Enhanced the Synergistic Effect of Tetracycline Adsorption and Photocatalytic Degradation on a Novel Mesoporous Carbon Nitride

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Abstract

A novel mesoporous g-C₃N₄ with guanidine hydrochloride as precursor was prepared by molten salt assisted hard template of silica (SiO₂) aerogel for photocatalytic degradation of tetracycline (TC). The textural structure, chemical composition, morphology and optical properties of mesoporous g-C₃N₄ were characterized by a series of means, and the synergistic effect of adsorption and photocatalytic degradation of TC was elucidated. The results show that the successfully synthesized mesoporous g-C₃N₄ presented a coral-like rod shaped and heptazine ring structure. When the amount of SiO₂ aerogel template was 1.4 g, the richer nitrogen defects of the sample (GM-1.4) with the lower band gap (2.42 eV) was displayed. The photocatalytic degradation rate of GM-1.4 for TC was reached to 83.4% under visible illumination for 120 min. Furthermore, the $\cdot\text{O}_2^-$ and h^+ were proved to be the main active species, and the reasons of TC photodegradation were associated with the destruction of TC molecular structure.

1 Introduction

Tetracycline (TC) antibiotics are considered to be a classical drug that can inhibit the growth of microbes such as bacteria and fungi, and it is widely used in human disease treatment, animal husbandry and aquaculture. After being discharged into water, TC are difficult to be degraded by microorganisms in the environment, resulting in toxic effects on aquatic organisms.[1] Therefore, the development of effective technology to remove TC from water environment has of great attention.

As an eco-friendly nonmetallic photocatalyst, graphitic carbon nitride (g-C₃N₄) with good morphology and optical properties has great prospects in photocatalytic applications. In recent years, photocatalytic degradation of g-C₃N₄ has attracted extensive attention in solving tetracycline pollution in water.[2, 3] Nevertheless, the photocatalytic activity of pure g-C₃N₄ is extremely limited by the low surface area and faster electron-hole recombination.[4] In order to enhanced the photocatalytic activity of g-C₃N₄, mostly morphology control methods of mesoporous g-C₃N₄ have been studied, which can not only make it have developed pore structure, but also provide more active sites, thus improving the photocatalytic performance of g-C₃N₄ effectively.[5]

At present, the mainly way to prepare mesoporous g-C₃N₄ stably is still hard template method.[6] The hard template method refers to the formation of mesoporous g-C₃N₄ material containing template agent by replicating the structure of template agent under the high temperature condition, and the mesoporous g-C₃N₄ was obtained after removing the template. Among them adopting mesoporous silica such as SBA-15 and KIT-6 as template agents and carbon-nitrogen containing materials as precursors.[7, 8] Zhao et al. took SBA-15 as the hard template and cyanamide as the precursor to successfully replicate the structure of mesoporous SiO₂ and synthesize mesoporous g-C₃N₄. The mesoporous g-C₃N₄ had large specific surface area and pore volume, and its photocatalytic degradation rate on methyl orange was 15.3 times that of pure g-C₃N₄. [9] Chen et al. introduced a novel mesoporous g-C₃N₄ nanospheres (MCNS) with excellent visible light response by using a monodisperse SiO₂ template and controlling the incomplete

polycondensation of cyanamide on the template, which had a unique nanosphere structure with a larger specific surface area possessed more abundant cyano groups.[10] Liu et al. used melamine as precursor and SiO_2 aerogels as template, the mesoporous $\text{g-C}_3\text{N}_4$ with hollow tubular porous structure was synthesized successfully, which has good photocatalytic degradation performance for Rhodamine B (RhB).[11] Bai et al. took melamine as precursor and SiO_2 spheres as template, and $\text{g-C}_3\text{N}_4$ with hollow microsphere morphology was obtained after removing the template with HF, which has excellent performance for gas storage, drug transportation and as a photocatalyst.[12] Hence, the different precursors and template have a great impact on the morphology and performance of mesoporous $\text{g-C}_3\text{N}_4$. [13, 14] Moreover, the preparation of mesoporous $\text{g-C}_3\text{N}_4$ with triazine ring structure can effectively reduce the bonding barrier and promote the extension of the planar network structure. However, compared with the mesoporous $\text{g-C}_3\text{N}_4$ with the heptazine ring structure, the energy of the mesoporous $\text{g-C}_3\text{N}_4$ with triazine ring structure is higher and less stable, which is not conducive to the separation and transport of electrons in $\text{g-C}_3\text{N}_4$. On the other hand, mesoporous $\text{g-C}_3\text{N}_4$ with heptazine ring structure has higher electron cloud delocalization, higher internal electron separation and transfer rate, and stronger photocatalytic performance.[4, 15-19] Therefore, in order to further improve the photocatalytic performance of mesoporous $\text{g-C}_3\text{N}_4$, the precursor of $\text{g-C}_3\text{N}_4$ will be optimized to synthesize mesoporous $\text{g-C}_3\text{N}_4$ with heptazine ring structure. It is found that the $\text{g-C}_3\text{N}_4$ with heptazine ring structure can be synthesized by polycondensation of guanidine hydrochloride at different polymerization temperature, and the gas released from guanidine hydrochloride during the polycondensation process at high temperature can also act as mesoporous templates, which can play a greater role in the preparation of mesoporous $\text{g-C}_3\text{N}_4$ with better photocatalytic performance.[20] Xia et al synthesized a belt-like carbon nitride by co-condensation of guanidine hydrochloride and dicyandiamide at low temperature. [21] However, the problems of uncontrollable morphology, poor crystallinity and high carrier recombination efficiency in the preparation process of $\text{g-C}_3\text{N}_4$ with different precursor still to be explored.

