized by XRD, TEM, DRS and VSM respectively. Methylene blue (MB) was selected as a target pollutant to investigate the photocatalytic activity of $g\text{-C}_3\text{N}_4/\text{NiFe}_2\text{O}_4$ composite with different content of $g\text{-C}_3\text{N}_4$. The degradation rate of MB can reach 87% in 4 h for the optimum ratio 7.5% $g\text{-C}_3\text{N}_4/\text{NiFe}_2\text{O}_4$ and more $g\text{-C}_3\text{N}_4$ (10%) would cause a decreasing activity under visible light irradiation. In the section of mechanism, the energy band matching of $g\text{-C}_3\text{N}_4/\text{NiFe}_2\text{O}_4$ heterojunction and the driving force of photocatalytic degradation for MB were discussed.

Experimental

2.1 Synthesis of NiFe_2O_4

All reagents were of analytical grade and were used without further purification. At first, 1 mmol $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 0.5 mmol $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added into 17 mL absolute ethanol in a 20 mL Teflon-lined autoclave and magnetically stirred for 30 min at room temperature. Secondly, the reddish brown emulsion was precipitated and adjusted to a pH of 13 by adding 6 M NaOH solution dropwise. Thirdly, the precursor was sealed in a stainless steel tank and heated at 180 °C for 20 h after stirring for another 30 min. When the reaction terminated, the product was cooled down at room temperature and washed three times by water and ethanol separately, and then dried at 60 °C for later use.

2.2 Synthesis of $g\text{-C}_3\text{N}_4/\text{NiFe}_2\text{O}_4$ composites

The preparation of $g\text{-C}_3\text{N}_4$ is according to the method from our previous work.³¹ The $g\text{-C}_3\text{N}_4/\text{NiFe}_2\text{O}_4$ products with varying $g\text{-C}_3\text{N}_4$ content were synthesized in the following process: 120 mg NiFe_2O_4 and $g\text{-C}_3\text{N}_4$ (mass fraction of $g\text{-C}_3\text{N}_4$: 5, 7.5, 10 wt%) were added into a beaker containing 20 mL absolute ethanol and kept magnetically stirring for 10 h at room temperature; then the obtained suspension was put in a 100 °C drying oven for 12 h without other operations. The obtained products are labeled as 5% $g\text{-C}_3\text{N}_4/\text{NiFe}_2\text{O}_4$, 7.5% $g\text{-C}_3\text{N}_4/\text{NiFe}_2\text{O}_4$ and 10% $g\text{-C}_3\text{N}_4/\text{NiFe}_2\text{O}_4$.

2.3 Characterization

XRD patterns of the samples were obtained on the X-ray diffractometer (Bruker D8) with Cu K α radiation ($\lambda=1.5418 \text{ \AA}$) in the range of $2\theta=10\text{-}80^\circ$. Transmission electron microscopy (TEM) micrographs were taken with a JEOL-JEM-2010 (JEOL, Japan) operated at 200 kV. The UV-vis diffuse reflectance spectra (DRS) of the samples were obtained on a UV-vis spectrophotometer (UV-2450, Shimadzu Corporation, Japan) using BaSO_4 as the reference. Infrared (IR) spectra of all the catalysts (KBr pellets) were recorded on the Nicolet Model Nexus 470 IR equipment. Elemental compositions were detected by X-ray photoelectron spectroscopy (XPS) analysis, which was performed on an ESCALab MKII X-ray photoelectron spectrometer using the Mg K α radiation. The magnetic property of NiFe_2O_4 and $g\text{-C}_3\text{N}_4/\text{NiFe}_2\text{O}_4$ composites was measured in a vibrating sample magnetometer (VSM) (Quantum Design Corporation, USA) with a maximum applied field of $\pm 2 \text{ T}$ at 300 K.

2.4 Photocatalytic activity measurement

The MB degradation experiment was performed to evaluate the photocatalytic activity of samples under a 300 W Xe lamp with a 400 nm cutoff filter. 0.05 g photocatalysts were added

into 50 mL MB (10 mg/L) in a Pyrex photocatalytic reactor connected to a circulating water system which could keep the reaction temperature at 30 °C. In addition, continuous aeration was pumped to provide the reaction with oxygen and mix the suspension as well. Prior to irradiation, dark reaction accompanied by magnetic stirring for 1 h was necessary to reach absorption-desorption equilibrium between the photocatalyst and MB solution. During irradiation, 4 mL suspension was taken at defined time intervals. Then the sample was tested with a UV-vis spectrophotometer (UV-2450, Shimadzu) after centrifuge at the wavelength of 664 nm which is the maximal absorption band of MB. In the H_2O_2 system, 1 mL H_2O_2 was injected into the reaction suspension as soon as the Xe lamp was turned on. Meanwhile the sampled specimen must be tested in time.

