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g-C₃N₄ nanosheet supported NiCo₂O₄ nanoparticles for boosting degradation of tetracycline under visible light and ultrasonic irradiation†

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The doping of semiconductor materials through some facile and appropriate methods holds significant promise in enhancing the catalytic performance of catalysts. Herein, NiCo₂O₄/g-C₃N₄ composite catalysts were synthesized via a high-energy ball milling method. The microstructure and physicochemical characterization of the as-prepared composites confirmed the successful loading of NiCo₂O₄ nanoparticles onto the g-C₃N₄ nanosheets. The NiCo₂O₄/g-C₃N₄ composites showed excellent catalytic effect under visible light/ultrasonic irradiation, and the efficiency of tetracycline hydrochloride (TCH) degradation reached 90% within 15 min. The optical properties of g-C₃N₄ nanosheets were improved by doping, and the diffusion of active materials and carrier migration rate were improved by ultrasonic assistance. Possible catalytic mechanisms and potential pathways of the NiCo₂O₄/g-C₃N₄ composites for the degradation of TCH triggered by visible light/ultrasonic irradiation were proposed. This study provides a new strategy for energy-assisted photocatalytic degradation of organic pollutants.

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1. Introduction

In recent years, a variety of antibiotics have been detected in surface water as emerging pollutants,^{1–3} drawing increasing attention to the pollution of water by antibiotics. Tetracycline is one of the most commonly used antibiotics for treatment of diseases due to its broad-spectrum antimicrobial properties.^{4,5} However, tetracycline cannot be fully absorbed, resulting in more than 70% being released into the environment. Tetracycline in water can also inhibit the normal growth of aquatic organisms and cause endocrine disorders in aquatic organisms.^{6,7} In addition, the carcinogenic activity of tetracycline is very harmful to human health.⁸ The existence of tetracycline in water damages water quality, posing a long-

term potential threat to the ecosystem and human health. Therefore, how to remove tetracycline from water is an urgent problem to be solved.

Many efforts have been devoted to the degradation of tetracycline pollutants in water, such as adsorption,⁹ advanced oxidation processes (AOPs),^{10,11} and electrochemical¹² and catalytic degradation.^{13–15} Among them, photocatalytic technology has attracted more attention owing to its effective utilization of sunlight. The band gap matching between a semiconductor material and solar energy is key to achieving efficient photocatalytic degradation. However, the lack of active sites and a high carrier recombination rate in semiconductor materials have greatly limited the development of photocatalytic technology. Ultrasonic technology is an emerging wastewater treatment solution with the advantages of high efficiency, fast speed and environmental protection.^{16–18} The principle of ultrasonic catalysis technology is mainly based on the phenomenon of acoustic cavitation. Cavitation bubbles are first formed on the catalyst surface through ultrasonic waves, and then the local high temperature and high pressure caused by the rupture of cavitation bubbles will promote the formation of strongly oxidizing monomers such as hydroxyl free radicals.^{19,20} The combination of ultrasonic waves and photocatalysis has enhanced the degradation of organic pollutants, overcoming the limitations of any single degradation method. The use of ultrasonic wave vibration results in more strongly

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oxidizing monomers, with an enhanced diffusion rate and a mass transfer effect in the liquid phase. As a result, the contact frequency and reaction rate of the photocatalyst and organic pollutant will be improved, so will the catalytic degradation effect.

As a typical polymer photocatalyst with non-toxicity, low cost, easy availability and high conductivity, graphitized carbon nitride (g-C₃N₄) is widely applied in photocatalytic degradation.^{21–24} Moreover, g-C₃N₄ with a two-dimensional layered structure has a high piezoelectric coefficient.^{25,26} However, it still face limitations such as low potential energy and easy recombination of electron-hole pairs.^{27,28} Thus, metals and non-metals have been doped in g-C₃N₄ to improve its photocatalytic performance. Different techniques have been adopted for g-C₃N₄ doping, such as thermal polycondensation synthesis,²⁹ solid phase synthesis,³⁰ a solvothermal method,³¹ and ball milling.^{32,33} Among them, the ball milling technique is the most suitable method for scaled production because it is simple, efficient and does not require organic solvents. More importantly, the ball milling method can significantly enhance the active sites and stability of nanocatalysts, ideal for the preparation of highly efficient nanocatalysts.

In this study, the NiCo₂O₄/g-C₃N₄ composite catalysts were synthesized *via* a high-energy ball milling method. NiCo₂O₄ nanoparticle doping improved the band-gap structure of g-C₃N₄ and enhanced the absorption of visible light, providing a way for electron transfer and enhancing the separation efficiency of photogenerated carriers. The microstructure and physicochemical properties of NiCo₂O₄/g-C₃N₄ composites were studied, and the catalytic activity and the mechanism of the composite catalysts under different catalytic conditions were investigated. The as-prepared NiCo₂O₄/g-C₃N₄ composite catalysts showed excellent catalytic activity under the synergistic effect of visible light/ultrasonic irradiation, suggesting that ball milling is a simple and reliable method for large-scale synthesis of nanocatalysts. This work has great practical application value for highly efficient degradation of organic pollutants in wastewater.

2. Experimental

2.1. Materials

Urea, cobalt(II) nitrate hexahydrate, nickel(II) nitrate hexahydrate, sodium hydroxide and tetracycline hydrochloride (TCH) were supplied by Sinopharm Chemical Reagent Co., Ltd (Shanghai, China).

2.2. Preparation of g-C₃N₄

10 g of urea and 30 mL of deionized water were mixed followed by drying. After drying, the mixture was transferred to a 100 mL muffle furnace for calcination at 550 °C for 3 h with a heating rate of 5 °C min^{−1}.