In this paper, a novel mesoporous $\text{g-C}_3\text{N}_4$ with guanidine hydrochloride as precursor was prepared by a molten salt-assisted SiO_2 aerogel template method. The effect of different ratio of precursor to template on the structure, morphology and optical property were analysed. At the same time, rare reports have studied the effect of mesoporous $\text{g-C}_3\text{N}_4$ prepared with guanidine hydrochloride as precursor on TC degradation. So TC was used as the model pollutant and mesoporous $\text{g-C}_3\text{N}_4$ was used as the catalyst, the adsorption and photocatalytic degradation experiments were carried out, and the synergistic mechanism of TC adsorption and photocatalytic degradation on mesoporous $\text{g-C}_3\text{N}_4$ was investigated.

2 Experimental Section

2.1 Preparation of materials

As a hard template, SiO_2 aerogel was synthesized firstly. 30 g rice husk ash was mixed with 200 mL of sodium hydroxide (NaOH , $1 \text{ mol}\cdot\text{L}^{-1}$, Tianjin Damao Chemical Reagent Factory, China) aqueous solution,

boiled to 100°C and maintained the temperature for 3.5 h. After cooled at room temperature, and the water glass solution was obtained by suction filtration. Subsequently, the water glass solution was adjusted to pH=5 with hydrochloric acid (HCl, 1 mol·L⁻¹, Chengdu Kelong Chemical Co.Ltd, China) and ammonia solution (NH₃·H₂O, 1 mol·L⁻¹, Guangdong Guanghua Sci-Tech Co.Ltd, China), then removed sodium ion from sodium silicate by cation exchange resin (particle size 95%, Sinopharm Chemical Reagent Co.Ltd, China). After static 24 h, hydrophobic modified SiO₂ aerogels were obtained by replacing the solvent with ethanol absolute (EtOH, 99.7% Guangdong Guanghua Sci-Tech Co.Ltd, China), n-hexane (Tianjin Beichen Fangzheng Reagent Factory) and chlorotrimethylsilane (TMCS, 98%, Aladdin Shanghai Aladdin Biochemical Technology Co.Ltd, China).

Guanidine Hydrochloride (4 g, 99%, Sinopharm Chemical Reagent Co.Ltd, China), SiO₂ aerogel (0.7/1.4/2.8 g), potassium chloride (KCl, 22 g, 99.5%, Guangdong Guanghua Sci-Tech Co.Ltd, China) and lithium chloride anhydrous (LiCl, 18 g, Shanghai Macklin Biochemical Co.Ltd, China) were milled and mixed in a Planet ball mill (QM-3SP2, Nanjing University Instrument Factory, China) for 30 min, then transferred to a crucible, heated to a suitable temperature (500°C) in a muffle furnace (SX2-5-12NP, Shanghai Heng Science Instrument Co.Ltd, China) and kept for 4 h. The calcined samples were cooled to room temperature, washed with deionized (DI) water, dried in a blast drying oven (DHG-9108A, Shanghai Jinghong Experimental Equipment Co.Ltd, China) and soaked in hydrofluoric acid (HF, 40%, Chengdu Jinshan Chemical Reagent Co.Ltd) for 24 h. Finally, the mixed solution soaked in HF was washed with DI water and dried to obtain mesoporous g-C₃N₄ which is denoted as GM-X, where GM represents mesoporous g-C₃N₄ which used guanidine hydrochloride as precursor, X represents the amount of SiO₂ aerogel (X = 0.7, 1.4, 2.8).

In order to compare with SiO₂ aerogel as hard template, the bulk g-C₃N₄ was synthesized by the above the process, the mixture of 4 g guanidine hydrochloride, 22 g KCl and 18 g LiCl was milled and calcined at 550°C for 4h, then bulk g-C₃N₄ was obtained after washing and drying, and named GB, where GB represents bulk g-C₃N₄ without SiO₂ aerogel.

