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Synthesis of a well-dispersed $\text{CaFe}_2\text{O}_4/\text{g-C}_3\text{N}_4/\text{CNT}$ composite towards the degradation of toxic water pollutants under visible light†

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Herein, we fabricated a ternary photocatalyst composed of CaFe_2O_4 , multiwalled carbon nanotubes (CNTs) and graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) via a simple hydrothermal route. CaFe_2O_4 acted as a photosensitizer medium and the CNT acted as a co-catalyst, which remarkably enhanced the photocatalytic performances of $\text{g-C}_3\text{N}_4$ towards the degradation of hexavalent chromium (Cr(VI)) and the antibiotic tetracycline (TC) under visible light irradiation. To investigate the morphological and topological features of the photocatalyst, field-emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) analyses were performed. The surface properties and oxidation state of the $\text{CaFe}_2\text{O}_4/\text{g-C}_3\text{N}_4/\text{CNT}$ composite were determined by X-ray photoelectron spectroscopy (XPS). The recombination rate of the charge carriers and the band gap values of the as-synthesized catalysts were analyzed by photoluminescence spectroscopy (PL) and diffused reflectance spectroscopy (UV/Vis DRS) studies, respectively. Besides the degradation reactions, the high hydrogen production rate of $1050 \mu\text{mol h}^{-1}$ under visible light using the $\text{CaFe}_2\text{O}_4/\text{g-C}_3\text{N}_4/\text{CNT}$ composite loaded with 5 wt% CNT was observed. The superior photocatalytic performances of the $\text{CaFe}_2\text{O}_4/\text{g-C}_3\text{N}_4/\text{CNT}$ composite can be ascribed to the effective heterojunction formed between $\text{g-C}_3\text{N}_4$ and the CaFe_2O_4 matrix, in which the CNT act as a conducting bridge in the system, promoting the production of photoinduced charge carriers in the semiconductor system. Finally, the plausible photocatalytic mechanism towards the degradation of pollutants and hydrogen production was discussed carefully.

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1. Introduction

In the past few decades, the reckless release of organic pollutants in water bodies has increased greatly, which cause severe environmental problems and health risks.^{1,2} Accordingly, the photocatalysis process using semiconductor photocatalysts has been proposed as a green technology to degrade the organic pollutants in water bodies, even at trace levels.³ Thus, semiconductor materials, such as TiO_2 , SnO_2 , and ZnO , have been investigated by various researchers owing to their low cost and ease of availability.⁴ However, their foremost drawbacks are their wide band gap energy, high recombination, and low visible light response, which limit their large-scale production in industry.

Recently, a polymeric semiconductor, $\text{g-C}_3\text{N}_4$, has emerged with visible light response, excellent quantum efficiency and photochemical stability, presenting a competitive candidate for the degradation of dyes, NO_x removal, CO_2 reduction, and water-splitting reactions.⁵ Unfortunately, the pure $\text{g-C}_3\text{N}_4$ semiconductor exhibits a sluggish performance due to its high recombination rate and poor absorption ability in the entire visible light region. Furthermore, its low quantum efficiency and turnover number (TON) are also considered a major obstacle.⁶ Thus, tremendous efforts have been made to resolve these problems, and a system mainly composed of well-matched semiconductors will be a good way to overcome these issues.⁷ The heterojunction between highly visible light active semiconductors with suitable band gap values is favorable for enhanced charge separation efficiency in $\text{g-C}_3\text{N}_4$ and dramatically enhances its light absorption ability in the entire visible region.⁸

Thus, calcium ferrite (CaFe_2O_4), as p-type visible light-active photocatalyst, has been investigated due to its low cost and toxicity with narrow band gap energy towards the degradation of pollutants in both the gaseous and liquid phase.⁹ Nevertheless, its major drawbacks such as inefficient hole transfer property, high recombination rate, and charge mobility result in

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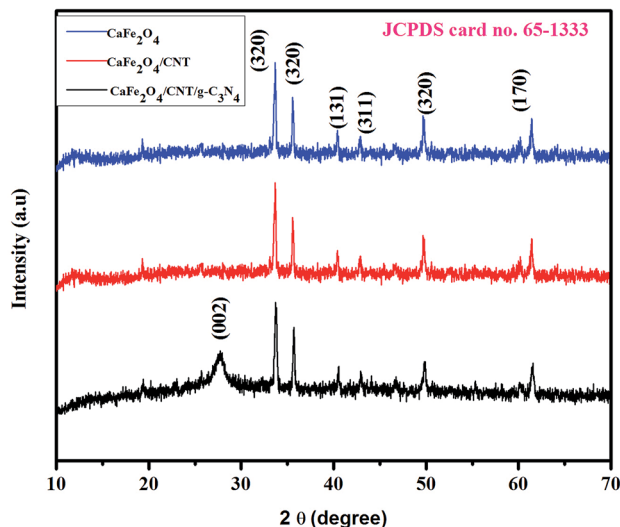


Fig. 1 XRD patterns of the as-prepared CaFe_2O_4 and $\text{CaFe}_2\text{O}_4/\text{g-C}_3\text{N}_4/\text{CNT}$ composite.

a sluggish performance.¹⁰ Therefore, the CaFe_2O_4 photocatalysts suffered severely during water-splitting reactions and the degradation of pollutants. To solve these issues, Luo *et al.* developed a novel $\text{CaFe}_2\text{O}_4/\text{Bi}_2\text{O}_3$ composite *via* a simple wet chemical route. The photocatalytic properties of the $\text{CaFe}_2\text{O}_4/\text{Bi}_2\text{O}_3$ composite was evaluated through the degradation of malachite green (MG) dye under visible light irradiation.¹¹ The higher photocatalytic efficiency can be attributed due to the improved separation of photogenerated electron-hole pairs through the incorporation of Bi_2O_3 , which can be beneficial for a higher degradation performance. Liu *et al.* prepared a carbon-modified CaFe_2O_4 composite towards the degradation of methylene blue dye.¹² The presence of carbon in CaFe_2O_4 greatly influenced the degradation rate of CaFe_2O_4 due to its excellent adsorption behavior.

Therefore, it is essential to develop simple and cost-effective methods to improve the photocatalytic ability of both CaFe_2O_4 and $\text{g-C}_3\text{N}_4$ without sacrificing their

crystalline nature and structural stability. CNT are outstanding 1D nano-sized materials with abundant surface hydroxyl and carboxyl groups, which enable their solubility in polar solvents.¹³ Thus, anchoring CNT on the surface of CaFe_2O_4 and $\text{g-C}_3\text{N}_4$ can lead to a superior performance than that of the CaFe_2O_4 and $\text{g-C}_3\text{N}_4$ binary system. Besides, CNT exhibit a high specific surface area, excellent electron transfer ability, and can act as a noble metal-free co-catalyst in heterojunction systems.¹⁴ The CNT-enabled heterojunction system can afford extra active sites for the adsorption of target pollutants in degradation reactions. Inspired by this mechanism and to further improve the photo-degradation efficiency of both CaFe_2O_4 and $\text{g-C}_3\text{N}_4$, herein, we demonstrate a simple method for the development of a ternary photocatalyst.¹⁵ Upon the incorporation of CNT, the photocatalytic efficiency was significantly improved towards the hydrogen evolution reaction, and $\text{Cr}(\text{vi})$ and TC degradation to a great extent.

2. Experimental

2.1. Materials

All the chemicals used in this work were of analytical reagent (AR) grade. Dicyandiamide, melamine ($\text{C}_3\text{H}_6\text{N}_6$), calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), iron(III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), potassium dichromate, tetracycline hydrochloride, glycerol, ethylene glycol, citric acid, ethanol, methanol and MWCNT were obtained from Sigma-Aldrich Corporation. Deionized (DI) was used throughout the synthesis and photocatalytic process.