2.3. Preparation of NiCo₂O₄

The co-precipitation method was used to synthesize NiCo₂O₄ nanoparticles. 0.87 g of Ni (NO₃)₂·6H₂O and 3.49 g of Co (NO₃)₂·6H₂O were dissolved in 50 mL of deionized water with a molar ratio of 1 : 4. After stirring for 1 h, 25 mL of 2 M NaOH was added to the mixture solution, and a large amount of Ni-Co hydroxide coprecipitate was rapidly formed. The coprecipitate was filtered and washed with water and then dried overnight at 60 °C. Finally, the powder was calcined at 300 °C for 3 h in air with a heating rate of 6 °C min^{−1}.

2.4. Preparation of NiCo₂O₄/g-C₃N₄

The NiCo₂O₄/g-C₃N₄ composite catalysts were prepared *via* a high-energy ball milling method, as shown schematically in Fig. 1. In a typical synthesis process, different mass ratios of NiCo₂O₄ and g-C₃N₄ were placed in a planetary ball milling machine in 250 mL zirconia jars, and 200 g of different sized zirconia balls were added to each jar. After that, the high energy ball milling machine was run at a rotational speed of 500 rpm for 6 h. The obtained powder was finally dried overnight at 60 °C.

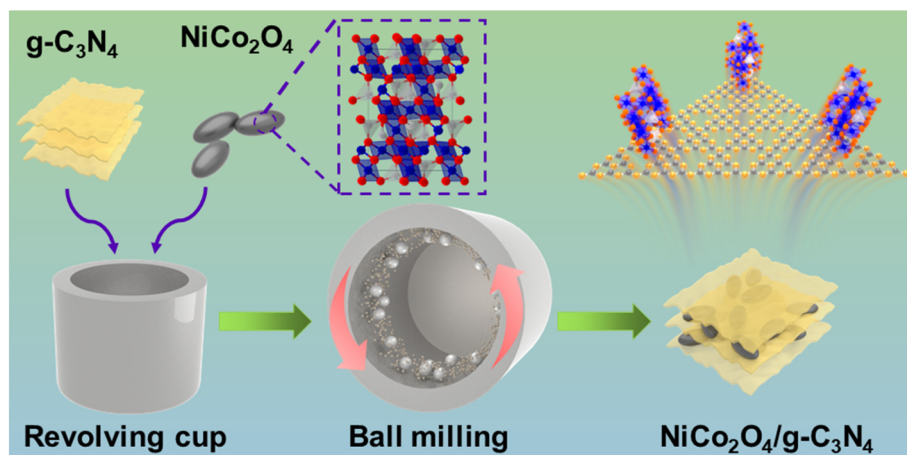


Fig. 1 Schematic illustration of the preparation of NiCo₂O₄/g-C₃N₄ composites.

2.5. Characterization

The surface morphology and elemental composition of the $g\text{-C}_3\text{N}_4$ samples were analyzed by transmission electron microscopy (TEM, Tecnai G220S-TWIN, FEI Co., Ltd, USA) with energy-dispersive X-ray spectroscopy (EDX, Oxford, UK). The chemical structure of samples was analyzed by Fourier transform infrared spectroscopy (FTIR, TENSOR 27, Bruker, USA) in the frequency range of $500\text{--}4000\text{ cm}^{-1}$. The crystal structure of the samples was analyzed using an X-ray diffractometer (XRD, D/max 2500, Rigaku, Japan) within the 2θ range from 10° to 70° . The specific surface area of $g\text{-C}_3\text{N}_4$ and $\text{NiCo}_2\text{O}_4/g\text{-C}_3\text{N}_4$ composites was obtained from a Micromeritics TriStar II 3020 sorption analyzer (Micromeritics Instrument Co., USA). The chemical composition of $\text{NiCo}_2\text{O}_4/g\text{-C}_3\text{N}_4$ composites was recorded by X-ray photoelectron spectroscopy (XPS, PHI-5000C ESCA, PerkinElmer, USA).

2.6. Catalytic activity measurements

Tetracycline solution was employed to evaluate the catalytic activity of the $\text{NiCo}_2\text{O}_4/g\text{-C}_3\text{N}_4$ composite catalysts. 50 mg of catalyst were added to the tetracycline solution (50 mL , 5 mg L^{-1}) under simultaneous xenon lamp ($\lambda > 420\text{ nm}$) irradiation and ultrasound actuation. The degradation degree of the tetracycline solution at different time intervals was measured by UV-vis spectroscopy (Analytik, Jena, Spe cord 210 plus). The test was adjusted accordingly to examine the effect of the amount of NiCo_2O_4 and catalytic conditions.

2.7. Electrochemical test

The electrochemical performance of the $\text{NiCo}_2\text{O}_4/g\text{-C}_3\text{N}_4$ composites was analyzed on an electrochemical workstation (CorrTest CS 310, Wuhan, China) through a standard three-electrode system. The working electrode was prepared as follows: 10 mg of catalyst was mixed with 1 mL of 5 wt%

Nafion solution followed by deposition on a fluorine-doped tin oxide (FTO) glass and drying in air. $0.1\text{ M Na}_2\text{SO}_4$ solution was used as the electrolyte, while Ag/AgCl and a Pt slice were used as the reference electrode and counter electrode, respectively. EIS measurements were performed using the same system over a frequency range of $10^5\text{--}10^{-2}\text{ Hz}$ with an AC amplitude of 0.27 V at the open circuit potential.

3. Results and discussion

3.1. Characterization

The color of the $g\text{-C}_3\text{N}_4$ powder changed from yellow to gray after the introduction of NiCo_2O_4 nanoparticles, as shown in Fig. 2a. The TEM images of $g\text{-C}_3\text{N}_4$ nanosheets showed a 2D thin nanosheet with a wrinkle-like structure (Fig. 2b). The TEM image (Fig. 2c) demonstrates that NiCo_2O_4 nanoparticles are well embedded on the surface of $g\text{-C}_3\text{N}_4$ nanosheets after doping with nanoparticles. At a higher magnification, the surface shows many elliptical NiCo_2O_4 nanoparticles, as shown by the red circles in Fig. 2d. Besides, the HRTEM image of the lattice fringe shows a separation of 0.25 nm (Fig. 2e), corresponding to the (311) plane of the NiCo_2O_4 phase.^{34,35} The EDS elemental mapping in Fig. 2f displays that $\text{NiCo}_2\text{O}_4/g\text{-C}_3\text{N}_4$ composites are composed of C, O, N, Ni and Co elements. The distribution of Ni and Co elements is clearly visible with an elliptical shape, indicating that NiCo_2O_4 nanoparticles have been successfully loaded onto $g\text{-C}_3\text{N}_4$ nanosheets.

