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1. Introduction

Graphitic carbon nitride (g- C_3N_4) has recently emerged as a promising metal-free photocatalyst for water splitting, CO₂ reduction, selective oxidation of alcohols and water purification.^{1–6} Two-dimensional (2D) conjugated planes and tri-s-triazine repeating units through Van der Waals interactions provide g- C_3N_4 with unique advantages such as good chemical stability as well as an appealing electronic structure with a medium-bandgap (2.7 eV).⁷ However, the limited light harvesting ability and fast recombination probability of the photogenerated charge carriers seriously restrict the application of g- C_3N_4 in the photocatalytic field.⁸ Therefore, fabrication of robust g- C_3N_4 material with excellent photocatalytic activity is still a challenge.

Nanopore enriched hollow carbon nitride nanospheres with extremely high visible-light photocatalytic activity in the degradation of aqueous contaminants of emerging concern[†]

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Construction of highly efficient hollow nanosphere photocatalytic systems has been strongly attracting the attention of researchers. In the present work, nanopore enriched hollow carbon nitride nanospheres (HCNNSs) with a smaller particle size (200 nm) and a thinner shell thickness (40 nm) are successfully fabricated by a silica-nanocasting strategy. Such unique structures possess many advantages such as large BET surface area (122 m² g⁻¹), high light-harvesting ability, fast charge separation and transfer efficiency, plentiful exposed active sites and enhanced oxidation ability of photogenerated holes (h_{VB}^+). Therefore, HCNNSs in smaller sizes (HCNNS-200) exhibit extremely excellent visible-light photocatalytic efficiency towards the degradation of contaminants of emerging concern, e.g. levofloxacin (LEVO), in comparison with bulk g-C₃N₄ and HCNNSs in larger sizes (HCNNS-500). And it takes less than 10 min to finish the degradation of LEVO. The experimental results including those from indirect chemical probing, electron spin resonance, ion chromatography and high performance liquid chromatography-mass spectrometry confirm that h_{VB}^+ and 'O₂⁻ are the active species that are responsible for the mineralization of LEVO to NO₃⁻, F⁻, H₂O and CO₂ under visible-light irradiation. Additionally, the degradation pathway of LEVO in the HCNNS-200 photocatalytic system is also proposed. It is expected that HCNNS-200 can be used as a promising photocatalyst for environmental remediation.

Inspired by the thylakoid membrane where plant photosynthesis occurs, hollow nanostructured materials, especially hollow g- C_3N_4 nanospheres, have been constructed *via* morphological engineering and have attracted much attention because of their unique structural, physical and chemical properties:^{9–19} i) the hollow structures can enhance the light harvesting efficiency owing to multiple light reflection events within their void space; additionally, hollow structures can facilitate mass transfer *via* shortening the transfer distance as compared with bulk catalysts; ii) the large surface areas of both exterior and interior surfaces can promote surfacedependent reactions by providing plentiful active sites.

Recently, much effort has been paid to fabricate hollow g-C₃N₄-based nanospheres *via* a nanostructured silica template, such as, hollow carbon nitride nanospheres (HCNSs),^{13,20} post-annealing reinforced HCNSs,²¹ Co₃O₄/HCNS/Pt,²² CdS/HCNS²³ and MoS₂/HCNS.²⁴ Constructing three-dimensional hollow nanospheres of g-C₃N₄ from two-dimensional conjugated packed g-C₃N₄ planes not only significantly enhances light harvesting but also facilitates the mass transfer of the reactants and products as well as the migration of the photogenerated charge carriers. Therefore, all



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these hollow g- C_3N_4 -based nanospheres achieve good H_2 or/ and O_2 evolution efficiency. In addition, by coupling the appropriate cocatalysts on the exterior or interior surfaces, the H_2 and O_2 evolution sites are spatially separated, and overall photocatalytic water splitting can be achieved.²² Unfortunately, such perfect hollow carbon nitride nanospheres are rarely studied in the photodecomposition of organic pollutants, which is seriously restricted by the lower oxidation ability of photogenerated holes, leading to slow photocatalytic efficiency and poor mineralization ability. In this context, it is highly desirable to develop hollow carbon nitride nanospheres with high photocatalytic and mineralization efficiency for pollutant removal.