2.2. Preparation of $\text{g-C}_3\text{N}_4$

$\text{g-C}_3\text{N}_4$ was prepared *via* a simple calcination route. In a typical synthesis, a stoichiometric amount of dicyandiamide and melamine (1 : 1 ratio) was added to a silica crucible and calcined at 550°C for 4 h under a nitrogen atmosphere. Finally, the silica crucible was cooled naturally to obtain porous $\text{g-C}_3\text{N}_4$ sheets.

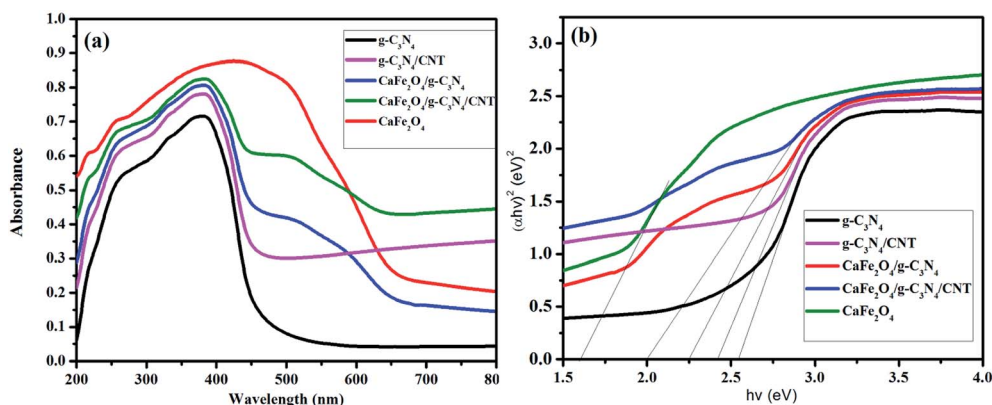


Fig. 2 (a) UV-vis diffuse reflectance spectra of CaFe_2O_4 , $\text{g-C}_3\text{N}_4$, $\text{g-C}_3\text{N}_4/\text{CNT}$ s, and $\text{CaFe}_2\text{O}_4/\text{g-C}_3\text{N}_4/\text{CNT}$ composite. (b) Optical band gap energy, E_g , of CaFe_2O_4 , $\text{g-C}_3\text{N}_4$, $\text{g-C}_3\text{N}_4/\text{CNT}$ s, and $\text{CaFe}_2\text{O}_4/\text{g-C}_3\text{N}_4/\text{CNT}$ composite.



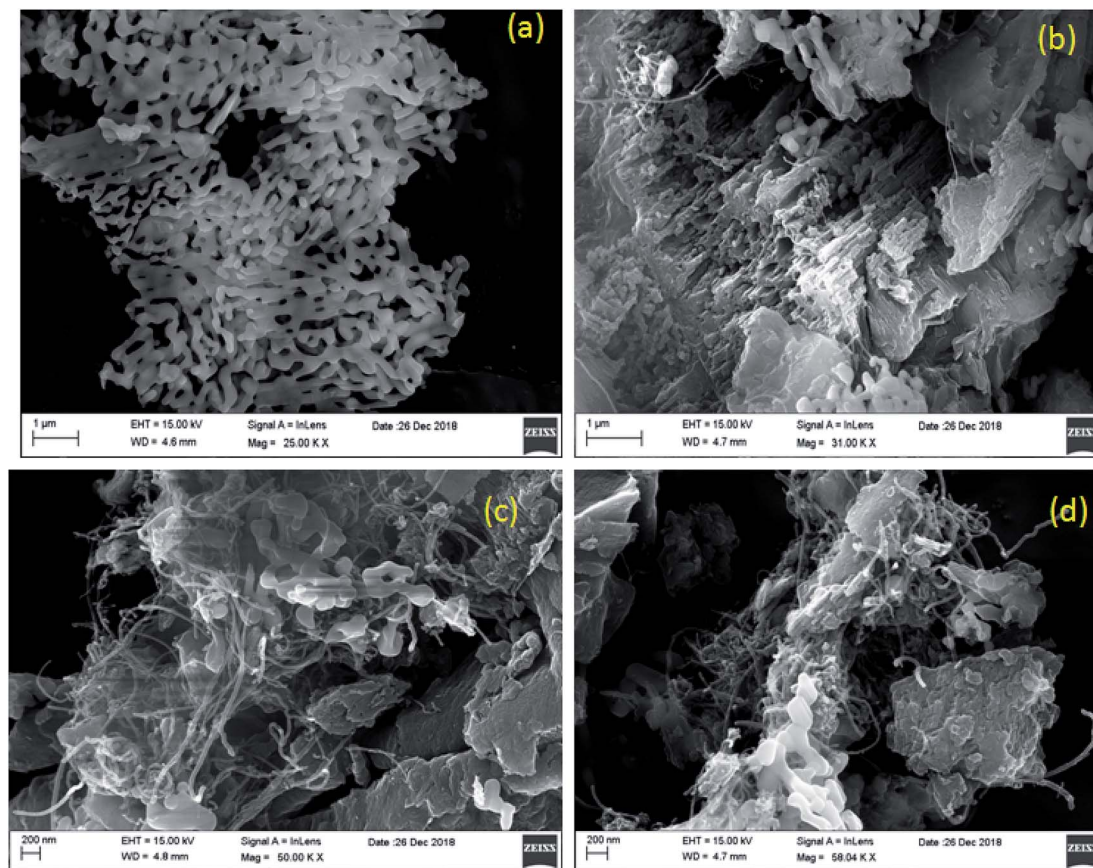


Fig. 3 (a–d) FE-SEM images of CaFe_2O_4 and $\text{CaFe}_2\text{O}_4/\text{g-C}_3\text{N}_4/\text{CNT}$ composite.

2.3. Preparation of CaFe_2O_4

CaFe_2O_4 was synthesized as follows method: a calculated amount of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, glycerol, ethylene glycol, and citric acid was mixed under ultrasound irradiation and stirred for 1 h at 80°C . The obtained red color fluffy product was further calcined at 850°C for 3 h under an air atmosphere to obtain the pure-phase CaFe_2O_4 .

2.4. $\text{CaFe}_2\text{O}_4/\text{g-C}_3\text{N}_4/\text{CNTs}$ composite

A simple hydrothermal route was adopted to synthesize the $\text{CaFe}_2\text{O}_4/\text{g-C}_3\text{N}_4/\text{CNT}$ composite. Typically, the CNT and as-synthesized $\text{g-C}_3\text{N}_4$ were dispersed in 20 mL of DI water with the help of ultrasonication for 2 h. Then, a calculated weight percentage of CaFe_2O_4 powder was mixed with the above solution and transferred to a Teflon-lined autoclave, which was heated at 120°C for 12 h. The final brown-colored precipitate was washed with DI water repeatedly and vacuum dried at 70°C overnight.

2.5. Characterization

The $\text{CaFe}_2\text{O}_4/\text{g-C}_3\text{N}_4/\text{CNT}$ composite was analyzed *via* X-ray diffraction (XRD) on a PANalytical X-ray diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) in the 2θ range of $10\text{--}70^\circ$. The elemental purity and surface properties of the $\text{CaFe}_2\text{O}_4/\text{g-C}_3\text{N}_4/\text{CNT}$ composite was examined *via* X-ray photoelectron spectroscopy (XPS) on an ESCALAB X-ray photoelectron spectrometer using $\text{MgK}\alpha$ radiation. The morphology and microstructures of the prepared samples were

recorded *via* TEM (Tecnai G2 F20 transmission electron microscope), and field-emission scanning electron microscopy using an EM, Quanta FEG 250. UV-Vis diffuse reflectance spectra (DRS) of the samples were analyzed on a UV/Vis spectrophotometer (Jasco-V750 Japan) in the wavelength range of 200–900 nm using BaSO_4 as an internal standard. Photoluminescence (PL) spectra were measured using a fluorescence spectrophotometer (F-7000, Japan).