The FT-IR spectra of $g\text{-C}_3\text{N}_4$ samples are shown in Fig. 3a. For original $g\text{-C}_3\text{N}_4$ and $\text{NiCo}_2\text{O}_4/g\text{-C}_3\text{N}_4$ composites, the vibration peak at 807 cm^{-1} was assigned to the tri-s-triazine unit structure of $g\text{-C}_3\text{N}_4$. The wide absorption peaks in the range of $1200\text{--}1800\text{ cm}^{-1}$ were ascribed to CN heterocycle skeletal vibration. The broad absorption peaks at $2900\text{--}3300\text{ cm}^{-1}$

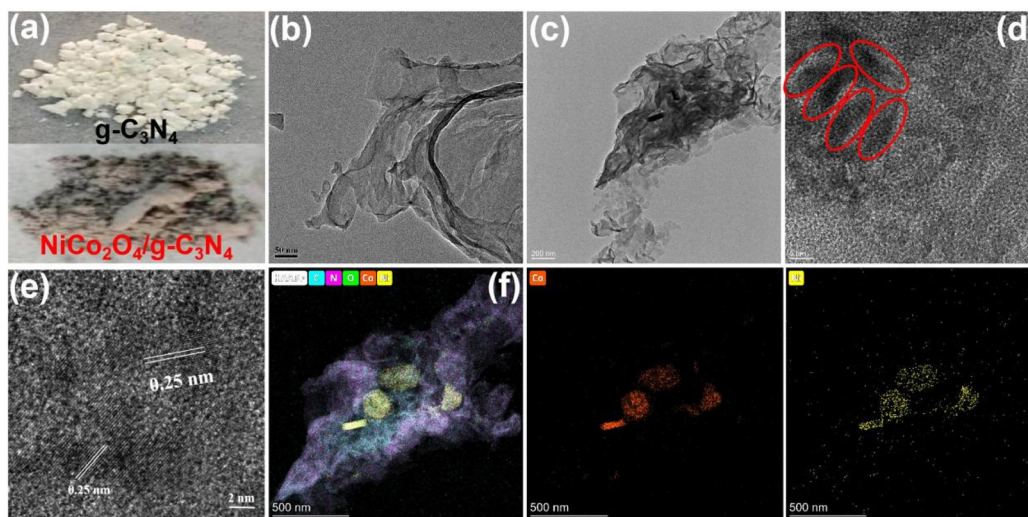


Fig. 2 Optical photos (a) and TEM images of $g\text{-C}_3\text{N}_4$ nanosheets and $\text{NiCo}_2\text{O}_4/g\text{-C}_3\text{N}_4$ composites at different magnifications (b–d), HRTEM image (e) of $\text{NiCo}_2\text{O}_4/g\text{-C}_3\text{N}_4$ composites and the corresponding elemental mapping (f).