In the present work, nanopore enriched hollow carbon nitride nanospheres (HCNNSs) with a smaller particle size (200 nm) and a thinner shell thickness (40 nm) are successfully fabricated by a silica-nanocasting strategy. Owing to their unique hollow nanostructure, the as-prepared HCNNSs possess enhanced light-harvesting efficiency, fast charge separation property and increased surface accessibility. What is more, the smaller size of the HCNNSs also enhance the quantum size effect, leading to increased oxidizing ability of photogenerated holes in the HCNNSs. Therefore, HCNNSs exhibit excellent visible-light photocatalytic activity in the photodegradation of aqueous organic pollutants, as well as deep oxidation of the organic pollutants into H_2O , CO_2 and inorganic anions.

The morphologies, phase and chemical structure, optical absorption and photoelectrochemical properties of the HCNNSs are well characterized, and the visible-light photocatalytic activity of the HCNNSs is evaluated by the degradation of contaminants of emerging concern including levofloxacin (LEVO) and trimethoprim (TMP) which are frequently detected at low concentration levels in natural water and can cause adverse effect in biota.²⁵ Meanwhile, the active species generated during the process of photodegradation are investigated by electron spin resonance spectroscopy and free radical and hole scavenging experiments. On the basis of the above results, the mechanism and pathway of the visiblelight photocatalytic degradation of LEVO over the HCNNSs are revealed, which is one of the most important issues for hollow carbon nitride nanosphere photocatalysts but is seldom studied up till now.

2. Experimental

2.1. Catalyst preparation

2.1.1. Silica templates. The monodisperse core–shell structured silica templates were synthesized through a modified Stöber method.¹³ Typically, an aqueous ammonia solution (7%, 16 or 30 mL) was added to ethanol (150 mL), and then tetraethoxysilane (TEOS, 3.4 or 5.1 mL) was added dropwise to the above basic ethanol solution with vigorous stirring at room temperature for 1 h to yield uniform nonporous colloidal silica spheres. A mixture of TEOS (5 or 7.5 mL) and *n*-octadecyltrimethoxysilane (C₁₈TMOS, 2.26 or 3.39 mL) was

then added dropwise to the above solution with vigorous stirring for 10 min to create a thin mesoporous silica shell around the dense silica core. The mixed solution was then kept at ambient temperature for 3 h without stirring to promote the cohydrolysis and condensation of the TEOS and C_{18} TMOS on the nonporous silica cores. The resulting white precipitate was recovered by filtration, dried at 80 °C for 12 h, and further calcined at 550 °C in air for 6 h with a heating rate of 5 °C min⁻¹. The as-prepared monodisperse silica templates were neutralized with 1 M HCl and then dried at 60 °C for 12 h. The final silica templates were denoted as Template-*x*, where *x* represented the particle size of the silica template. Here, *x* = 200 and 500, respectively.

2.1.2. HCNNS. A mixture of the Template-*x* powder (1 g) and an aqueous cyanamide solution (50%, 1.5 mL) was sonicated for 2 h in a flask connected to a vacuum line, followed by stirring at 60 °C for 14 h and then drying at 80 °C for 24 h. The resulting white powder was transferred to an alumina crucible and calcined at 550 °C under flowing N₂ for 2 h with a heating rate of 5 °C min⁻¹. Afterwards, the obtained yellow g-C₃N₄/SiO₂ hybrids were treated with NH₄HF₂ (4 M, 10 mL) for 12 h to remove the silica template. The final yellow powder was obtained by drying at 80 °C overnight. The product is denoted as HCNNS-*x* with *x* = 200 and 500, respectively.

2.1.3. Bulk g- C_3N_4 **.** Bulk g- C_3N_4 was synthesized as the reference sample by calcination of cyanamide at 550 °C under flowing N_2 atmosphere for 2 h with a heating rate of 5 °C min⁻¹.