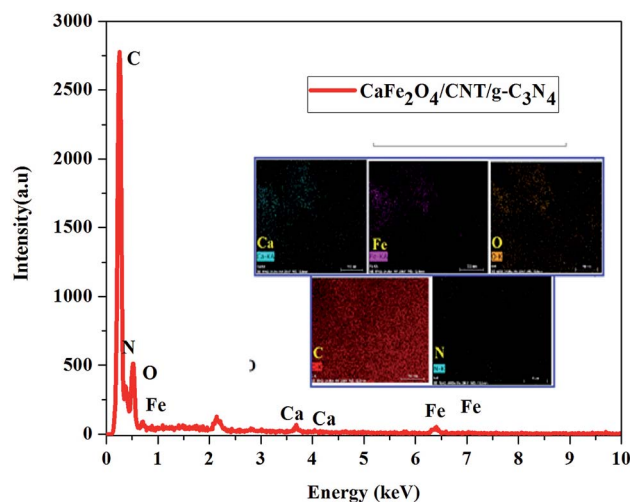


Fig. 4 EDS and elemental mapping analysis of the $\text{CaFe}_2\text{O}_4/\text{g-C}_3\text{N}_4/\text{CNT}$ composite.



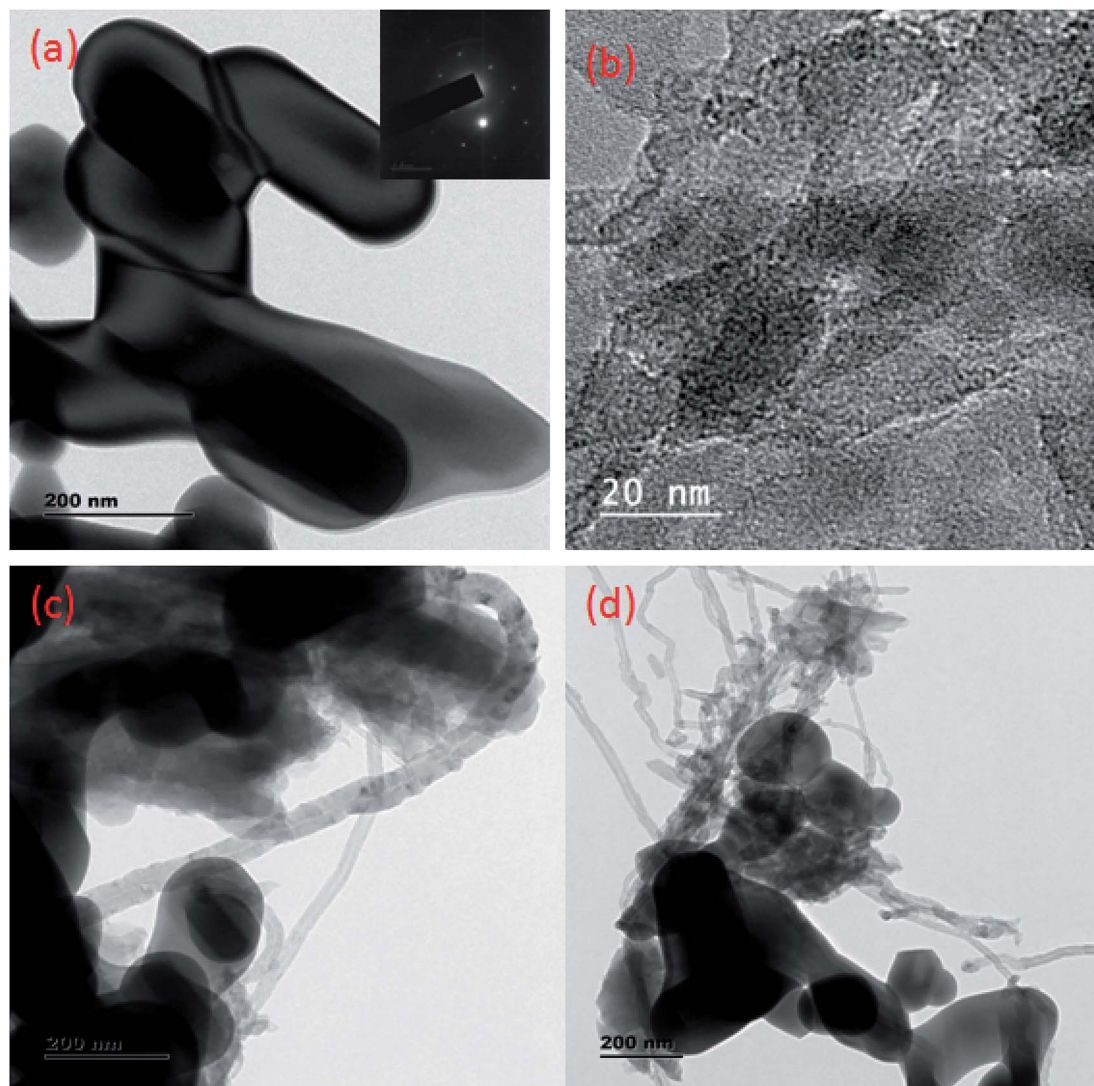


Fig. 5 (a) TEM images of CaFe_2O_4 (b) $\text{g-C}_3\text{N}_4$ and (c and d) $\text{CaFe}_2\text{O}_4/\text{g-C}_3\text{N}_4/\text{CNT}$ composite.

2.6. Photocatalytic degradation reactions

The aqueous phase degradation of $\text{Cr}(\text{vi})$ and TC was performed in a quartz reactor under visible light irradiation ($\lambda \geq 420 \text{ nm}$) generated by a 300 W Xe lamp. The distance between the test solution and the lamp was fixed at 15 cm. In the degradation process, 0.1 g of powdered photocatalyst was mixed in 100 mL of $\text{Cr}(\text{vi})$ and TC with a concentration of 10 ppm. Before visible light irradiation, the suspension was kept in the dark with constant stirring for 20 min to attain equilibrium between the pollutants and photocatalyst. Subsequently, the degraded suspension was collected at given time periods and the absorbance maxima were analyzed by a UV-vis spectrophotometer.