Results and discussion

3.1 XRD analysis

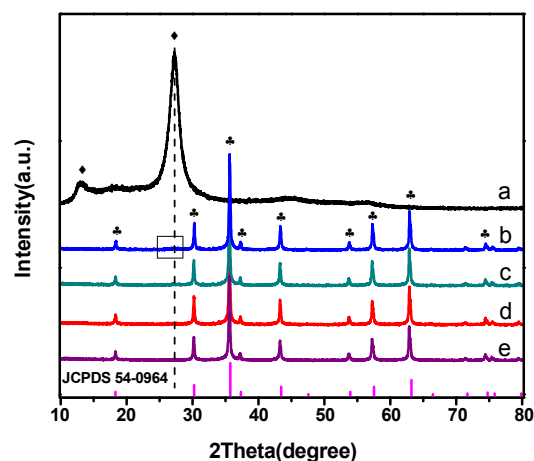


Fig. 1 XRD patterns of (a) $g\text{-C}_3\text{N}_4$, (b) 10% $g\text{-C}_3\text{N}_4/\text{NiFe}_2\text{O}_4$, (c) 7.5% $g\text{-C}_3\text{N}_4/\text{NiFe}_2\text{O}_4$, (d) 5% $g\text{-C}_3\text{N}_4/\text{NiFe}_2\text{O}_4$, (e) NiFe_2O_4 .

Fig. 1 displays the XRD patterns of samples and all of the peaks have been marked with two kinds of symbols (\blacklozenge for $g\text{-C}_3\text{N}_4$ and \clubsuit for NiFe_2O_4). As shown in Fig. 1, the diffraction peaks at 18.4° , 30.3° , 35.7° , 37.3° , 43.3° , 53.8° , 57.3° , 63.0° and 74.5° were matching well with (111), (220), (311), (222), (400), (422), (511), (440) and (533) crystalline planes of NiFe_2O_4 respectively (JCPDS 54-0964). It was noteworthy that there was no peak of impurity for samples b, c, d and e, which proved pH=13 can hinder the formation of Fe_2O_3 . Besides, the peaks at 27.4° and 13° can be indexed as (002), (100) diffraction plane of $g\text{-C}_3\text{N}_4$, respectively.³² Obviously no peak shift occurred for NiFe_2O_4 , so the chemisorption process did not have an influence on the crystal structure. More importantly, when the content of $g\text{-C}_3\text{N}_4$ increased to 10%, the peak at 27.4° appeared while for other proportions the peak was not observed because of the low $g\text{-C}_3\text{N}_4$ content.

3.2 TEM analysis

In order to figure out the origin of activity changes before and after NiFe_2O_4 combined with $g\text{-C}_3\text{N}_4$, the particle size and morphology of catalysts were investigated by means of TEM. In Fig. 2(a), it can be clearly observed that NiFe_2O_4 had two totally different types of grain morphologies: the large polygon

plates (about 100nm) and the nanoscale particles (about 8 nm). So, the crystallite size distribution of NiFe_2O_4 could be properly bimodal.^{33,34} Fig. 2(b) illustrated that NiFe_2O_4 polygon plates and nanoparticles adhered to the $\text{g-C}_3\text{N}_4$ flake and the dispersion of NiFe_2O_4 nanoparticles was better than that of pure NiFe_2O_4 , which would be beneficial to form the heterojunction structure and promote the separation efficiency of photoinduced carriers.

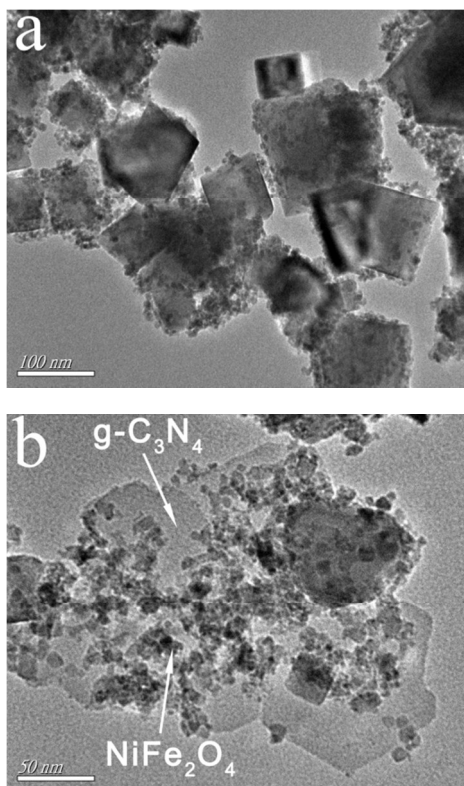


Fig. 2 TEM images of (a) NiFe_2O_4 , (b) 7.5% $\text{g-C}_3\text{N}_4/\text{NiFe}_2\text{O}_4$.