2.2. Catalyst characterization

Transmission electron microscopy (TEM) images were recorded on a JEM-2100F high resolution transmission electron microscope at an accelerating voltage of 200 kV. Nitrogen porosimetry measurements were performed on a Micromeritics ASAP 2020 M surface area and porosity analyzer. Powder X-ray diffraction (XRD) patterns were obtained on a Japan Rigaku D/max 2000 X-ray diffractometer (Cu K α , λ = 1.5418 Å). Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet Magna 560 IR spectrophotometer. X-ray photoelectron spectroscopy (XPS) was performed on a VG-ADES 400 instrument with a Mg K-ADES source. UV-vis diffuse reflectance spectra (UV-vis/DRS) were recorded on a Cary 500 UV-vis-NIR spectrometer. Photoelectrochemical measurements were carried out on Chenhua CHI 660E electrochemical station. Photoluminescence (PL) spectra were obtained with a Photon Technology International (PTI) TimeMasterTM 400 with an excitation wavelength of 337 nm. DMPO (5,5-dimethyl-1-pyrroline-N-oxide) spin-trapping EPR spectra were recorded on a JES-FA200 electron spin resonance spectrometer.

2.3. Photocatalytic performance evaluation

The adsorption and photocatalytic activity of the as-prepared photocatalysts were evaluated by the degradation of LEVO and TMP under visible-light irradiation (400–680 nm) using a 300 W Xe lamp. For all adsorption and photocatalytic tests, 50 mL of the aqueous target pollutant solution with an initial concentration of 20 mg L⁻¹ was used, and the catalyst amount was 50 mg. All tests were performed in a self-made quartz photoreactor fitted with a circulation water system to maintain a constant temperature. Prior to irradiation, the adsorption-desorption equilibrium between the target compound and the catalyst was monitored by the determination of the concentrations of the target pollutant for a certain time interval. During the photocatalytic tests, a fixed amount of the reaction solution was taken out at given time intervals, followed by centrifugation to remove the photocatalyst completely. The concentrations of LEVO and TMP were determined using an Agilent 1200 high performance liquid chromatograph (HPLC): C18 column, UV detector. The concentraorganic acids during tions of the produced the photodegradation process were determined using a Dionex DX-300 ion chromatograph (IC), while the concentrations of inorganic anions were determined using a Metrohm 881 Compact IC. The intermediates produced during the photodegradation process were identified using an Agilent 1200 HPLC-micro TOFESI-TOF-MS high-resolution electrospray ionization time-of-flight mass spectrometer equipped with HPLC (HPLC-MS).

2.4. Photoelectrochemical measurements

All electrochemical measurements were performed on a conventional three-electrode electrochemical workstation equipped with Ag/AgCl (saturated KCl) and a Pt wire as the reference electrode and the counter electrode, respectively. FTO coated with the as-prepared photocatalyst film was used as the working electrode for the electrochemical impedance spectroscopy (EIS) Nyquist analysis, photocurrent test and Mott–Schottky plot determination.

3. Results and discussion

3.1. Preparation and characterization of HCNNSs

The preparation of HCNNSs includes two main steps. As illustrated in Scheme 1, a modified Stöber method is applied to produce monodisperse core-shell structured silica templates with a dense core covered by a nanopore enriched shell. Colloidal silica cores are firstly obtained by the hydroly-



Scheme 1 Illustration of the route of the preparation of the HCNNSs.

sis and condensation of TEOS in a mixture of ethanol and ammonia aqueous solution; moreover, the particle size of the silica cores can be adjusted by changing the initial concentrations of TEOS and NH₄OH in the preparation system. The higher the TEOS and NH4OH concentrations, the larger the particle size of the silica cores. Here, two silica cores are prepared at different initial TEOS and NH4OH adding amounts, which directly influence the particle sizes of the silica templates. After further cohydrolysis and condensation of the TEOS and C18TMOS around the silica core followed by calcination, core-shell structured silica templates with a thin porous silica shell around the silica core are therefore fabricated because of the removal of octadecyl groups from the silica/carbon framework. In the next step, the as-prepared silica templates are used to cast the HCNNSs. Before adding the g-C₃N₄ precursor of cyanamide (CY), the silica templates are post-acidified with dilute HCl to enhance the surface reactivity of the silica to the NH2-rich CY molecules via acid-base interaction. Subsequently, a combined technology of sonication and vacuum is applied to extract the air trapped in the silica matrix as well as to pump the aqueous CY solution (50%) sufficiently into the pore channels. Compared with molten state CY as the precursor, the aqueous CY solution possesses better liquidity so that the CY molecules can access the pore channels of the silica templates more easily under milder reaction conditions. After calcination of the dried CY/ SiO₂ hybrids at 550 °C followed by the removal of silica template via NH₄HF₂ treatment, HCNNS-200 (particle size of 200 nm) and HCNNS-500 (particle size of 500 nm) are fabricated.