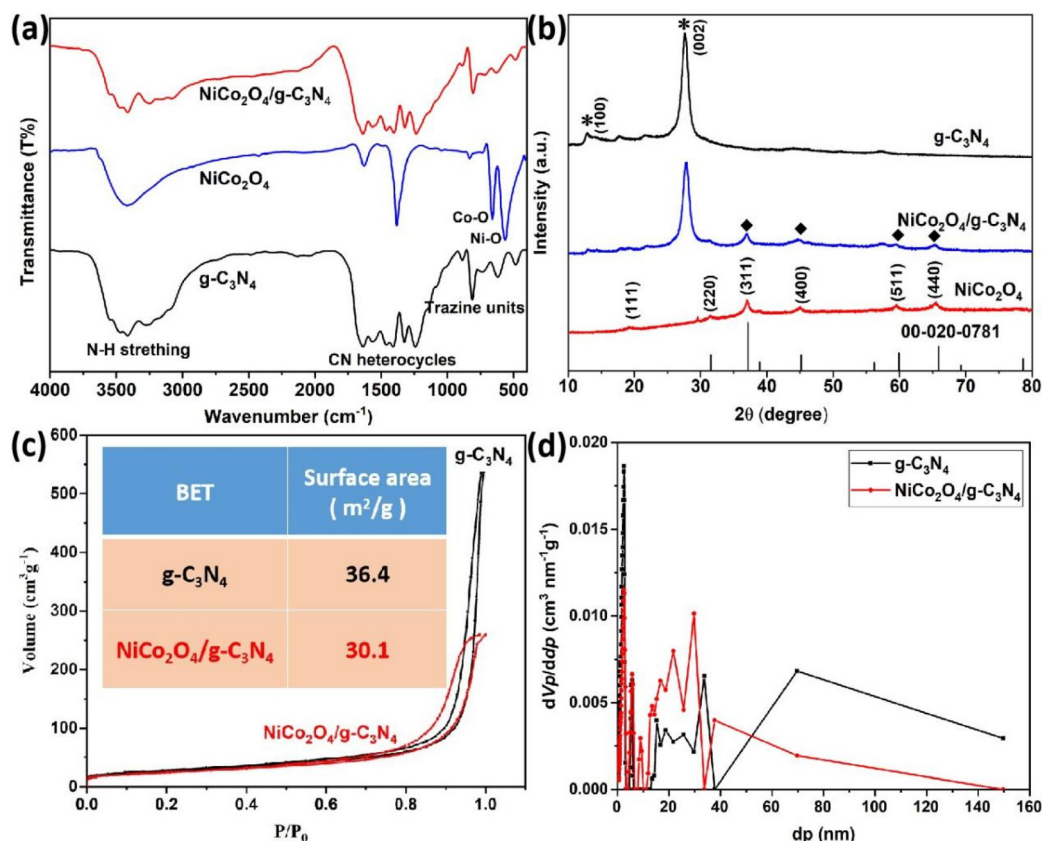


Fig. 3 FT-IR spectra (a) and XRD pattern (b) of $\text{g-C}_3\text{N}_4$, NiCo_2O_4 and $\text{NiCo}_2\text{O}_4/\text{g-C}_3\text{N}_4$. The adsorption-desorption isotherm curves (c) and porosity scale distribution (d) of $\text{g-C}_3\text{N}_4$ and $\text{NiCo}_2\text{O}_4/\text{g-C}_3\text{N}_4$.

were due to N-H stretching.³⁶ In the FT-IR spectra of NiCo_2O_4 nanoparticles, there are two strong metal-oxygen peaks at 659.6 and 563.2 cm^{-1} corresponding to Co-O and Ni-O, respectively.³⁷ However, the metal-oxygen peaks were not detected in $\text{NiCo}_2\text{O}_4/\text{g-C}_3\text{N}_4$ composites, which may be due to the small amount of NiCo_2O_4 nanoparticles and their heterogeneous dispersion on the $\text{g-C}_3\text{N}_4$ surface.

The crystal structure of $\text{g-C}_3\text{N}_4$, NiCo_2O_4 and $\text{NiCo}_2\text{O}_4/\text{g-C}_3\text{N}_4$ composites was studied by XRD (Fig. 3b). The XRD pattern of NiCo_2O_4 nanoparticles displays six characteristic peaks at $2\theta = 19.8^\circ$, 31.1° , 36.6° , 44.6° , 59.1° and 64.9° corresponding to the (111), (220), (311), (400), (511) and (440) planes, respectively. These peaks match the standard JCPDS of NiCo_2O_4 (No. 20-0781).³⁸ The XRD patterns of $\text{g-C}_3\text{N}_4$ and $\text{NiCo}_2\text{O}_4/\text{g-C}_3\text{N}_4$ composites show two peaks at 13.0° and 27.5° corresponding to the (100) and (002) planes of $\text{g-C}_3\text{N}_4$ (marked with *). In addition, $\text{NiCo}_2\text{O}_4/\text{g-C}_3\text{N}_4$ composites exhibit NiCo_2O_4 characteristic peaks (marked with $\blacklozenge$), indicating that NiCo_2O_4 has been successfully loaded onto $\text{g-C}_3\text{N}_4$ nanosheets.

The pore size distribution of the original $\text{g-C}_3\text{N}_4$ and $\text{NiCo}_2\text{O}_4/\text{g-C}_3\text{N}_4$ composites was further analyzed using the N_2 adsorption/desorption isotherm (Fig. 3c). Both samples display a type IV isotherm with a H3 hysteresis loop. The surface area of the $\text{NiCo}_2\text{O}_4/\text{g-C}_3\text{N}_4$ composites was calculated to be $30.1 \text{ m}^2 \text{ g}^{-1}$ (Fig. 3c inset), which is a little less than that

of $\text{g-C}_3\text{N}_4$ ($36.4 \text{ m}^2 \text{ g}^{-1}$). This may be due to the introduction of NiCo_2O_4 nanoparticles which have filled the pores of $\text{g-C}_3\text{N}_4$ nanosheets. In addition, the pore size distribution of $\text{NiCo}_2\text{O}_4/\text{g-C}_3\text{N}_4$ composites as shown in Fig. 3d further suggests a mesoporous structure of the composites.

The chemical composition of the $\text{NiCo}_2\text{O}_4/\text{g-C}_3\text{N}_4$ composites was analyzed by XPS. The XPS wide scan spectrum of the composites (Fig. 4a) is composed of five elements (Ni, Co, O, C and N), where Ni and Co elements are derived from metal oxides and the N element from $\text{g-C}_3\text{N}_4$ nanosheets. In the Co 2p spectra, two kinds of Co species and two shakeup satellites were detected as shown in Fig. 4b. The peaks at 782.6 and 797.4 eV are assigned to Co^{2+} , and the peaks at 780.3 and 795.4 eV to Co^{3+} . In the Ni 2p spectra (Fig. 4c), the high-resolution spectrum of Ni 2p can be fit to two spin-orbit doublets characteristic of Ni^{2+} (857.7 and 875.7 eV) and Ni^{3+} (855.7 and 873.3 eV). The peaks located at around 862.1 and 880.4 eV are indexed to the two shake-up satellites of nickel.³⁹ The O 1s high-resolution spectra (Fig. 4d) are separated into three peaks at 529.4, 530.8 and 532.6 eV, attributed to metal oxygen bonds, adsorbed water on the surface and the hydroxyl group, respectively. The C 1s XPS peaks at 285.3, 286.8 and 288.8 eV are attributed to graphitic carbon (C-C), C-N bonds and the sp^2 -hybridized carbon bond, respectively (Fig. 4e).⁴⁰ In Fig. 4f, for N 1s, the three peaks located at 398.6, 399.8 and 401.2 eV are