2.7. Photocatalytic H_2 evolution reactions

To measure the hydrogen production rate, the following procedure was adopted. Exactly 50 mg of $\text{CaFe}_2\text{O}_4/\text{g-C}_3\text{N}_4/\text{CNT}$ composite was dispersed in 75 mL of 15 vol% lactic acid solution, and then purged with N_2 for 30 min to remove the oxygen

in the reactor vessel. A 4 W LED was applied as the visible-light source and continuous stirring was maintained to keep the photocatalyst suspended in the medium. The amount of hydrogen produced was measured by a gas chromatograph with a TCD detector. The AQY of the $\text{CaFe}_2\text{O}_4/\text{g-C}_3\text{N}_4/\text{CNTs}$ was calculated using the following equation:

$$\text{AQY}\% = \frac{\text{no. of evolved hydrogen molecules} \times 2}{\text{no. of incident photons}} \times 100$$

3. Results and discussion

Fig. 1 shows the XRD patterns of $\text{g-C}_3\text{N}_4$, CaFe_2O_4 , and $\text{CaFe}_2\text{O}_4/\text{g-C}_3\text{N}_4/\text{CNT}$ composite. Two apparent distinguishing peaks of $\text{g-C}_3\text{N}_4$ appeared at the 2θ values of 13.1° and 27.8° , which can be perfectly matched with the JCPDS card number 87-1526.¹⁶ All the peaks of CaFe_2O_4 correspond to the orthorhombic crystal phase and matched the standard card (JCPDS 32-0168).¹⁷ The



strong interference peak of $g\text{-C}_3\text{N}_4$ at 27.5 was observed in the $\text{CaFe}_2\text{O}_4/g\text{-C}_3\text{N}_4/\text{CNT}$ composite, confirming the successful formation of the heterojunction. Furthermore, the characteristic peaks of the CNT were not observed in the system, which can be attributed to their low concentration and poor crystallinity. Thus, the optical properties of the as-synthesized catalyst samples were recorded by UV-vis DRS analysis. Fig. 2a presents the typical UV-vis DRS spectrum of $g\text{-C}_3\text{N}_4$, CaFe_2O_4 and $\text{CaFe}_2\text{O}_4/g\text{-C}_3\text{N}_4/\text{CNT}$ composite. It can be observed that the absorption maximum of CaFe_2O_4 is about 466 nm, while the pure $g\text{-C}_3\text{N}_4$ exhibits poor visible light absorption about 470 nm. From the Tauc plot, the band gap energies of CaFe_2O_4 and $g\text{-C}_3\text{N}_4$ were calculated to be 1.55 eV and 2.57 eV, respectively. Comparing the absorption maxima of $g\text{-C}_3\text{N}_4$, $g\text{-C}_3\text{N}_4/\text{CNT}$ and $g\text{-C}_3\text{N}_4/\text{CaFe}_2\text{O}_4$ nanocomposites, the $\text{CaFe}_2\text{O}_4/g\text{-C}_3\text{N}_4/\text{CNT}$ composite exhibited a significant red shift with the characteristic absorption edge at 585 nm and band gap energy of 2.02 eV, as shown in Fig. 2b. This may be attributed to the successful formation of an active heterojunction between the $g\text{-C}_3\text{N}_4$ and CaFe_2O_4 interface and strong electron conducting nature of CNT.¹⁸ Moreover, the enhanced visible light absorption confirmed that the $\text{CaFe}_2\text{O}_4/g\text{-C}_3\text{N}_4/\text{CNT}$ composite can absorb the visible light effectively, which is favorable for the production of hydrogen and degradation of pollutants.¹⁹

The morphologies of the as-synthesized composites were analyzed by FE-SEM and TEM analysis. The SEM images in Fig. 3a–d show the morphology and structure of CaFe_2O_4 and the $\text{CaFe}_2\text{O}_4/g\text{-C}_3\text{N}_4/\text{CNT}$ composite. Fig. 3a shows that the CaFe_2O_4 particles are well-dispersed with an average size of 200–300 nm.²⁰ Fig. 3b–d show the FE-SEM images of the $\text{CaFe}_2\text{O}_4/g\text{-C}_3\text{N}_4/\text{CNT}$ composite, which contains CaFe_2O_4 , CNT and $g\text{-C}_3\text{N}_4$ nanosheets, respectively. Furthermore, the FE-SEM images reveal that $g\text{-C}_3\text{N}_4$ exhibited a porous structure with few aggregations. The tube-like CNT were interlinked effectively on the surface of the $g\text{-C}_3\text{N}_4$ and CaFe_2O_4 matrices.²¹ The existence of this heterojunction was further confirmed by the representative elemental mapping images (EDS) in Fig. 4, which show an even distribution of carbon (C), nitrogen (N), calcium (Ca), oxygen (O) and iron (Fe).

Further, to investigate the microstructure of the obtained samples, TEM characterization was performed. Fig. 5a–d present the typical TEM images of CaFe_2O_4 , $g\text{-C}_3\text{N}_4$, and the $\text{CaFe}_2\text{O}_4/g\text{-C}_3\text{N}_4/\text{CNT}$ composite. For the composite, grey part can be assigned to the sheet-like $g\text{-C}_3\text{N}_4$, and the dark particles can be assigned to CaFe_2O_4 nanoparticles, which were dispersed effectively on the exterior surface of $g\text{-C}_3\text{N}_4$.²² Furthermore, the TEM images display the existence of a heterojunction stuck between $g\text{-C}_3\text{N}_4$ and CaFe_2O_4 , and the tubular CNT acting as a connecting bridge between these materials. In the SAED patterns, the lattice fringes have a spacing of 0.231 nm, which is consistent with the (131) planes of CaFe_2O_4 (JCPDS 32-0168). Thus, these results are in accordance with the XRD analysis. Upon further analysis of the HRTEM images, as shown in Fig. 6, close contact interfaces between CaFe_2O_4 , $g\text{-C}_3\text{N}_4$ and CNT were observed. From the TEM results, it can be concluded that an apparent interface was formed between the $g\text{-C}_3\text{N}_4$, CNT, and CaFe_2O_4 matrices. Therefore this ternary

$\text{CaFe}_2\text{O}_4/g\text{-C}_3\text{N}_4/\text{CNT}$ composite is promising for the transport of charge carriers towards the degradation of Cr(VI) and TC.²³

The chemical binding energies and oxidation states of the $\text{CaFe}_2\text{O}_4/g\text{-C}_3\text{N}_4/\text{CNT}$ composite were confirmed by XPS (Fig. 7), which was also used to study the valence state properties of the semiconductors. Fig. 7a displays the XPS survey spectrum of the $\text{CaFe}_2\text{O}_4/g\text{-C}_3\text{N}_4/\text{CNT}$ composite. The major peaks of the Ca, Fe, O, C and N elements appeared in the XPS spectra. Fig. 7b displays the elemental scan of the Ca 2p element, where the major peaks at 346.4 eV and 350.2 eV correspond to the Ca 2p_{3/2} and Ca 2p_{1/2} spins, respectively.²⁴ The elemental XPS spectrum of Fe 2p in Fig. 7c mainly shows peaks at 710.8 eV and 724.8 eV, representing the Fe 2p_{3/2} and Fe 2p_{1/2} spins, which indicate the oxidation of Fe was 3+ in CaFe_2O_4 .²⁵ The O 1s spectrum in Fig. 7d was deconvoluted into two main peaks at 529.7 eV and 531.8 eV, corresponding to the lattice oxygen in ferrites and surface-adsorbed OH groups, respectively.²⁶ The C 1s peaks of the composite were located at 288.6 eV and 284.5 eV, which correspond to the C–N and C–C hybridization in the carbon matrix, respectively (Fig. 7e). The peaks observed at 398.7 eV and 398.5 eV are attributed to the sp²-hybridized nitrogen atoms in the triazine rings. Furthermore, the sharp peak observed at 401.4 eV corresponds to the strong binding of nitrogen with carbon atoms such as N–(C)₃ (Fig. 7f).²⁷ Thus, the structural analysis with XRD, FE-SEM, TEM, UV-vis DRS, and XPS suggests that the $\text{CaFe}_2\text{O}_4/g\text{-C}_3\text{N}_4/\text{CNT}$ composite was successfully synthesized.