3.3 IR analysis

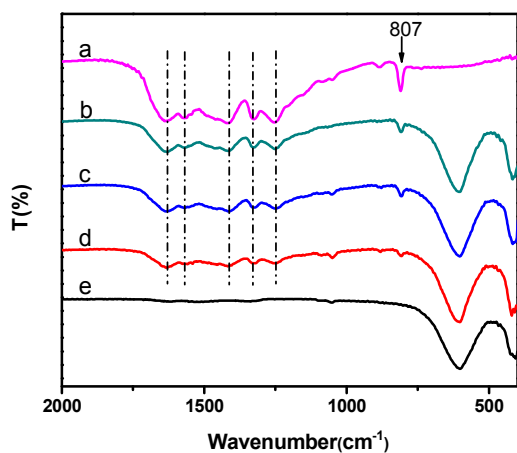
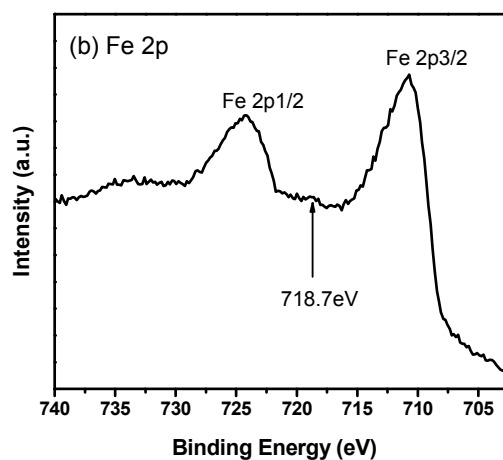
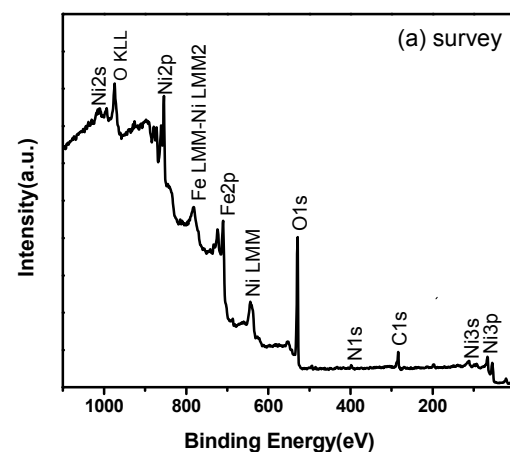


Fig. 3 IR spectra of (a) $\text{g-C}_3\text{N}_4$, (b) 10% $\text{g-C}_3\text{N}_4/\text{NiFe}_2\text{O}_4$, (c) 7.5% $\text{g-C}_3\text{N}_4/\text{NiFe}_2\text{O}_4$, (d) 5% $\text{g-C}_3\text{N}_4/\text{NiFe}_2\text{O}_4$, (e) NiFe_2O_4 .

The IR spectrum enables us to distinguish molecular structure of $\text{g-C}_3\text{N}_4$ from other organic chemicals easily and

sensitively. In Fig. 3, $\text{g-C}_3\text{N}_4$ and $\text{g-C}_3\text{N}_4/\text{NiFe}_2\text{O}_4$ samples all had a group of absorption peaks in the 1200-1650 cm^{-1} region, corresponding to the stretching vibration modes of C=N and C-N heterocycles and the peak at 807 cm^{-1} to the breathing mode of triazine units.^{35,36} Additionally the strong absorption peak at 608 and 417 cm^{-1} can be ascribed to the stretching vibrations of Fe-O bonds in tetrahedral positions and Metal-O bonds in octahedral positions respectively.^{37,38} Moreover, as the mass fraction of $\text{g-C}_3\text{N}_4$ increased from 5% to 10% the peak at 807 cm^{-1} appeared and became sharp gradually which demonstrated $\text{g-C}_3\text{N}_4$ and NiFe_2O_4 have been integrated together.