3.1.1. Morphological characteristics and textural properties. The morphological characteristics of the as-prepared two silica templates and the corresponding HCNNSs are revealed by TEM observation (Fig. 1). Both silica templates exhibit a monodispersed spherical nanostructure with a condensed core and a porous shell (Fig. 1a-d). The diameter and shell thickness of the smaller template (Template-200) is ca. 200 nm and ca. 40 nm, while the diameter and shell thickness of the larger one (Template-500) is ca. 500 nm and ca. 130 nm (data presented in Table 1). Removing the silica templates yields highly uniform hollow carbon nitride nanospheres (HCNNS-200 and HCNNS-500) that inherit most of their geometrical features from the parent silica templates (Fig. 1e-h). The estimated shell thickness of HCNNS-200 is 40 nm, which is strongly related to the thickness of the porous silica shell over the condensed core of the template. However, the shell thickness of HCNNS-500 is only ca. 100 nm, smaller than the shell thickness of its silica templates. The result implies that 50% aqueous CY is hard to penetrate sufficiently into the pore channels of the thick shell of the silica template due to the long diffusion path and air trapped in the deep hole of Template-500. It should be noted that the bright-dark patterns existing in the shell of HCNNS-200 or HCNNS-500 suggest well-kept porous structures after removal of the silica templates.

The textural properties of various g-C₃N₄ samples are studied by nitrogen gas porosimetry measurements. As shown in



Fig. 1 TEM images of Template-200 (a and b), Template-500 (c and d), HCNNS-200 (e and f), and HCNNS-500 (g and h).

Table 1 Particle size (*a*), shell thickness (δ), BET surface area (S_{BET}) and band gap (E_{g}) of various g-C₃N₄ samples

Catalyst	<i>d</i> (nm)	δ (nm)	$S_{\rm BET} \left({{ m m}^2 ~{ m g}^{ - 1}} ight)$	$E_{\rm g} \left({\rm eV} \right)$
Bulk g-C ₃ N ₄	_	_	22	2.74
HCNNS-200	200	40	122	2.89
HCNNS-500	500	100	116	2.85

Fig. 2a, bulk g- C_3N_4 prepared by direct thermal condensation of cyanamide exhibits type IV isotherms with a very small H3 hysteresis loop, signifying its poor mesoporosity owing to its bulk morphology (Fig. S1†). Correspondingly, bulk g- C_3N_4 possesses a very small BET surface area (22 m² g⁻¹, Table 1). As for the HCNNSs prepared by the silica casting method, their isotherms show combined characteristics of a rapidly increasing nitrogen gas adsorbed amount at relative pres-



Fig. 2 Nitrogen gas adsorption–desorption isotherms (a), nitrogen gas adsorption isotherm at $P/P_0 < 0.1$ (inset of a), and corresponding BJH pore-size distribution curves (b) of g-C₃N₄ and the HCNNSs.

sures (*P*/*P*₀) lower than 0.1 (type I isotherm) and a type IV isotherm with a H3 hysteresis loop at *P*/*P*₀ = 0.45–1.0 (Fig. 2a), indicating their interesting micro/mesoporosity.^{26–28} Compared with HCNNS-500, HCNNS-200 with a smaller particle size and thinner shell exhibits a larger hysteresis loop, indicating that more abundant mesopores are created in the shell of the hollow structure. This excellent hierarchical porosity renders HCNNS-200 a larger BET surface area (122 m² g⁻¹) than HCNNS-500 (116 m² g⁻¹).