2.2 Characterization

The crystal structure of the GM-X was measured by X-ray diffraction (XRD, Rigaku D/MAX 2500 V, Japan) with Cu/Kα light source at 40 mA and 100 KV, 2θ range was from 10 to 80°. The functional groups of the samples were analysed by Fourier transform infrared spectrum (FT-IR, IRTTracer-100, Shimadzu company of Japan) with a scan wavelength of 3500-500 cm⁻¹. The specific surface area and pore size were tested by Brunauer–Emmett–Teller (BET, TriStarII3020, MAC, USA) of N₂ adsorption/desorption analyses.

Surface morphologies and particle sizes of the samples were observed using scanning electron microscopy (SEM, Hitachi SU8220, Japan) and all samples were pre-coated with gold before being introduced into the vacuum chamber. High-resolution transmission electron microscopy (HRTEM) images were obtained on a JEOL JEM 2100F and all samples were sonicated in an ethanol solution for 30 min

before being transferred to copper supports. X-ray photoelectron spectroscopy (XPS, Thermo Fisher USA) was taken to investigate the selected element contents and the surface chemical composition of the samples. The optical properties of the samples were characterized by diffuse reflectance spectroscopy (DRS, uv-2600, Shimadzu Instruments Co.Ltd, Suzhou, China) in a spectral range of 200–800 nm and photoluminescence (PL, omni-fluo-960, Zhuo Lihan optical instruments Co.Ltd, Beijing, China) with a 355 nm excitation wavelength. The Zeta potential under different pH values was detected with Zeta-sizer Nano-ZS90X (Malvern, UK).

2.3 Adsorption test

30 mg of as-prepared sample was dispersed into 50 mL ($10 \text{ mg}\cdot\text{L}^{-1}$) TC solution and stirred magnetically at room temperature to reach adsorption-desorption equilibrium under dark conditions. An appropriate amount of suspension was taken every 5 min, and filtered through a $0.45 \mu\text{m}$ filter membrane. The concentration of TC was measured by ultraviolet visible spectrophotometer (UV-Vis 722 g, Shanghai Precision Scientific Instrument Co.Ltd, China) at the wavelength of 357.5 nm. $1 \text{ mol}\cdot\text{L}^{-1}$ NaOH and $1 \text{ mol}\cdot\text{L}^{-1}$ HCl were used to adjust the pH value of TC solution to 3, 5, 7 respectively, and then, the concentration of TC was measured after 24 h equilibrium in the dark via UV-Vis spectrophotometer. The effect of pH on the adsorption of TC by mesoporous $\text{g-C}_3\text{N}_4$ was investigated.

2.4 Photocatalysis test

The photocatalytic properties of the prepared materials were evaluated by degradation of TC solution under visible-light irradiation, and a 300 W xenon lamp with UV-cutoff filter ($\lambda \geq 420 \text{ nm}$) was used as the visible light source. Firstly, 10 mg, 20 mg, 30 mg and 40 mg of as-prepared sample were dispersed into 50 mL ($10 \text{ mg}\cdot\text{L}^{-1}$) TC solution, respectively. Before irradiation, the mixture was stirred magnetically for 1.5 h in the dark situation to ensure adsorption-desorption equilibrium. After dark reaction, the suspension was withdrawn every 5 min during the photocatalytic reaction. The TC concentration was tested by UV-Vis after filtration. The optimum dosage of catalyst can be determined by this experiment.

In addition, under the same experimental conditions as above, 30 mg photocatalyst was added into $5 \text{ mg}\cdot\text{L}^{-1}$, $10 \text{ mg}\cdot\text{L}^{-1}$, $15 \text{ mg}\cdot\text{L}^{-1}$ and $20 \text{ mg}\cdot\text{L}^{-1}$ TC solution (50 mL) respectively for photocatalytic reaction to determine the optimal initial concentration of TC solution.

The cyclic adsorption experiments of photocatalyst on TC solution were as follows: 30 mg photocatalyst was added into TC solution (50 mL, $10 \text{ mg}\cdot\text{L}^{-1}$, pH = 3/11) and stirred magnetically in the dark for 24 h. The mixed solution was filtered by a $0.45 \mu\text{m}$ filter membrane to collect the photocatalyst adsorbed TC, rinsed with deionized water (pH = 3/11) and dried for later use. Then, 30 mg of photocatalyst adsorbed TC was added into TC solution (50 mL, $10 \text{ mg}\cdot\text{L}^{-1}$, pH = 3/11) and magnetic stirred again in the dark for 24 h to reach adsorption equilibrium. The TC concentration was measured by UV-Vis.

To further investigate the photocatalytic degradation mechanism of TC over the photocatalyst, the UV-Vis absorption spectrum of TC solution ($10 \text{ mg}\cdot\text{L}^{-1}$, $\text{pH} = 7$) after different periods of the photocatalytic reaction over the photocatalyst was measured.