3.4 XPS



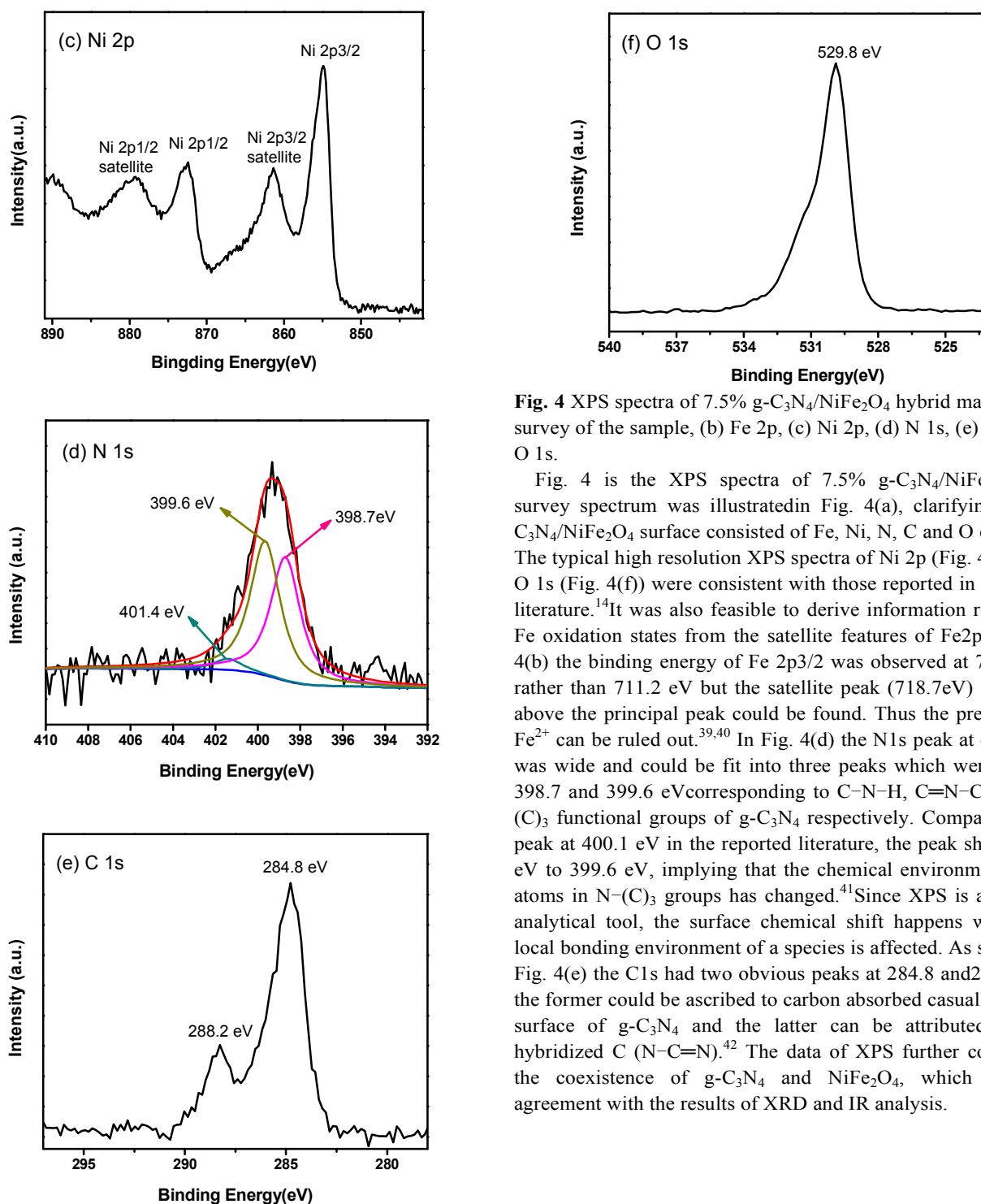


Fig. 4 XPS spectra of 7.5% g-C₃N₄/NiFe₂O₄ hybrid material (a) survey of the sample, (b) Fe 2p, (c) Ni 2p, (d) N 1s, (e) C 1s, (f) O 1s.

Fig. 4 is the XPS spectra of 7.5% g-C₃N₄/NiFe₂O₄. The survey spectrum was illustrated in Fig. 4(a), clarifying that g-C₃N₄/NiFe₂O₄ surface consisted of Fe, Ni, N, C and O elements. The typical high resolution XPS spectra of Ni 2p (Fig. 4(c)) and O 1s (Fig. 4(f)) were consistent with those reported in previous literature.¹⁴ It was also feasible to derive information regarding Fe oxidation states from the satellite features of Fe 2p. In Fig. 4(b) the binding energy of Fe 2p_{3/2} was observed at 710.7 eV rather than 711.2 eV but the satellite peak (718.7 eV) at 8.0 eV above the principal peak could be found. Thus the presence of Fe²⁺ can be ruled out.^{39,40} In Fig. 4(d) the N 1s peak at ~399 eV was wide and could be fit into three peaks which were 401.4, 398.7 and 399.6 eV corresponding to C-N-H, C=N-C and N-(C)₃ functional groups of g-C₃N₄ respectively. Compared with peak at 400.1 eV in the reported literature, the peak shifted 0.5 eV to 399.6 eV, implying that the chemical environment of N atoms in N-(C)₃ groups has changed.⁴¹ Since XPS is a surface analytical tool, the surface chemical shift happens when the local bonding environment of a species is affected. As shown in Fig. 4(e) the C 1s had two obvious peaks at 284.8 and 288.2 eV, the former could be ascribed to carbon absorbed casually on the surface of g-C₃N₄ and the latter can be attributed to sp² hybridized C (N-C=N).⁴² The data of XPS further confirmed the coexistence of g-C₃N₄ and NiFe₂O₄, which was in agreement with the results of XRD and IR analysis.