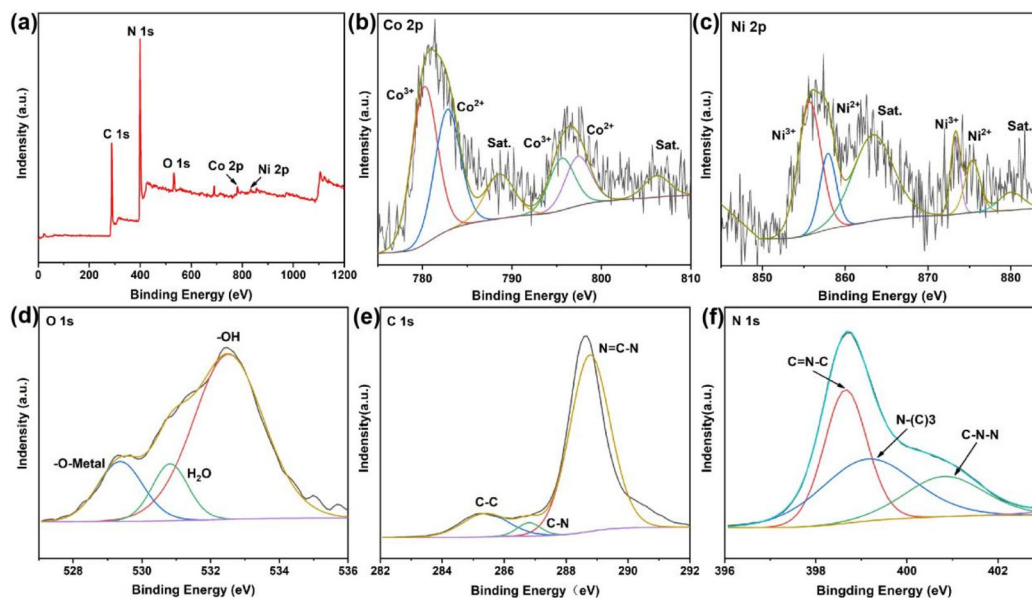


Fig. 4 Wide-scan XPS spectra of $\text{NiCo}_2\text{O}_4/\text{g-C}_3\text{N}_4$ composites (a) and detailed resolution of Co 2p, Ni 2p, O 1s, C 1s, and N 1s peaks (c–f).

ascribed to sp^2 -hybridized nitrogen ($\text{C}=\text{N}-\text{C}$), sp^3 -hybridized nitrogen ($\text{N}-(\text{C})_3$) and amino functional group coupled carbon ($\text{C}-\text{N}-\text{H}$), respectively.⁴¹ The XPS spectra further demonstrated that the NiCo_2O_4 nanoparticles were successfully anchored onto the $\text{g-C}_3\text{N}_4$ nanosheets.

3.2. Optical properties

The optical properties of the $\text{g-C}_3\text{N}_4$, NiCo_2O_4 and $\text{NiCo}_2\text{O}_4/\text{g-C}_3\text{N}_4$ samples were analyzed using UV-vis spectra. Fig. 5a shows that the absorption peak of pure $\text{g-C}_3\text{N}_4$ decreases

rapidly after 400 nm, indicating a narrow visible-light response range. In sharp contrast, NiCo_2O_4 nanoparticles present a wide absorption spectrum in the visible-light region. As a result, the $\text{NiCo}_2\text{O}_4/\text{g-C}_3\text{N}_4$ composites also exhibit a wide absorption spectrum from the UV to visible-light region.

The optical band gap of the samples can be estimated from Tauc plots following the equation:⁴²

$$(ah\nu) = A(h\nu - E_g)^{1/2} \quad (1)$$

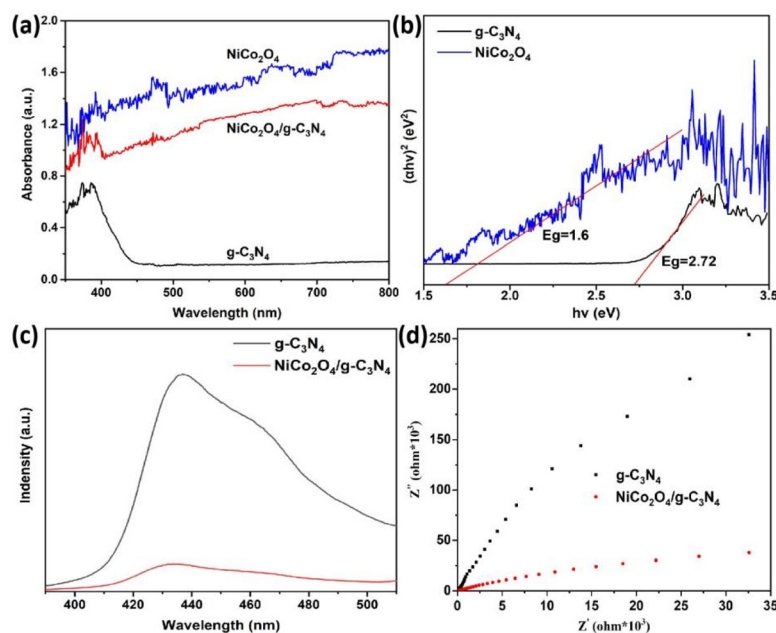


Fig. 5 UV-vis spectra (a) and the corresponding Tauc plots (b) of $\text{g-C}_3\text{N}_4$, NiCo_2O_4 and $\text{NiCo}_2\text{O}_4/\text{g-C}_3\text{N}_4$ composites. PL spectra (c) and EIS Nyquist plots (d) of $\text{g-C}_3\text{N}_4$ and $\text{NiCo}_2\text{O}_4/\text{g-C}_3\text{N}_4$ composites.

where α , ν , E_g and A represent the absorption coefficient, light frequency, band gap energy and proportionality constant, respectively.

From the estimated results in Fig. 5b, the band gaps of g-C₃N₄ and NiCo₂O₄ were determined to be 2.72 and 1.60 eV, respectively. The small energy gap will facilitate the absorption of visible light, resulting in excellent photocatalytic properties of NiCo₂O₄/g-C₃N₄ composites.