2.5 Active group capture experiment

In order to determine the main active species involved in mesoporous $\text{g-C}_3\text{N}_4$ photocatalytic degradation, the quenching experiments were conducted in this work. Generally, IPA, TEOA and BQ were used as the capture agents to scavenge hydroxyl radical ($\cdot\text{OH}$), hole (h^+) and superoxide radical ($\cdot\text{O}_2^-$), respectively. Firstly, 10 mmol IPA, 10 mmol TEOA and 1 mmol BQ were added into TC solution (50 mL , $10 \text{ mg}\cdot\text{L}^{-1}$), respectively, and then 30 mg mesoporous $\text{g-C}_3\text{N}_4$ was added for adsorption and photocatalytic experiments. The main active substances of photocatalytic reaction were determined with the degradation of TC. Furthermore, electron spin resonance (ESR, Bruker-A300, Germany) was conducted for the trapping experiments in dark and light conditions to probe the reactive radicals in the process of photocatalytic reaction. Among them, DMPO was selected as the generated capture agent of $\cdot\text{OH}$ and $\cdot\text{O}_2^-$, and TEMPO was selected as the capture agent of h^+ .

2.6 Cycle experiment

The photocatalytic experiment was repeated five times to evaluate the reusability and stability of mesoporous $\text{g-C}_3\text{N}_4$. 30 mg mesoporous $\text{g-C}_3\text{N}_4$ was added in TC solution (50 mL , $10 \text{ mg}\cdot\text{L}^{-1}$) for dark adsorption and photocatalytic reaction, respectively. According to the steps of the above photocatalytic experiment, mesoporous $\text{g-C}_3\text{N}_4$ was reused for photocatalytic degradation of TC. The mesoporous $\text{g-C}_3\text{N}_4$ after each dark reaction and photocatalytic experiment was collected with $0.45 \mu\text{m}$ filter membrane, then washed with deionized water and absolute ethanol for several times. The recovered catalysts were dried at 60°C for 6h, and then reused for photocatalytic degradation of TC. The absorbance after dark adsorption equilibrium and light reaction were measured to calculate the repeated degradation efficiency of mesoporous $\text{g-C}_3\text{N}_4$ in TC solution.

3 Results And Discussion

3.1 Characterization analysis

The XRD patterns of the samples are shown in Fig. 1. For GB and GM-1.4, the XRD pattern showed a major peak at $2\theta = 27.7^\circ$, which can be indexed to the (002) plane.[22, 23] However, the weak diffraction peak indexed to the (100) facet of GB and GM-1.4 disappeared, it may be due to the formation of $\text{g-C}_3\text{N}_4$ in the sample similar to the structure of the heptazine ring[24] and the plane size of the CN layer was small.[25] Compared with GB, the characteristic peaks at the (002) plane of the GM-X samples slightly

shifted to high angles. The results indicated that the SiO₂ template promoted the molecular gap and interlayer spacing of the GM-X, and restrained the formation of the stack structure.[26]

Fig. 2 showed the FT-IR spectra of the samples. The characteristic peaks in the range of 1000-1700 cm⁻¹ were attributed to the stretching vibration and in-plane bending vibration of C- N or C=N aromatic heterocycle compounds.[24, 27] The peak located at 810 cm⁻¹ could be contributed to the inner-ring bending vibration of the heptazine ring unit.[24, 28] In addition, for GB and GM-X, the characteristic bands observed at 2173 cm⁻¹ and 2192 cm⁻¹ could be assigned to asymmetric vibration of cyano (–C≡N), which was caused by the loss of NH₃ group.

The nitrogen adsorption and desorption isotherm curves and pore size distribution curves of GB and GM-X were shown in Fig. 3. As shown in Fig. 3(a), all isotherm curves exhibited type Ⅲ isotherms, suggesting that they all possessed macro-meso porous structure.[29, 30] The type H3 hysteresis loop in the isotherm of GM-0.7 and GM-2.8 are more obvious than those of GB, which indicated that the SiO₂ template makes the structure of mesoporous g-C₃N₄ change greatly. However, there was no obvious hysteresis loop in GM-1.4, and the specific surface area and pore volume were shown relatively small from Table 1, which may be caused by the collapse of the structure of GM-1.4 to a certain extent, and the mesopores with small pore sizes were interconnected to form mesopores with larger pore size. From Fig. 3(b), the pore sizes of all the materials were concentrated in the range of 2–50 nm, while the average pore size of the sample materials shown in Table 1 was in the range of 18-25 nm, it was also concluded that all g-C₃N₄ samples were found to be mesoporous materials.

Table 1

specific surface area, total pore volume and average pore size of the samples.