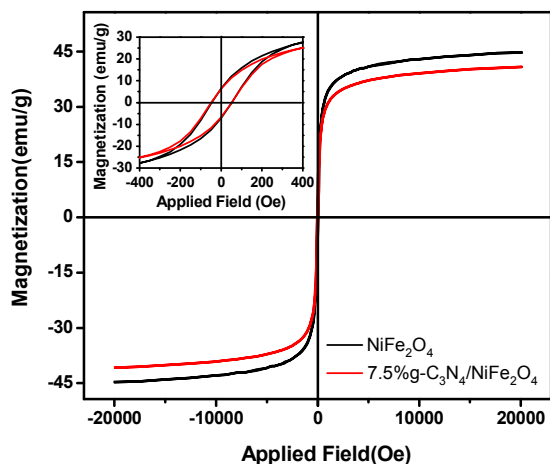


Fig. 5 Magnetization curves of the photocatalysts.

3.5 Magnetic property

When this photocatalytic material was designed, its magnetic characteristic attracted us from beginning to end. Fig. 5 illustrates magnetization curves of pure NiFe_2O_4 and 7.5% $\text{g-C}_3\text{N}_4/\text{NiFe}_2\text{O}_4$: X-axis represents the applied magnetic field H and Y-axis represents magnetization M . It could be estimated that the saturation magnetization M_s of NiFe_2O_4 and 7.5% $\text{g-C}_3\text{N}_4/\text{NiFe}_2\text{O}_4$ was about 45 and 40 emu/g respectively and the coercivity H_c was around 50 Oe without much difference between two samples in the insert figure. The presence of low-content $\text{g-C}_3\text{N}_4$ less influenced the composite magnetism so that the collection and recycle of photocatalyst could be readily available by the external magnet. The photo in Fig. 7(b) exhibited the separation of 7.5% $\text{g-C}_3\text{N}_4/\text{NiFe}_2\text{O}_4$ photocatalyst from the reaction system after the fifth recycle of MB degradation.

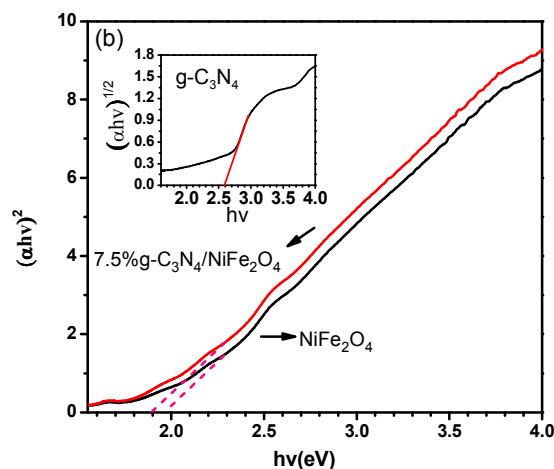
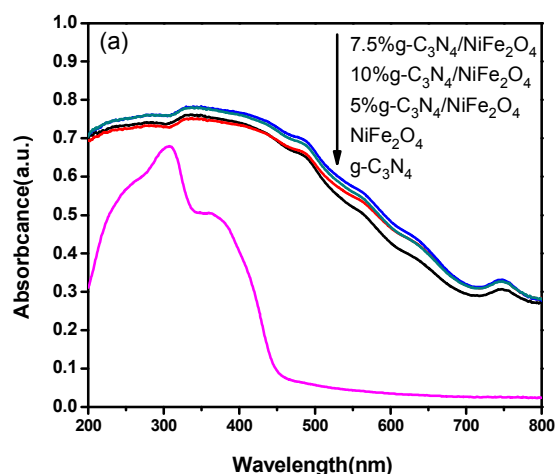


Fig. 6(a) UV-vis diffuse reflectance spectra, (b) $(\alpha h\nu)^2$ versus $h\nu$ curves of NiFe_2O_4 and 7.5% $\text{g-C}_3\text{N}_4/\text{NiFe}_2\text{O}_4$.