It is worth mentioning that highly proficient visible light-active photocatalytic reactions are mainly a result of fast separation efficiency, good redox reactions and high visible light absorption.²⁸ The electron–hole separation and charge transfer properties of $g\text{-C}_3\text{N}_4$ and the $\text{CaFe}_2\text{O}_4/g\text{-C}_3\text{N}_4/\text{CNT}$ composite was confirmed by PL analysis, and the data is shown in Fig. 8. $g\text{-C}_3\text{N}_4$ showed the highest PL peak intensity, which confirms that

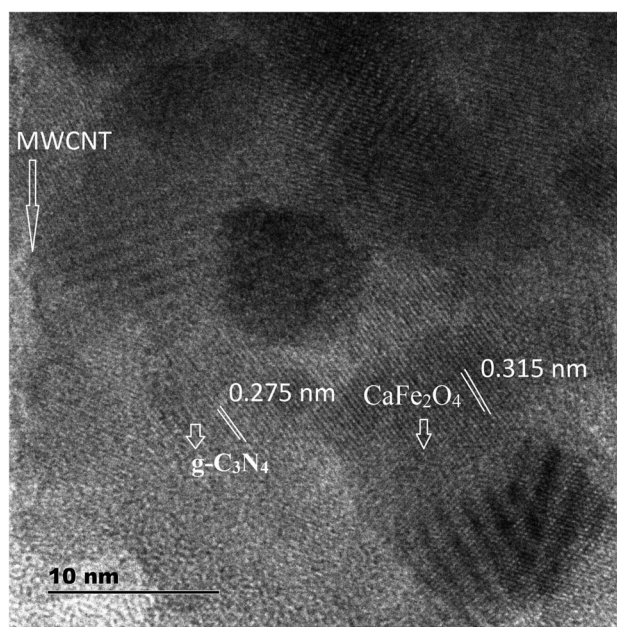


Fig. 6 HRTEM images of the $\text{CaFe}_2\text{O}_4/g\text{-C}_3\text{N}_4/\text{CNT}$ composite.



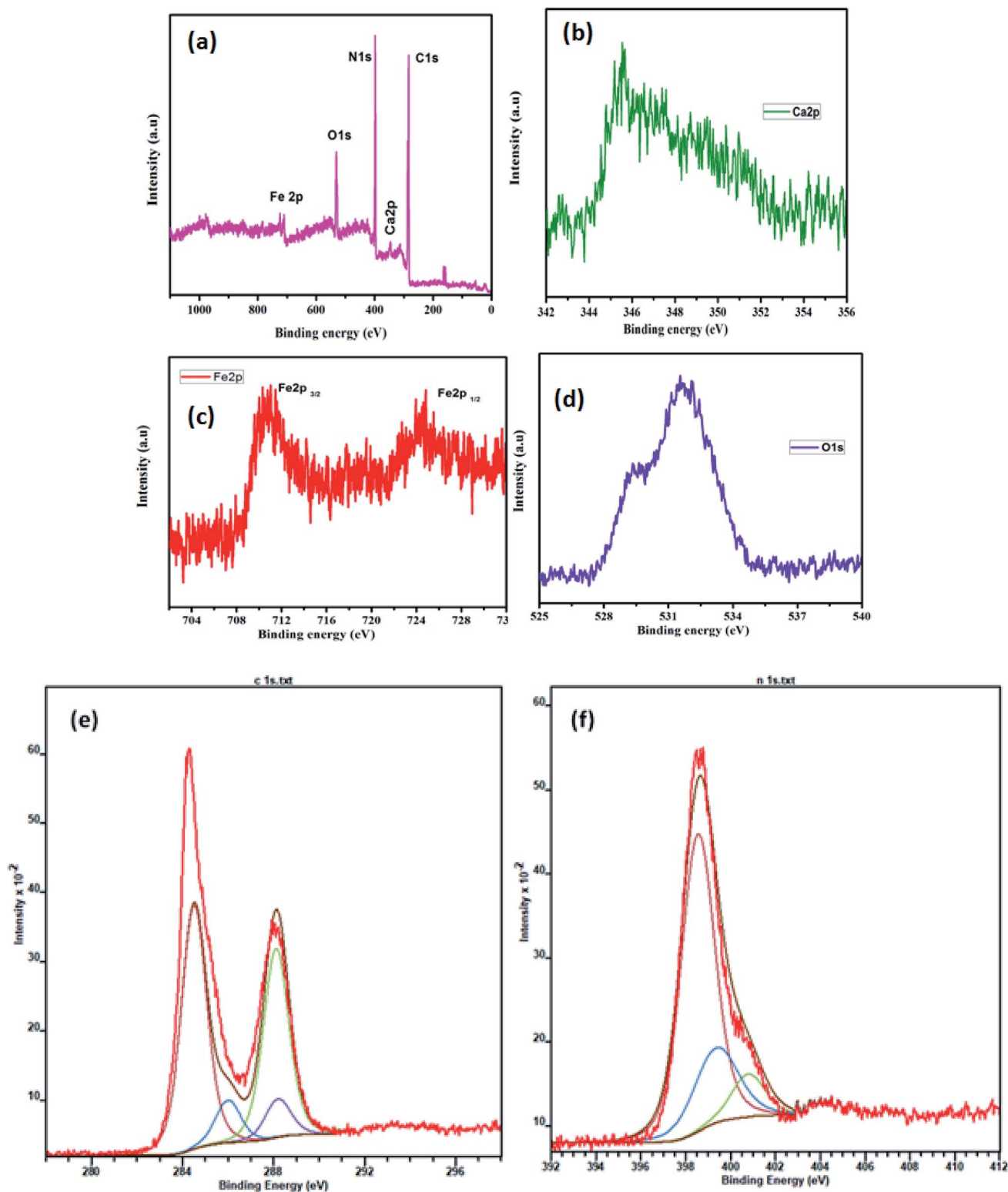


Fig. 7 XPS spectra of the as-prepared $\text{CaFe}_2\text{O}_4/\text{g-C}_3\text{N}_4/\text{CNT}$ composite: (a) survey scan, (b) Ca 2p, (c) Fe 2p, (d) O 1s, (e) C 1s, and (f) N 1s.

it has a very high recombination rate. However, the PL intensity of the $\text{CaFe}_2\text{O}_4/\text{g-C}_3\text{N}_4/\text{CNT}$ composite was remarkably compared with that of $\text{g-C}_3\text{N}_4$. The lower recombination rate in the photocatalytic system can be beneficial for the complete degradation of pollutions within a minimum time.²⁹

The BET surface area and average pore size of CaFe_2O_4 , $\text{g-C}_3\text{N}_4$, $\text{CaFe}_2\text{O}_4/\text{CNTs}$, and the $\text{CaFe}_2\text{O}_4/\text{g-C}_3\text{N}_4/\text{CNT}$ nanocomposite were obtained from N_2 adsorption-desorption studies, as shown in Fig. 9. The N_2 adsorption-desorption curves of the prepared samples exhibit type IV isotherms,



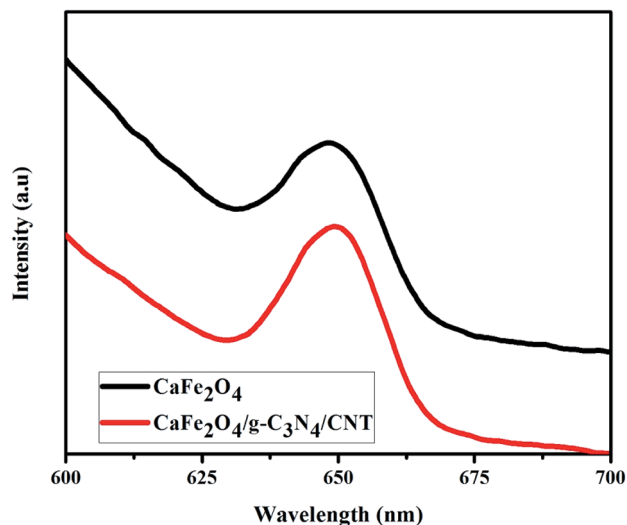


Fig. 8 PL analysis of CaFe_2O_4 and $\text{CaFe}_2\text{O}_4/\text{g-C}_3\text{N}_4/\text{CNTs}$ composite.

indicating the pore size of the samples is mesoporous in nature using the BJH method. It was evident that the $\text{CaFe}_2\text{O}_4/\text{g-C}_3\text{N}_4/\text{CNTs}$ photocatalyst exhibited the highest specific surface area, which is beneficial for higher photocatalytic activity.