Samples	S _{BET} /m ² ·g ⁻¹	V _{TP} /cm ³ ·g ⁻¹	D _P (nm)
GB	19.16	0.07	18.55
GM-0.7	40.52	0.16	18.30
GM-1.4	1.94	0.091	23.24
GM-2.8	32.2	0.14	20.75

The optical properties of GB and GM-X were characterized by the UV diffuse reflectance spectra and the results were showed in Fig. 4. The GB showed a clear absorption edge at around 475 nm, while the absorption edges of the GM-X presented blue shift compared with GB.[31] The band gap values of all samples was calculated using Eq. (1) as follows:

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

where A is the absorption coefficient, ν is the incident light frequency, a is a constant, E_g is the band gap width and n is the constant of the $g\text{-C}_3\text{N}_4$ electron transfer indirectly, $n = 1$.

The calculation results can be seen from the Fig. 4, the band gap values of GB and GM-X($X=0.7, 1.4, 2.8$) were estimated to 2.53, 2.62, 2.42 and 2.66, respectively. It was indicated that the proper introduction of template could improve the electron transport capacity of photocatalyst and increase the separation efficiency of photogenerated electrons.[32] In this paper, the sample of GM-1.4 improved the photoelectric transmission performance of mesoporous $g\text{-C}_3\text{N}_4$ better.

Fig. 5 presents PL spectra of sample characterized by fluorescence analysis under 355 nm excitation wavelength. the PL peaks of GM-X are both lower than GB, indicating that the SiO_2 aerogel template can effectively inhibit the recombination of photogenerated carriers and improve the separation ability of photoelectric charge.[23, 33] Compared with GM-0.7 and GM-2.8, the PL peak of GM-1.4 was the lowest, which indicated the lowest recombination rate of photogenerated electron hole pairs of the samples,[34] it was reasonably concluded that the introduction of 1.4 g SiO_2 aerogel template had a stronger promoting effect on the separation rate of photogenerated carriers of mesoporous $g\text{-C}_3\text{N}_4$ to improve the photocatalytic activity.

The morphology of mesoporous $g\text{-C}_3\text{N}_4$ was observed using SEM and TEM images in Fig. 6. Fig. 6(a) and (b) shows the nanorod shaped morphologies of GB, and that for GM-1.4, Fig. 6(e) and (f) displays a coral-like rod and a protruded dot morphology on the surface.[35] This morphological feature can increase the number of active sites of GM-1.4 and enhance the photocatalytic performance. In addition, the morphology and structure of the samples was further observed by TEM in Fig. 6 (c) (d) (g) (h). Light and dark rod-like images were presented in Fig. 6 (c) and (g), which may be caused by the parallel and scattered arrangement of samples. it was further verified that the samples have the rod morphology. Moreover, as shown in Fig. 6 (d), the lattice fringe spacing is 0.73nm, it was attributed to the (100) crystal plane, which was consistent with the characterization of XRD. However, the lattice fringe of GM-1.4 could not be captured in Fig. 6 (h), it was deduced that the thin pore wall of the samples was shattered by the ultrasonic pre-treatment before TEM test, which made the fringes difficult to photograph.

C1s, N1s and O1s of GB and GM-1.4 measured by XPS were shown in Fig. 7, respectively. Fig. 7(a) showed that the GB and GM both have distinct characteristic peaks of C1s, N1s and O1s.[36] According to Fig. 7(b), For C1s spectra, the $g\text{-C}_3\text{N}_4$ showed three typical characteristic peaks at 284.8 eV, 286.8 eV and 288.1 eV, which could be attributed to C–C bonds of graphitic impurities in $g\text{-C}_3\text{N}_4$, C–O species of SP^2 hybrid carbon defect and SP^2 hybridized carbon bonded to the N atoms of the aromatic heterocycles ($\text{N}=\text{C}=\text{N}$), respectively.[37-39] Besides, it is worth noting that the peak intensities of GM-1.4 is lower than that of GB at located of 286.8 eV, indicating that there were fewer C–O species in the GM-1.4. As shown in Fig. 7(c), the spectrum of N1s was fitted into three distinct peaks at 399.4 eV, 401.6 eV and 405.0 eV, corresponding to the nitrogen atoms in the aromatic rings ($\text{N}=\text{C}=\text{N}$), tertiary nitrogen $\text{N}-(\text{C})_3$ groups[40] and π bond[32], respectively. It is indicated that the mesoporous $g\text{-C}_3\text{N}_4$ was synthesized to the structure

of heptazine ring, which can be also confirmed by the XRD spectra in Fig. 1. Furthermore, the O1s spectra of the samples in Fig. 7(d) shows two peaks with the binding energies of 532.2 eV and 533.5 eV, where refers to the H-O bond and N-C-O bond of the mesoporous g-C₃N₄, respectively.[21, 41, 42] In addition, the characteristic peaks of GM-1.4 moved to a larger band, and the peak intensity at 534.0 eV was weaker than GB, indicating that there were less N-C-O species in the GM-1.4.