3.6 UV-vis analyses

In Fig. 6(a) the UV-vis diffuse reflectance spectra reflected the samples' optical properties: $\text{g-C}_3\text{N}_4$ had an absorption edge around 460 nm while NiFe_2O_4 and its composites had much stronger, wider absorption in the visible region. The distinct band gap, molecular structure and color of catalysts were considered to explain the difference in absorption range and intensity. It was also noted that 7.5% $\text{g-C}_3\text{N}_4/\text{NiFe}_2\text{O}_4$ composite had the strongest absorption intensity, which suggested that the integration of $\text{g-C}_3\text{N}_4$ and NiFe_2O_4 could promote the photoabsorption ability.⁴³ Commonly a classic Tauc plot is carried out to estimate the amorphous semiconductor's band gap energy according to the relation: $(\alpha h\nu)^n$ versus $h\nu$. In Fig. 6(b) the results indicated that NiFe_2O_4 was one direct band gap semiconductor and E_g of $\text{g-C}_3\text{N}_4$ and NiFe_2O_4 was about 1.98 and 1.9 eV respectively. The narrowed band gap of $\text{g-C}_3\text{N}_4/\text{NiFe}_2\text{O}_4$ would reinforce the visible light absorption intensity. Besides, the illustration in the upper left demonstrated $\text{g-C}_3\text{N}_4$ was an indirect transition and its band gap energy was around 2.6 eV close to the reported paper.²³

4.1 Photocatalytic decomposition of MB

Fig. 7(a) shows the MB degradation curves with varying catalysts under visible light illumination. It can be seen that after 4 h of visible light irradiation the proportion C/C_0 reached 57%, 66%, 87% and 76% for NiFe_2O_4 , 5% $\text{g-C}_3\text{N}_4/\text{NiFe}_2\text{O}_4$, 7.5% $\text{g-C}_3\text{N}_4/\text{NiFe}_2\text{O}_4$ and 10% $\text{g-C}_3\text{N}_4/\text{NiFe}_2\text{O}_4$ with H_2O_2 respectively. The result clearly revealed that 7.5% $\text{g-C}_3\text{N}_4/\text{NiFe}_2\text{O}_4$ exhibited the best photocatalytic performance with H_2O_2 and the photocatalytic degradation efficiency of MB for pure NiFe_2O_4 was no more than 10% when there was no H_2O_2 . Thereby it can be concluded that the obtained NiFe_2O_4 and $\text{g-C}_3\text{N}_4/\text{NiFe}_2\text{O}_4$ can effectively activate H_2O_2 along with the visible light illumination. Furthermore the activation can be enhanced by the heterojunction structure. Besides, the best photocatalytic performance for 7.5% $\text{g-C}_3\text{N}_4/\text{NiFe}_2\text{O}_4$ can be attributed to the proper adsorption of MB and the enough active sites on the photocatalyst surface. In Fig. 7(b) MB degradation for the mechanically mixed sample was 65% lower than 7.5% $\text{g-C}_3\text{N}_4/\text{NiFe}_2\text{O}_4$ composite, which directly verified the successful combination of $\text{g-C}_3\text{N}_4$ and NiFe_2O_4 . At the same time the rate of photocatalytic reaction was also studied by fitting the zero order kinetic ($C_0 - C = kt$) and the results were

displayed in Fig. 7(c) and Table. 1. The photodegradation rate of 7.5% g-C₃N₄/NiFe₂O₄ under visible light irradiation was 1.5 times higher than those of pure NiFe₂O₄. To further study the recyclability of g-C₃N₄/NiFe₂O₄ composite, five runs of photodegradation experiment were carried out. As can be seen in Fig. 7(d), g-C₃N₄/NiFe₂O₄ photocatalyst could keep unequivocally high photocatalytic activity after five repeating uses so the heterojunction structure was stable.