The high photogenerated electron-hole pair recombination rate is one of the main factors hindering the development of photocatalysis technology. Photoluminescence (PL) properties of g-C₃N₄ and NiCo₂O₄/g-C₃N₄ composites were analyzed by spectral resolution spectroscopy. Fig. 5c shows that the photoluminescence intensity of NiCo₂O₄/g-C₃N₄ is lower than that of g-C₃N₄. The decrease of PL intensity indicates that the doping with nanoparticles promotes efficient electron-hole separation and inhibits the carrier recombination process, resulting in an enhanced photocatalytic efficiency of the NiCo₂O₄/g-C₃N₄ composites.

The electrochemical performance of the samples was measured by electrochemical impedance spectroscopy (EIS) in a 0.1 M Na₂SO₄ solution. The semicircle radius of NiCo₂O₄/g-C₃N₄ composites was significantly smaller than that of pure g-C₃N₄ (Fig. 5d). It is well known that the smaller the semicircle in the EIS Nyquist plot, the faster the charge transfer rate and the lower the electron-hole recombination rate. This

is mainly due to the excellent conductivity of NiCo₂O₄ nanoparticles, which act as a bridge for electron transfer and promote the migration of charge carriers.

3.3. Photocatalytic activity

A tetracycline aqueous solution (5 mg L⁻¹) was employed to evaluate the catalytic activity of the NiCo₂O₄/g-C₃N₄ composites. The effects of ultrasonic power, content of NiCo₂O₄ and illumination on the catalytic performance of the composites were investigated. It can be seen from the experimental results that the degradation rate decreases slightly without light irradiation (Fig. S1†). This is because the catalyst sample was placed in the solution at this stage, and the dye molecules were adsorbed onto the surface to reach an adsorption equilibrium. As shown in Fig. 6a, when the ultrasonic power was 150 W, the ultrasonic degradation efficiency of the NiCo₂O₄/g-C₃N₄ composites was 70%. The degradation efficiency slightly increased when the power was 250 W. With a further increase of ultrasonic power to 400 W, the ultrasonic degradation rate significantly increased with the degradation efficiency reaching 80% within 15 min. These findings suggest that the ultrasonic power has a direct impact on the degradation efficiency. The increase in ultrasonic power will increase the energy of cavitation, leading to more cavitation bubbles and active free radicals. At the same time, ultrasonic

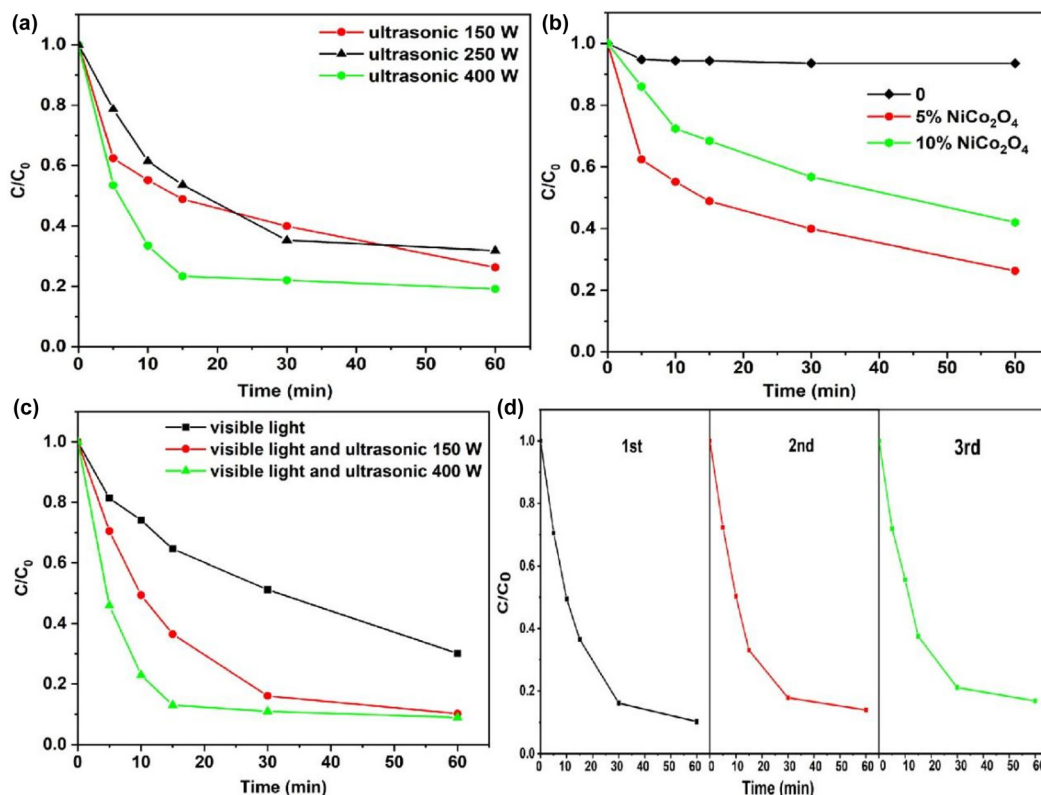


Fig. 6 Decomposition of residuary TCH solution by NiCo₂O₄/g-C₃N₄ composites under different ultrasonic powers (a), different contents of NiCo₂O₄ (b) and different illumination conditions (c); stability of the NiCo₂O₄/g-C₃N₄ composite catalyst (d).

waves accelerate the carrier migration rate and reduce the electron–hole recombination.

The stability of photocatalysts has been considered as an essential aspect for their practical applications. The photocatalytic cyclability of the $\text{NiCo}_2\text{O}_4/\text{g-C}_3\text{N}_4$ composites was studied by a cycling test. As shown in Fig. 6d, the photocatalytic activity rate exhibits good stability after three cycles, which has proved the good stability of the $\text{NiCo}_2\text{O}_4/\text{g-C}_3\text{N}_4$ composite catalyst. Moreover, the XRD pattern of the $\text{NiCo}_2\text{O}_4/\text{g-C}_3\text{N}_4$ composite catalyst remains basically unchanged after the reaction (Fig. S2[†]), indicating the good stability of the catalyst.