3.2 Adsorption and photocatalytic degradation of TC on mesoporous g-C₃N₄

3.2.1 Photocatalytic degradation performance of TC on mesoporous g-C₃N₄

Fig. 8(a) shows the photocatalytic degradation curve of 10 mg·L⁻¹ TC solution by different dosage of GB and GM-1.4. As can be observed from the figure, with the increasing of mesoporous g-C₃N₄ dosage, the photocatalytic degradation performance of TC was also enhanced. However, compared with the dosage of 30 mg mesoporous g-C₃N₄, adding 40 mg mesoporous g-C₃N₄ did not significantly improve the degradation effect of TC. Therefore, the optimal dosage of mesoporous g-C₃N₄ in the subsequent experiments were carried out at 30 mg. Fig. 8(b) shows the photocatalytic degradation curves of 30 mg mesoporous g-C₃N₄ on TC solutions with different concentrations (5 mg·L⁻¹, 10 mg·L⁻¹, 15 mg·L⁻¹ and 20 mg·L⁻¹). Although the optimal efficiency of degradation was displayed at the TC concentration of 5 mg·L⁻¹, this concentration is too low to adjust exactly. With careful comparison the, TC concentration of 10 mg·L⁻¹ were determined for the subsequent studies on the synergistic effect of adsorption and photocatalysis. As shown in Fig. 8 (c), the photocatalytic degradation rate of TC solution with pH = 7 by GM-1.4 was about 83.4% after 120 min visible light irradiation, indicate that the mesoporous g-C₃N₄ also has a good photocatalytic degradation effect on TC. In addition, the blank experiment results show that the degradation of TC was negligible in the absence of mesoporous g-C₃N₄ catalyst. The standard deviation of all data is within 3.9%, which indicates that there is no significant error in the experiment.

3.2.2 Effect of pH on TC adsorption properties

The effect of pH value on the adsorption of TC by mesoporous g-C₃N₄ was investigated by adsorption experiments of mesoporous g-C₃N₄ on TC solution with pH value of 3,5,7. Fig. 8 (d) shows the variation in the adsorption capacity of GB and GM-1.4 for TC solution under different pH conditions after processing the experimental data. The error analysis of the experimental data shows that the standard deviation of all data was within 7.1%, which indicated that the experimental results were well conducted and the experimental results have no obvious deviation. As shown in Fig. 8 (d), the adsorption capacity of GB and GM-1.4 for TC solution reached the maximum at pH = 3, with the increasing of the pH value, the

adsorption capacity of GB and GM-1.4 for TC solution decreases gradually. In addition, the adsorption capacity of TC on GM-1.4 at different pH value was greater than that GB, this indicated that the adsorption capacity of TC is not only related to the specific surface area and pore size, but also depended on the surface charge, electrostatic force interaction and ion interaction between mesoporous g-C₃N₄ and TC molecules. The zeta potential of GB and GM-1.4 samples in deionized aqueous solution systems at different pH values are shown in Table 2. As shown in Table 2, The zeta potential of GB and GM-1.4 in pH = 3 solution was -30.8 and 15.0 mV, respectively. With the increase of pH value, the absolute value of zeta potential is between 30-60 mV, it means that the ionization degree of TC solution decreased, and the mesoporous g-C₃N₄ shows good stability at pH 3, 5,7,9,11. Moreover, the mesoporous g-C₃N₄ is more stable in aqueous solution at pH = 5/7 than that at pH = 3, and more difficult to react with other charged ions. According to previous studies, TC solution mainly exists in the form of TCH₃⁺ in a highly acidic environment (pH = 2).[43] However, the electrostatic repulsion between mesoporous g-C₃N₄ and TC is relatively large and the adsorption effect is very weak. Therefore, the study of TC solution with pH ≤ 2 is not carried out in this study. TC mainly exists in the form of amphoteric ions in the solution of pH = 3-6, [44] and the electrostatic repulsion between TC and mesoporous g-C₃N₄ is weakened, so the adsorption capacity is enhanced. In this experiment, GB and GM-1.4 displayed the highest adsorption capacity of TC solution at pH = 3, so the subsequent experiments on the synergistic effect of adsorption and photocatalysis were carried out with TC solution at pH = 3.

Table 2

zeta potential (mV) of GB and GM-1.4.

Samples	3	5	7	9	11
GB	-30.8	-46.0	-50.5	-44.2	-31.7
GM-1.4	15.0	-44.6	-47.0	-44.3	-48.6

3.2.3 Synergistic Effect of Mesoporous g-C₃N₄ on Adsorption of TC and Photocatalysis

Fig. 9(a), (b) and (c) shows the dark adsorption kinetics, the degradation kinetics and the cyclic adsorption of GM-1.4 on TC solution at pH = 3, respectively. The kinetic fitting equations used in Fig. 9 (a) is as follows:

The pseudo-first order: $q_t = q_e \cdot (1 - e(-k_1 t))$
(2)

The pseudo-second order: $q_t = (q_e \cdot k_2 \cdot t) / (1 + q_e \cdot k_2 \cdot t)$ (3)

where t represents the reaction time, q_t and q_e represent the adsorption capacity of the adsorbent to TC at adsorption time t (min) and adsorption equilibrium, k_1 and k_2 are the pseudo-first-order and pseudo-second-order rate constant, respectively.