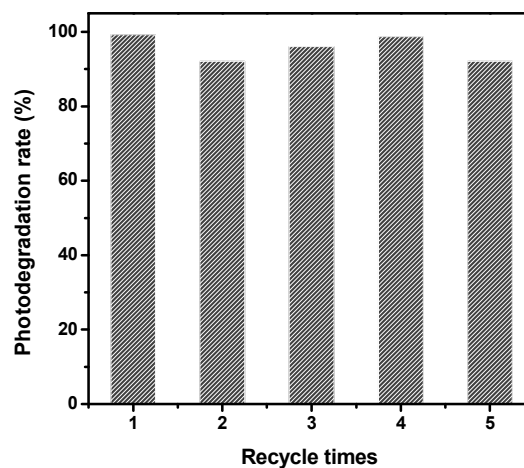
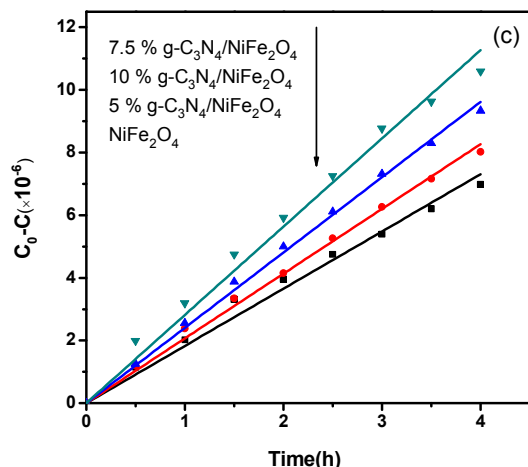
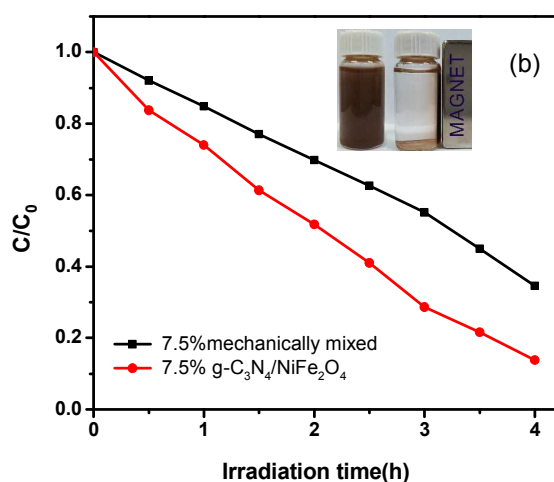
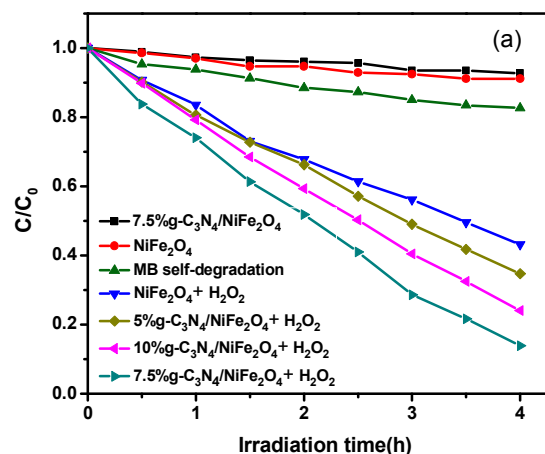


Fig. 7 (a) Photocatalytic performance of samples, (b) activity comparison between 7.5% g-C₃N₄/NiFe₂O₄ and 7.5% mechanically mixed, (c) kinetic fit diagram, (d) cycling runs of 7.5% g-C₃N₄/NiFe₂O₄ photocatalyst for MB degradation.

Table. 1 Zero-order kinetic constant for MB degradation with different photocatalyst.

Samples	$k(1 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1} \cdot \text{h}^{-1})$	R^2
NiFe ₂ O ₄	1.83	0.9954
5% g-C ₃ N ₄ /NiFe ₂ O ₄	2.07	0.9986
10% g-C ₃ N ₄ /NiFe ₂ O ₄	2.40	0.9990
7.5% g-C ₃ N ₄ /NiFe ₂ O ₄	2.82	0.9958

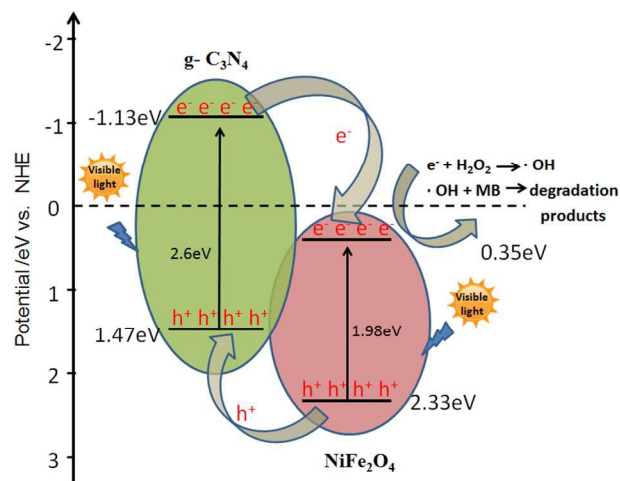


Fig. 8 Heterojunction diagram for electrons transfer in g-C₃N₄/NiFe₂O₄ composite.

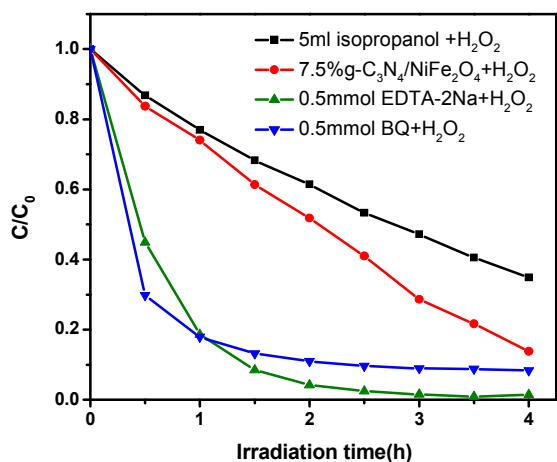


Fig. 9 Photocatalytic performance of 7.5% g-C₃N₄/NiFe₂O₄ with different scavengers for MB degradation.