The photogenerated charge carrier capability and separation nature of the composite were investigated by EIS measurements. Both CaFe_2O_4 and the $\text{CaFe}_2\text{O}_4/\text{g-C}_3\text{N}_4/\text{CNT}$ composite exhibited semicircular Nyquist plots, but the diameter of the $\text{CaFe}_2\text{O}_4/\text{g-C}_3\text{N}_4/\text{CNT}$ composite plot was smaller (Fig. 10), further confirming the faster interfacial charge transfer rate and outstanding separation rate of photogenerated charge carriers between $\text{g-C}_3\text{N}_4$ and CaFe_2O_4 due to the incorporation of CNT.

The spin-trapping ESR measurements were used to confirm the presence of active oxidation species produced over the $\text{CaFe}_2\text{O}_4/\text{g-C}_3\text{N}_4/\text{CNT}$ composite during the photocatalytic process, and the results are shown in Fig. 11. Under visible light

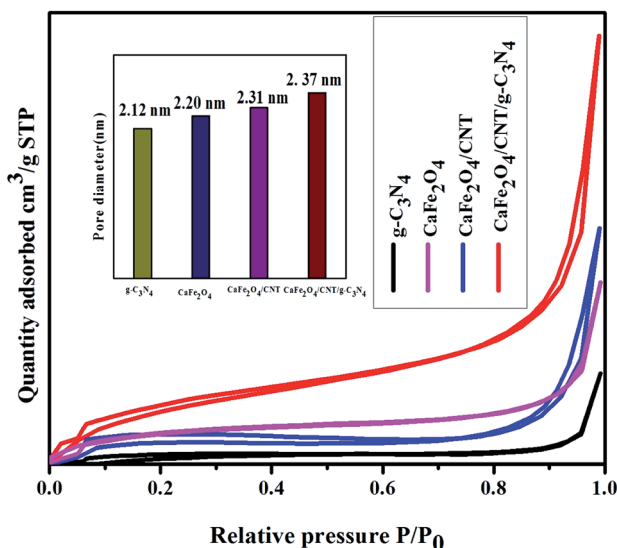


Fig. 9 BET analysis of CaFe_2O_4 , $\text{g-C}_3\text{N}_4$, $\text{CaFe}_2\text{O}_4/\text{CNTs}$, and $\text{CaFe}_2\text{O}_4/\text{g-C}_3\text{N}_4/\text{CNT}$ composite.

irradiation, the characteristic peaks of $\text{DMPO}\cdot\cdot\text{O}_2^-$ and $\text{DMPO}\cdot\text{OH}$ were clearly observed, and the peak intensities were obvious when the irradiation time was increased up to 3 min. The ESR results confirmed that the $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ radicals were mainly generated during the photocatalytic process.

3.1. Photocatalytic activities and stability tests

The photocatalytic activity of $\text{g-C}_3\text{N}_4$, CaFe_2O_4 , and $\text{CaFe}_2\text{O}_4/\text{g-C}_3\text{N}_4/\text{CNT}$ composite for the visible light degradation of $\text{Cr}(\text{vi})$ and TC is shown in Fig. 12a. The photolysis of $\text{Cr}(\text{vi})$ and TC under visible light without photocatalysts was negligible. Using the pure $\text{g-C}_3\text{N}_4$ and CaFe_2O_4 , the degradation rate was not appreciable due to their high recombination rate of charge carriers. Furthermore, using the binary systems of $\text{g-C}_3\text{N}_4/\text{CNT}$ and $\text{CaFe}_2\text{O}_4/\text{CNT}$, the degradation rate of $\text{Cr}(\text{vi})$ and TC moderately increased. We found that the introduction of CNT in the $\text{g-C}_3\text{N}_4/\text{CaFe}_2\text{O}_4$ heterojunction enhanced the degradation rate for Cr and TC, and the best degradation efficiency was achieved upon the incorporation of CNT in the system, which confirms the importance of CNT in the ternary structure. The $\text{CaFe}_2\text{O}_4/\text{g-C}_3\text{N}_4/\text{CNT}$ composite exhibited a photocatalytic efficiency of 97% (at 120 min) for the degradation of $\text{Cr}(\text{vi})$ and 98% (at 60 min) for TC under visible light (Fig. 13a). As shown in Fig. 13b, the photodegradation rate of the $\text{CaFe}_2\text{O}_4/\text{g-C}_3\text{N}_4/\text{CNT}$ composite decreased slightly after five reaction cycles, indicating the excellent reusability of the photocatalytic material. The role of pH strongly interferes with the photocatalytic removal of $\text{Cr}(\text{vi})$; thus, the effect of pH was also studied in the pH range of 3–9 with the $\text{CaFe}_2\text{O}_4/\text{g-C}_3\text{N}_4/\text{CNT}$ composite. At a higher pH, the photocatalytic reduction rate for $\text{Cr}(\text{vi})$ was significantly reduced (Fig. 12b) due to the formation of $\text{Cr}_2\text{O}_7^{2-}$. At a lower pH value, $\text{Cr}(\text{vi})$ was easily removed due to the formation of HCrO_4^- and the protonated surface of the catalyst, which is more favorable for $\text{Cr}(\text{vi})$ removal.³⁰ Moreover, the reaction rate constant of the $\text{CaFe}_2\text{O}_4/\text{g-C}_3\text{N}_4/\text{CNTs}$ ternary photocatalyst, as shown in Fig. 14, for the removal of $\text{Cr}(\text{vi})$ is $65 \times 10^{-4} \text{ min}^{-1}$ and removal of TC is $73 \times 10^{-4} \text{ min}^{-1}$.

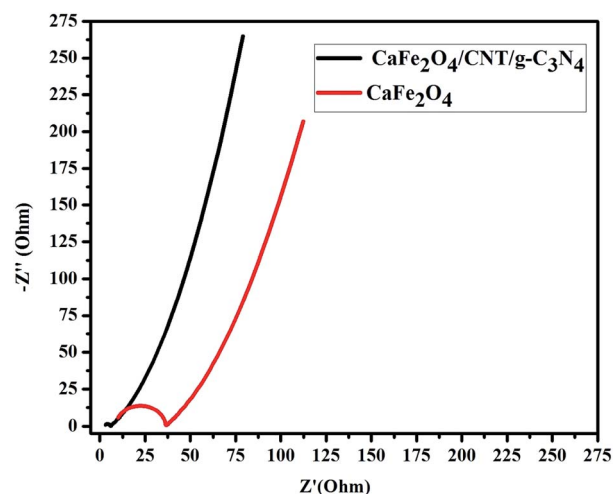


Fig. 10 EIS spectra CaFe_2O_4 and $\text{CaFe}_2\text{O}_4/\text{g-C}_3\text{N}_4/\text{CNT}$ composite.