Here, the efficiency comparison of the $\text{g-C}_3\text{N}_4$ composite catalyst for degradation of TCH is listed in Table S1.[†] As can be seen from Table S1,[†] the catalytic efficiency could be significantly increased through the synergistic effect of ultrasound and illumination.

3.4. Catalytic mechanism

The generated main active species during the catalytic process were investigated by electron paramagnetic resonance spectroscopy. 5,5-Dimethyl-1-pyrroline-*N*-oxide (DMPO) as the most frequently used spin trapping agent was employed for the detection of reactive oxygen radicals.⁴³ As shown in Fig. S3,[†] when the $\text{NiCo}_2\text{O}_4/\text{g-C}_3\text{N}_4$ composite was exposed to visible light, typical patterns of both $\text{DMPO}\cdot\text{O}_2^-$ (Fig. S3a[†]) and $\text{DMPO}\cdot\text{OH}$ (Fig. S3b[†]) were observed in the EPR spectrum, indicating the generation of reactive oxygen species (ROS)

during the photosensitizing process of the $\text{NiCo}_2\text{O}_4/\text{g-C}_3\text{N}_4$ composite under visible light irradiation.

The possible catalytic mechanism of $\text{NiCo}_2\text{O}_4/\text{g-C}_3\text{N}_4$ composites under the combination of visible light and ultrasonic irradiation is shown in Fig. 7. NiCo_2O_4 doping improves the optical properties of $\text{g-C}_3\text{N}_4$ nanosheets, resulting in a smaller band gap of $\text{NiCo}_2\text{O}_4/\text{g-C}_3\text{N}_4$ composites with increased utilization of light energy. Besides, the metal compounds have good electrical conductivity to promote the efficient separation of electron–hole pairs. Meanwhile, ultrasonic waves accelerate the carrier migration rate and promote the diffusion of oxygen to the surface of the catalyst, resulting in more active free radicals due to electrons combining with oxygen molecules. When the two semiconductors with different Fermi levels come into contact with each other, e^- will flow from $\text{g-C}_3\text{N}_4$ with a higher Fermi level to NiCo_2O_4 , and h^+ will flow from NiCo_2O_4 with a lower Fermi level to $\text{g-C}_3\text{N}_4$, resulting in a built-in electric field (as shown in Fig. 7). However, the CB base of $\text{g-C}_3\text{N}_4$ forms upward “spikes” at the interface and barrier region, which will hinder the migration of electrons (e^-) from the CB of NiCo_2O_4 to the CB of $\text{g-C}_3\text{N}_4$. In addition, the Coulomb repulsion at the interface can also hinder the migration of photogenerated carriers.^{44,45} Based on the above discussion, both $\text{g-C}_3\text{N}_4$ and NiCo_2O_4 can be excited to produce photogenic e^- and holes (h^+) under light irradiation. Some e^- in the CB of $\text{g-C}_3\text{N}_4$ and h^+ in the VB of NiCo_2O_4 recombine in the space charge region as a result of the interaction between the built-in electric field, band bending and

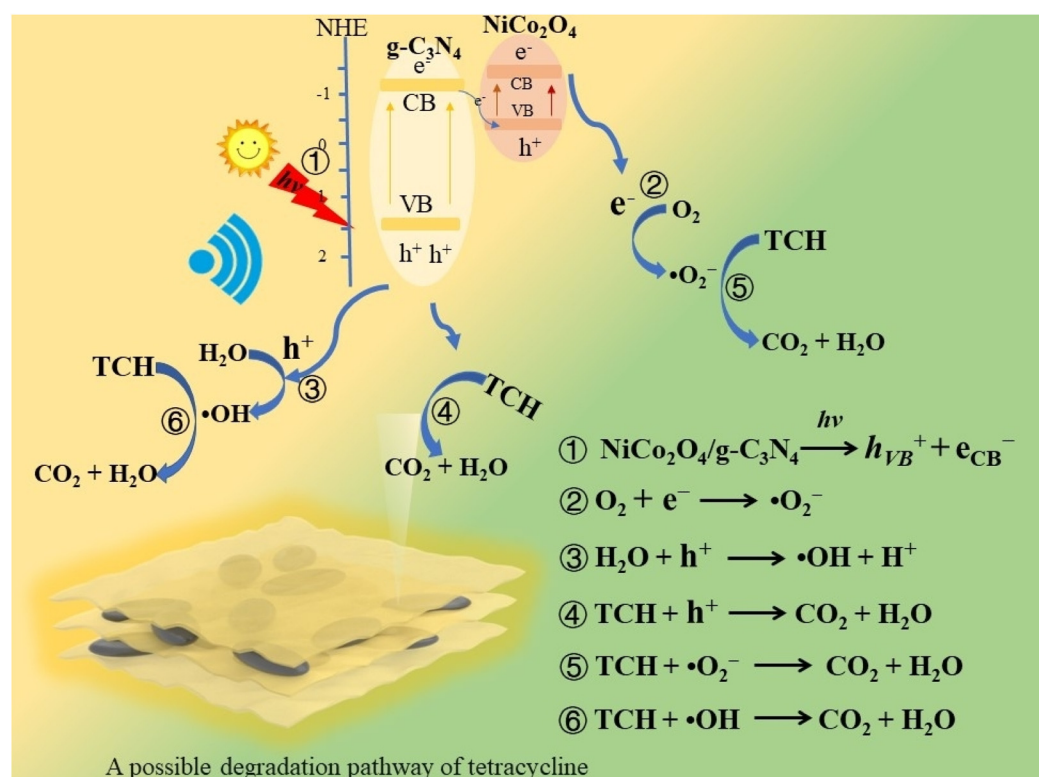


Fig. 7 Possible catalytic mechanism of $\text{NiCo}_2\text{O}_4/\text{g-C}_3\text{N}_4$ composites under the synergistic effect of visible light and ultrasonic irradiation.