5 Photocatalytic mechanism discussions

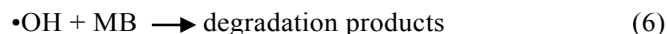
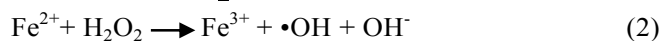
As mentioned above MB photodegradation capability has been improved by the heterojunction structure in the interfacial of g-C₃N₄/NiFe₂O₄ composite. Then we calculated NiFe₂O₄'s conduction band $E_{CB} = 0.35$ eV and $E_{VB} = 2.33$ eV according to equation (1) where X is semiconductor's electronegativity and E_c is the energy of free electron on the hydrogen scale.³² On the basis of experimental data, the scheme of a possible photocatalytic mechanism is presented in Fig. 8. Firstly, electrons on the VB position were excited to the CB position for both g-C₃N₄ and NiFe₂O₄ under visible light irradiation. Secondly, electrons on the CB of g-C₃N₄ moved to the CB of NiFe₂O₄ and holes on the VB of NiFe₂O₄ transferred to the VB of g-C₃N₄. As a result, the redistribution of electrons and holes prevented photoinduced carriers from recombination quickly. On the other hand, the CB value of NiFe₂O₄ (0.35 eV) is less negative than $E^0(\text{O}_2/\cdot\text{O}_2^-)$ (-0.046 eV vs NHE),⁴⁴ so O₂ would not be reduced by electrons to generate $\cdot\text{O}_2^-$ on the photocatalyst surface. Additionally, compared with the $E^0(\cdot\text{OH}/\text{OH}^-)$ (2.38 eV vs NHE),⁴⁵ the VB potential of g-C₃N₄ (1.47 eV) is less positive, which implied that $\cdot\text{OH}$ would not be yielded by the oxidation of OH⁻ with holes.

For the purpose of confirming the main active species, trapping experiments were carried out and isopropanol, 1,4-benzoquinone (BQ) and disodium ethylenediaminetetraacetate (EDTA-2Na) was added to capture hydroxyl radical ($\cdot\text{OH}$), superoxide radical ($\cdot\text{O}_2^-$) and hole (h^+) respectively. It can be clearly observed in Fig. 9 that the addition of 5 mL isopropanol caused the suppression of MB degradation rate while the addition of 0.5 mmol EDTA-2Na and BQ improved the degradation activity of MB. The results may reveal that the main active species should be $\cdot\text{OH}$ instead of $\cdot\text{O}_2^-$ and h^+ , which is in agreement with the hypothesis of photocatalytic mechanism diagram above. Additionally Wang analyzed the photo-Fenton reaction routes and proved that $\cdot\text{OH}$ played an vital role in the oxidation process of benzene to phenol for

FeCl₃/mpg-C₃N₄ hybrids.⁴⁶ There are related studies supporting the trapping experiment and mechanism research as well.^{47,48}

In Fenton and photo-Fenton reaction, iron-based species can generate highly reactive hydroxyl radicals ($\cdot\text{OH}$) to treat a large variety of water pollutants. Owing to the quick conversion from Fe³⁺ into Fe²⁺, the degradation activity in photo-Fenton reaction becomes many times higher than the classical Fenton reaction under visible light illumination.^{28,49} Here the photocatalytic process and photo-Fenton reaction both function: electrons and holes transfer to opposite direction under visible light irradiation; electrons on CB of NiFe₂O₄ can react with H₂O₂ and Fe³⁺ to produce $\cdot\text{OH}$ for the oxidation of MB, the photodegradation reaction can be expressed as follows:

$$(E)_{CB} = X - E_c - \frac{1}{2} E_g \quad (1)$$



Conclusions

In conclusion a simple chemisorption technique was applied to fabricate the magnetic g-C₃N₄/NiFe₂O₄ for MB degradation. With a matching energy band, g-C₃N₄/NiFe₂O₄ possessed favorable optical property and could activate H₂O₂ to produce effective oxidizing reagent realizing MB discoloration. Heterojunction established in the composite accelerated the process of electron-hole pair separation and boosted H₂O₂ activation and photo-Fenton reaction. As a whole, the uniformity of particle size and morphology still needs improved by adjusting synthesis conditions. The magnetic character of NiFe₂O₄ can be introduced to other composite for repeating use photocatalyst and enhancing photodegradation ability simultaneously.

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