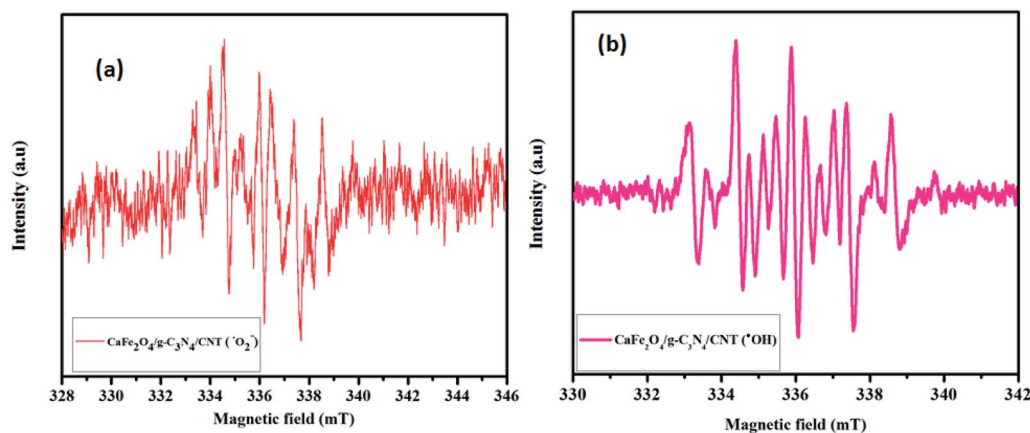


Fig. 11 EPR spectrum of $\text{CaFe}_2\text{O}_4/\text{g-C}_3\text{N}_4/\text{CNT}$ composite using DMPO.

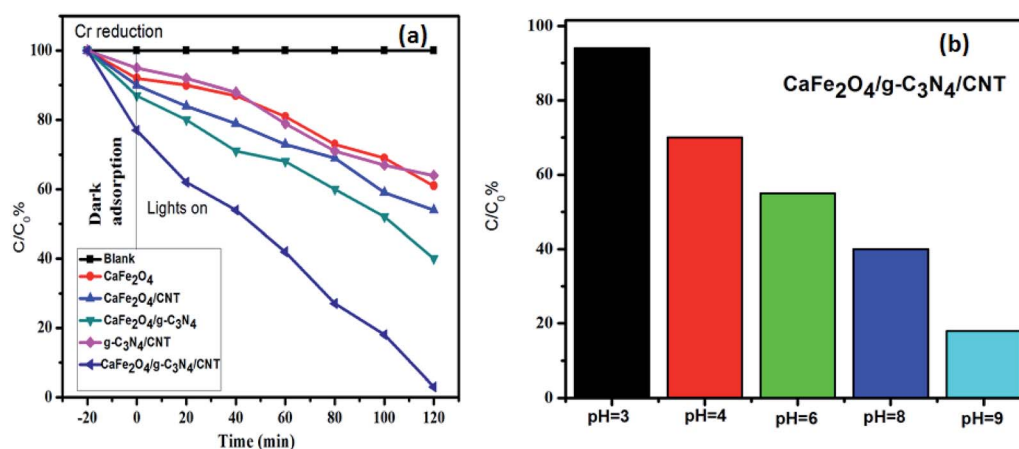


Fig. 12 (a) Adsorption and visible light photocatalytic performance of the samples for the degradation of $\text{Cr}(\text{VI})$ and (b) effect of pH on the removal of $\text{Cr}(\text{VI})$ using the $\text{CaFe}_2\text{O}_4/\text{g-C}_3\text{N}_4/\text{CNT}$ s composite.

3.2. Photocatalytic hydrogen production tests

In this work, the feasibility of using the $\text{CaFe}_2\text{O}_4/\text{g-C}_3\text{N}_4/\text{CNT}$ composite as a versatile photocatalyst for the production of hydrogen was studied. As shown in Fig. 15, the loading of CNT

on $\text{g-C}_3\text{N}_4$ and CaFe_2O_4 resulted in a significant enhancement in the photocatalytic hydrogen production rate. Initially, with an increase in the loading of $\text{g-C}_3\text{N}_4$ in CaFe_2O_4 , the hydrogen generation rate showed a remarkable improvement. In

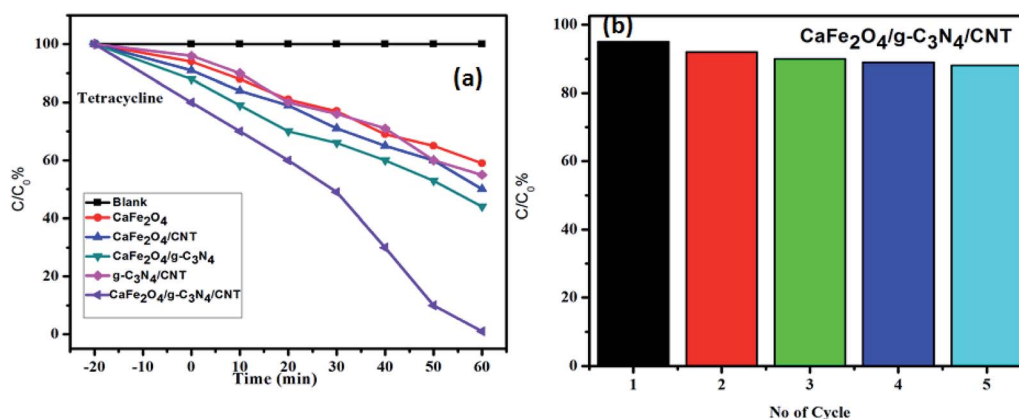


Fig. 13 (a) Adsorption and visible light photocatalytic performance of the samples in the degradation of TC and (b) stability test of the $\text{CaFe}_2\text{O}_4/\text{g-C}_3\text{N}_4/\text{CNT}$ composite in recycling degradation of TC.



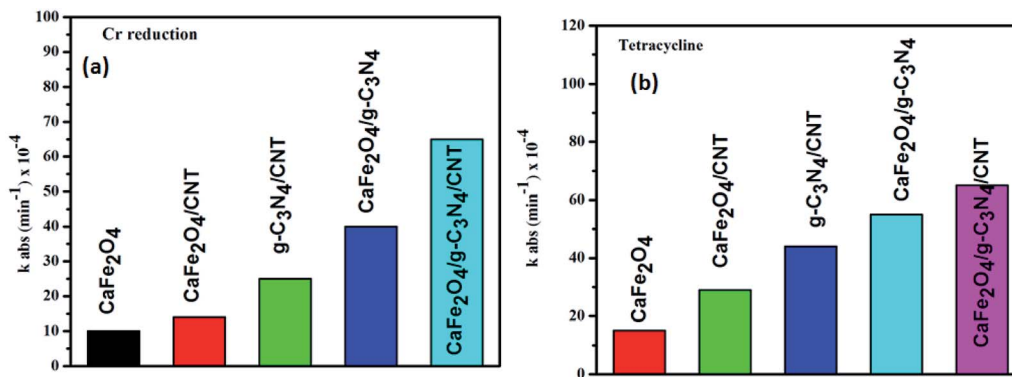


Fig. 14 Photodegradation kinetics of Cr and TC over the $\text{CaFe}_2\text{O}_4/g\text{-C}_3\text{N}_4/\text{CNT}$ composite under visible light.