As shown in Fig. 9(a), the adsorption equilibrium of TC by GM-1.4 was achieved within 10 min, the k_2 values are larger than the k_1 values, and the R^2 values of them are the opposite, which indicates that the pseudo-first-order model was much better than the pseudo-second-order model.

In order to investigate the photocatalytic performance under visible light irradiation more intuitively. The reaction kinetics of photodegradation of TC was evaluated by fitting the quasi-first order kinetic equation. The formula is as follows:

$$\ln(C_0 / C_t) = k_3 \cdot t \quad (4)$$

where C_0 and C_t are the initial concentration of TC and the concentration at t (min), respectively, and k_3 is the pseudo-first-order kinetic constant. K_{ad} is the kinetic constant of light removal after dark adsorption, and k_{wd} is the kinetic constant of direct light removal without dark reaction; both of them are equal to k_3 .

As shown in Fig. 9(b), the rate of photodegradation (K_{ad}) after dark adsorption is faster than the rate of photodegradation (K_{wd}) without dark adsorption, while the R^2 of the former is a little less than that of the latter, indicating that the photocatalytic degradation of TC solution on mesoporous g-C₃N₄ is caused by the synergistic effect of adsorption and photocatalysis.

The fitting residual error of the above model is within 11.1%, indicating that the experimental data is in good agreement with the model prediction, and the model used can well explain the co-degradation process of GM-1.4 adsorption photocatalytic TC solution at pH = 3. Fig. 9(c) shows the comparison of the TC adsorption capacity on GM-1.4 in twice adsorptions, the TC adsorption capacity on GM-1.4 in the second time is not much different from that of in the first time. The results showed that the first adsorption on TC was almost completely degraded after 120 min of visible light irradiation, while the adsorption on the samples surface accelerated the photodegradation. What's more, the standard deviations of the adsorption experiment data are all within the range of 4.7%, it can be deduced that the experimental results have no obvious errors.

3.2.3 Active group capture experiment

The results of active group capture experiments were shown in the Fig. 10. Fig. 10 (a) showed the photocatalytic activity of mesoporous g-C₃N₄ under irradiation with the addition of different trapping agents. The active species trapping agents used in the experiments included TEOA, BQ and IPA, which were used to scavenge the holes (h⁺), superoxide radicals (·O₂⁻) and hydroxyl radicals (·OH) for photocatalytic reaction system, respectively. Obviously, the photodegradation efficiency remained unchanged in the presence of IPA. However, when BQ and TEOA trapping agents were added, the photodegradation efficiency reduced significantly, and BQ had the most obvious quenching effect on the reaction. It was indicated that ·O₂⁻ and h⁺ were the main oxidative species in the photocatalytic reaction. Meanwhile, the ESR spectra of GB and GM-1.4 was shown in Fig. 10 (b) and (c). It can be seen from the ESR spectra that DMPO·OH and DMPO·O₂⁻ of GB and GM-1.4 had no obvious signal peak under dark conditions. However, four signal peaks of DMPO·OH and DMPO·O₂⁻ were appeared in the light condition, and the peak intensity of DMPO·O₂⁻ was stronger than that of DMPO·OH. These results indicated that ·O₂⁻ and ·OH were both the active species, and the influence of ·O₂⁻ species was greater. Compared to the dark state, TEMPO-h⁺ has weaker peak intensity in the light state, this may be because the mesoporous g-C₃N₄ produces more holes and neutralizes the trapping agent under light conditions, indicating that h⁺ also has a great influence on the photocatalytic reaction. This conclusion was also consistent with the results of the active group capture experiments.

3.2.4 Cycle performance test.

The results of photodegradation cycle experiments of GM-1.4 photocatalytic degradation on TC was shown in Fig. 11. It can be observed that the photocatalytic efficiency of GM-1.4 on tetracycline showed no significantly decrease after repeated for five times. Although the degradation rate decreased gradually with the increase of reaction times, this may be because the loss of catalyst in the process of recovery resulted in the reduction of mesoporous g-C₃N₄, thus leading to the decline of photodegradation rate.