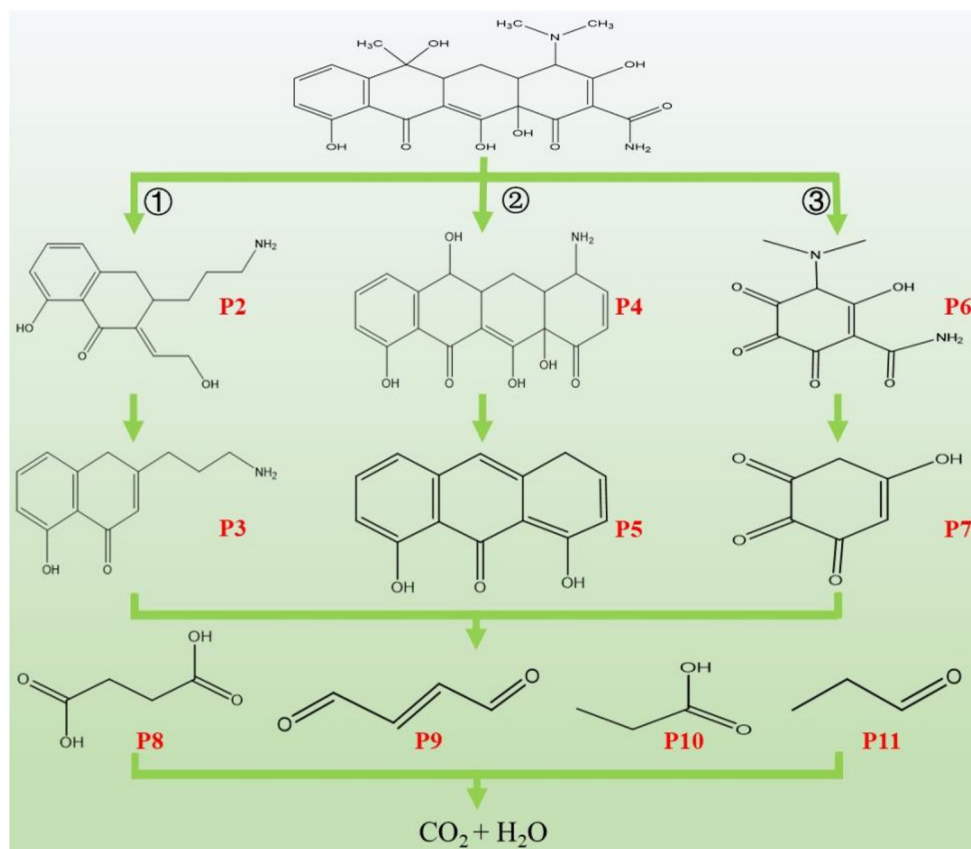


Fig. 8 Possible degradation pathways of tetracycline hydrochloride through the $\text{NiCo}_2\text{O}_4/\text{g-C}_3\text{N}_4$ composite system.

Coulomb repulsion. At the same time, e^- in the CB of NiCo_2O_4 and h^+ in the VB of $\text{g-C}_3\text{N}_4$ will be retained and react with O_2 and H_2O , respectively, to form superoxide radicals (O_2^-) and hydroxyl radicals ($\text{OH}^\bullet$). Due to the combined involvement of active free radicals such as h^+ , O_2^- and $\text{OH}^\bullet$, TCH is eventually degraded into CO_2 and H_2O (as shown in eqn ①–⑥). In summary, $\text{NiCo}_2\text{O}_4/\text{g-C}_3\text{N}_4$ composites have excellent catalytic performance under the synergistic effect of visible light and ultrasonic irradiation.

3.5. Potential TCH degradation pathways

The most common degradation pathways of tetracycline hydrochloride include demethylation, dehydroxylation, deamination and ring-opening.^{46,47} Three possible degradation pathways are shown in Fig. 8. In pathway ①, the tetracycline molecule loses the hydroxyl and methyl groups, thus opening the ring to form P2. The branched double bond of P2 is subsequently broken by oxidation to obtain P3. In pathway ②, the tetracycline molecule loses $-\text{CONH}_2$ and $-\text{CH}_3$ to obtain P4, which is then converted to P5 by a ring-opening reaction. In pathway ③, the third six-membered ring of tetracycline is oxidized to form P6, which is then transformed to P7 by the removal of $-\text{N}(\text{CH}_3)_2$ and $-\text{CONH}_2$. Furthermore, small molecule intermediates (P8, P9, P10 and P11) can be further oxidized by the above three pathways. Finally, all the intermediates are eventually

oxidized to CO_2 and H_2O under the action of reactive oxygen species. In summary, the $\text{NiCo}_2\text{O}_4/\text{g-C}_3\text{N}_4$ composite system does not produce any dangerous compounds during the TCH degradation process.

4. Conclusions

NiCo_2O_4 nanoparticles were successfully loaded onto the $\text{g-C}_3\text{N}_4$ nanosheet surface by a facile ball milling process. The doping with NiCo_2O_4 improved the optical properties of $\text{g-C}_3\text{N}_4$ with a narrower band gap, resulting in an enhanced efficiency in utilization of visible light. The metal compounds introduced new pathways for electron transfer and hence improved the efficiency of photogenerated carrier separation. The results demonstrated that the catalytic efficiency of $\text{NiCo}_2\text{O}_4/\text{g-C}_3\text{N}_4$ composite catalysts under the synergistic effect of visible light and ultrasonic irradiation was much higher than that of a single effect. Ultrasonic waves accelerated the carrier migration rate with enhanced diffusion of oxygen to the catalyst surface, resulting in more active free radicals. Possible catalytic mechanisms and potential pathways for the degradation of tetracycline hydrochloride have been proposed. The ultrasonic assisted photocatalysis demonstrated to be an environmentally friendly catalytic technology with a wide application prospect in the field of pollution control.

Conflicts of interest

The authors declare that the publication of this paper has no conflicts of interest.

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