particular, the hydrogen generation rate of the $\text{CaFe}_2\text{O}_4/g\text{-C}_3\text{N}_4/\text{CNT}$ composite sample increased to $1085 \mu\text{mol h}^{-1}$, which is about nearly 3 times higher than that of bare CaFe_2O_4 ($417 \mu\text{mol h}^{-1}$). The AQY of $\text{CaFe}_2\text{O}_4/g\text{-C}_3\text{N}_4/\text{CNTs}$ was calculated to be 7.2%. These results indicate that the CNT act as an effective co-catalyst for $g\text{-C}_3\text{N}_4/\text{CaFe}_2\text{O}_4$ and heterojunctions, and the loading ratio of CNT needs to be controlled within an appropriate range. Therefore, as a noble metal-free catalyst, $\text{CaFe}_2\text{O}_4/g\text{-C}_3\text{N}_4/\text{CNT}$ composite can potentially be used as an economically feasible catalyst to replace precious metals such as Pt and Pd industrially to produce hydrogen. As shown in Fig. 16, to study the stability of the $\text{CaFe}_2\text{O}_4/g\text{-C}_3\text{N}_4/\text{CNT}$ composite, cyclic runs for photocatalytic hydrogen production using the $\text{CaFe}_2\text{O}_4/g\text{-C}_3\text{N}_4/\text{CNT}$ composite sample were performed. A slight decrease in the hydrogen production rate of the $\text{CaFe}_2\text{O}_4/g\text{-C}_3\text{N}_4/\text{CNT}$ composite was observed in the last cycle, which confirms that the $\text{CaFe}_2\text{O}_4/g\text{-C}_3\text{N}_4/\text{CNT}$ composite has excellent stability during the photocatalytic production of hydrogen besides the degradation reactions. Furthermore, the sample was collected after the cycle test and then characterized by XRD analysis. The XRD patterns of the reused catalyst exhibited no significant changes in the crystal structure after five consecutive cycles. Thus, the $\text{CaFe}_2\text{O}_4/g\text{-C}_3\text{N}_4/\text{CNT}$ composite was determined to display good cyclic stability during the photocatalytic

production of hydrogen.³¹ Using all the characterization results, the plausible photocatalytic degradation mechanism with the $\text{CaFe}_2\text{O}_4/g\text{-C}_3\text{N}_4/\text{CNT}$ composite for a high degradation rate and hydrogen production was proposed. Also, a comparison of the present work with previous reported catalysts is presented in Table 1.

3.3. Photocatalytic mechanisms

Under visible light illumination, both CaFe_2O_4 and $g\text{-C}_3\text{N}_4$ can be quickly excited to generate the corresponding photoinduced electrons and holes due to their moderate band gaps of 1.55 eV and 1.55 eV, respectively. Since the E_{CB} value of $g\text{-C}_3\text{N}_4$ (-1.15 eV)³² is highly negative compared to that of CaFe_2O_4 ($+1.57 \text{ eV}$), the ejected electrons towards the CB of $g\text{-C}_3\text{N}_4$ can be simply transferred to the CB of CaFe_2O_4 . Meanwhile, the generated holes on the VB of CaFe_2O_4 may be transferred to the VB of $g\text{-C}_3\text{N}_4$ because the E_{VB} of CaFe_2O_4 ($+1.98 \text{ eV}$) was more positive than that of $g\text{-C}_3\text{N}_4$ ($+0.89 \text{ eV}$).³³ Furthermore, the additional impact of the CNT results in the transfer of more electron-hole pairs through the effective linkage, leading to an improvement in the lifetime of the carriers. In this mode, the charge separation of photogenerated electron-hole pairs can be drastically enhanced and the recombination rate can be minimized, thus

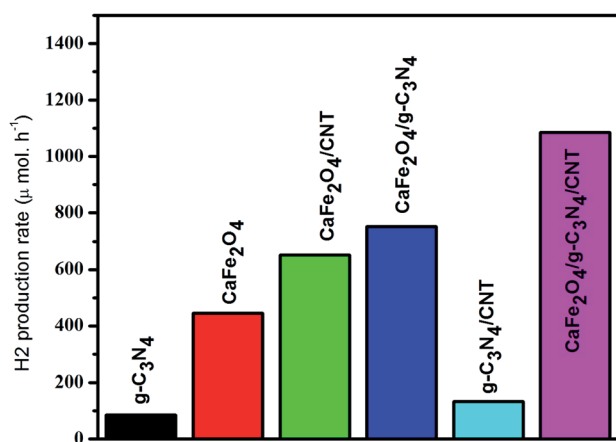


Fig. 15 Time-dependent photocatalytic hydrogen production rate of the $\text{CaFe}_2\text{O}_4/g\text{-C}_3\text{N}_4/\text{CNT}$ composite under visible light.

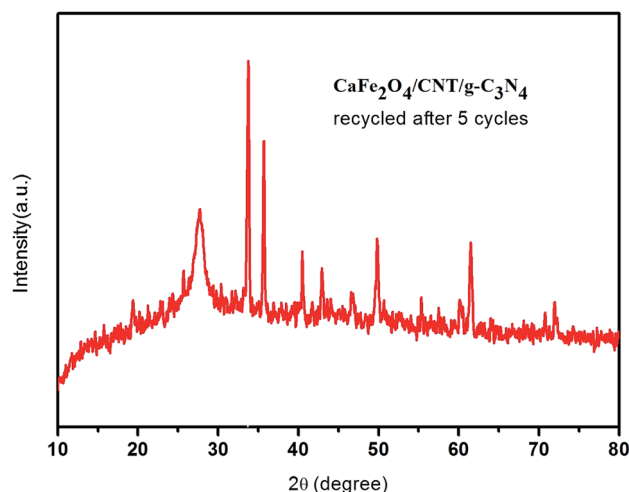


Fig. 16 XRD spectrum of the reused $\text{CaFe}_2\text{O}_4/g\text{-C}_3\text{N}_4/\text{CNT}$ composite towards hydrogen production after three cycles.



Table 1 Catalytic, photocatalytic and post-illumination activities of different catalysts

Photocatalyst	Target pollutant	Irradiation time (min)	Decomposition (%)	Ref.
Biochar-coupled g-C ₃ N ₄	Cr(vi)	300	100	41
TiO ₂ /g-C ₃ N ₄ @diatomite hybrid photocatalyst	Cr(vi)	300	100	42
N ₂ -g-C ₃ N ₄ photocatalyst	Bisphenol-A	120	79	43
g-C ₃ N ₄ /Na-bentonite composites	Cr(vi) and RhB	120	88.6	44
0D/2D bismuth molybdate homojunction	Cr(vi)	80	100	45
Ag/BiVO ₄ p-n junction photocatalyst	Tetracycline and Cr(vi)	100	70	46
CaFe ₂ O ₄ /g-C ₃ N ₄ /CNT composite	Tetracycline and Cr(vi)	120	98	This study

improving the photocatalytic ability of the CaFe₂O₄/g-C₃N₄/CNT composite.^{34–40} The possible photocatalytic mechanism for the photodegradation of Cr(vi) and TC as well as hydrogen generation using the ternary CaFe₂O₄/g-C₃N₄/CNT composite under visible light irradiation is proposed in Fig. S1.†

4. Conclusion

In conclusion, we demonstrated a simple hydrothermal strategy for the fabrication of a ternary CaFe₂O₄/g-C₃N₄/CNT composite. The addition of CNT in the system outstandingly promoted the separation of photogenerated charge carriers. The as-synthesized CaFe₂O₄/g-C₃N₄/CNT composite exhibited improved light-harvesting capability, more proficient charge transfer capability and improved hydrogen production performance. The hydrogen production rate of the optimal CaFe₂O₄/g-C₃N₄/CNT composite was superior to that of pure CaFe₂O₄ and previous works. Furthermore, the optimal CaFe₂O₄/g-C₃N₄/CNT composite photocatalyst exhibited excellent performances for the photodegradation of Cr(vi) and TC with high stability. This work may inspire the development of rare earth- and noble metal-free catalysts for the degradation of pollutants and production of hydrogen in the near future.

Conflicts of interest

There are no conflicts of interest in this paper.

Acknowledgements

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