3.2.5 Mechanism analysis of photocatalytic degradation of TC by mesoporous g-C₃N₄.

The UV-Vis spectra of blank experiments without catalyst and TC photocatalytic degradation with GM-1.4 under visible light at different periods are shown in Fig. 12 (a) and (b). As shown in Fig. 12(a), the UV-Vis absorption spectra of TC without catalyst unchanged after 120 min of xenon lamp irradiation, indicating that TC is relatively stable under light conditions and would not be degraded by itself. Fig. 12 (b) shows the spectra variation in the process of GM-1.4 photocatalytic degradation of TC. When the GM-1.4 was added to the TC solution, the absorption peak intensity of TC at the wavelength of about 357.5nm gradually decreases with the increase of illumination time, and the peak position of GM-1.4 curve in each time has barely moved, indicating that the decreasing of absorption peak intensity of TC mainly due to

the destruction of the structure of TC molecule caused by the photocatalytic reduction reaction to produce CO_2 and H_2O directly.[45-47] What's more, the variation of peak intensity presents a slight change after 60 min photocatalytic reaction, it meant that the TC molecules were mostly degraded within an hour, and also illustrated that the special coral-like rod shaped and porous structure of mesoporous g- C_3N_4 could enhance the above reaction process. As shown in Fig. 12 (c), the prepared mesoporous g- C_3N_4 with rich porous structure in this paper can provide more active sites, then to be excited by visible irradiation, and inhibit the recombination of electron and photogenerated hole, the photocatalytic efficiency of TC will be enhanced.

4 Conclusions

In this work, using guanidine hydrochloride as precursor, a novel mesoporous g- C_3N_4 with shaped heptazine ring structure was synthesized by molten salt assisted SiO_2 aerogel template method, and the heptazine ring structure and rich nitrogen defects was prepared successfully. The sample (GM-1.4) displayed the lower band gap (2.42 eV) and more plentiful active sites. The photocatalytic degradation rate of GM-1.4 for TC solution with pH = 7 was about 83.4% after 120 min visible light irradiation. Meanwhile, the TC adsorption capacity of GM-1.4 was both decreased with the increase of pH value, and the kinetic model verified that the photocatalytic degradation rate of TC on mesoporous g- C_3N_4 was promoted with the synergistic effect of adsorption. The active group capture experiment and ESR spectra showed that the $\cdot\text{O}_2^-$ and h^+ were the primary reactive species in the TC photodegradation, and the main reason of photocatalytic degradation of TC by mesoporous g- C_3N_4 was the TC molecular structure fracture.

Declarations

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Declarations

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled.

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There are no conflicts to declare.

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All the authors listed have approved the manuscript that is enclosed.

Availability of data:

The authors confirm that the data supporting the findings of this study are available within the article. Raw data supporting the findings of this study are available from the corresponding author [Zheng Liu] on request.

Authors' contributions:

Zheng Liu: Conceptualization, Methodology, Writing-Reviewing & Editing. Hekun Ding: Investigation, Data Curation, Writing-Original draft preparation. Xiao He: Data Curation, Formal analysis. Dongbo Wang: Supervision. Qingge Feng: Funding acquisition, Resource and Supervision.

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Figures

Figure 1

FT-IR spectra of the samples.

Figure 2

XRD patterns of the samples.

Figure 3

(a) N2 adsorption desorption isotherm curve of the samples, (b) pore size distribution curve of the samples.

Figure 4

UV diffuse reflectance spectra (a), band gap curves (b-e) of GB and GM-X

Figure 5

PL spectra of the samples.

Figure 6

SEM images of GB (a) (b), TEM images of GB (c) (d); SEM images of GM-1.4 (e) (f), TEM images of GM-1.4 (g) (h).

Figure 7

7 XPS spectra of GB and GM-1.4: (a) survey spectra, (b) C 1s spectra, (c) N 1s spectra, (d) O 1s spectra.

Figure 8

(a) Degradation curve of 10 mg·L⁻¹ TC solution with different dosage of GB and GM-1.4, (b) degradation curve of TC solution with different concentration by 30 mg GB and GM-1.4, (c) degradation curve of 10 mg·L⁻¹ TC solution with GB and GM-1.4, (d) changes of TC adsorption capacity of GB and GM-1.4 under different pH conditions.

Figure 9

GM-1.4 photocatalytic degradation of TC cycle experiment.

Figure 10

(a) Effects of different trapping agents on TC photodegradation by mesoporous g-C₃N₄, (b) ESR spectrum of GB, (c) ESR spectrum of GM-1.4.

Figure 11

(a) Dark adsorption kinetics of TC solution on GM-1.4 at pH = 3, (b) Light degradation kinetics of TC solution on GM-1.4 at pH = 3, (c) cyclic adsorption of TC solution on GM-1.4 at pH = 3.

Figure 12

(a) UV-Vis spectra of TC without mesoporous g-C₃N₄, (b) UV-Vis spectra of TC photo-catalytic degradation on GM-1.4, (c) Photocatalytic mechanism of TC on mesoporous g-C₃N₄ under visible light irradiation.