The interesting textural properties of the hollow carbon nitride nanospheres are also reflected in their corresponding BJH pore size distribution curves (Fig. 2b). HCNNS-200 exhibits a sharp BJH pore size distribution curve centering at 3.6 nm, suggesting its uniform mesopores within the polymer shell. As for HCNNS-500, its mesopores mainly center at 3.4 nm.

Compared with HCNNS-200, the pore size of HCNNS-500 is less well-distributed; meanwhile, its pores are less abundant. This is because the thicker shell of Template-500 results in the poor permeation of CY molecules. Uniform mesopores combined with the thin shell of HCNNS-200 may increase the accessibility of the reactants to the active sites by bridging the exterior and interior surfaces, which is expected to improve the heterogeneous photocatalytic activity.

3.1.2. Composition and structural information. The crystal structures of various $g-C_3N_4$ are characterized by XRD measurements. As shown in Fig. 3a, bulk $g-C_3N_4$ shows the typical graphitic stacking structure with the (100) diffraction peak at



Fig. 3 XRD patterns (a) and FT-IR spectra (b) of $g\text{-}C_3N_4$ and the HCNNSs.

13.1° and (002) peak at 27.5°, which represent the characteristic interlayer stacking and in-plane repeating structural motifs of the conjugated aromatic systems, respectively.^{29,30} The graphite-like structure can also be detected for the HCNNSs. Nevertheless, compared with the XRD pattern of the bulk $g-C_3N_4$, the (100) diffraction peaks of both HCNNSs become somewhat weak, suggesting the decreased order degree of the in-plane structural motif.³¹ The result is ascribed that the narrowed porous channels within the template may confine the polymerization degree of carbon nitride. In addition, the (002) diffraction peak for both HCNNSs shifts from 27.5° (g- C_3N_4) to 27.9°, suggesting that the average interlayer distance of the HCNNSs is shortened,^{13,21} leading to the compact carbon nitride framework with the porous structures in it. Interestingly, a new diffraction peak at 17.8° appears, which is assigned to the (600) crystal plane of mesoporous g-C₃N₄.^{32,33} The result further indicates the mesoporous structure within the shell of the HCNNSs.

FTIR further confirms the graphic structure of the HCNNSs (Fig. 3b). The peaks at 1200–1600 cm⁻¹ are typical stretching vibration modes of CN heterocycles, while the peak at 810 cm⁻¹ originated from the bending vibration of the triazine unit, illustrating the tri-s-triazine motifs of both g-C₃N₄ and HCNNSs.²⁷ Moreover, the broad absorption band located in the range of 3000–3300 cm⁻¹ is assigned to the stretching vibration of the N–H and O–H groups.

A high-resolution XPS surface probe technique is carried out to investigate the chemical states of the as-prepared samples (Fig. 4). As shown in Fig. 4a, three elements, O, N and C, are detected in both $g-C_3N_4$ and HCNNSs. Compared with bulk $g-C_3N_4$, the peak intensity of O 1s in the HCNNSs decreases, indicating the lower O content in the HCNNSs, while the intensity ratio of N 1s to C 1s increases, resulting in a C/



Fig. 4 XPS survey (a) and high-resolution spectra in O 1s (b), C 1s (c) and N 1s (d) binding energy regions of $g-C_3N_4$ and the HCNNSs.

N atom ratio closer to 4/3. It is speculated that HCNNSs may possess a much better structured CN framework with lower oxygen-content.

Fig. 4b shows the XPS of bulk $g-C_3N_4$ and HCNNSs in the O 1s binding energy region. For $g-C_3N_4$, the peaks centering at 531.2 and 533.1 eV are assigned to oxygen species from the C=O and C-O groups of $g-C_3N_4$.²⁷ These two peaks can also be detected in the O 1s spectra of the HCNNSs. However, the peak intensity of the HCNNSs is much weaker than that of the bulk $g-C_3N_4$, which is attributed to the fact that the condensation of cyanamide is much more thorough within the mesopores of the silica template, further reducing the content of the C=O and C-O groups.

The C 1s XPS spectra of the tested g- C_3N_4 samples display three characteristic peaks centering at 284.6, 286.3 and 288.1 eV (Fig. 4c), corresponding to carbon species from the adsorbed carbon, C-NH₂ group and sp² carbon atoms bonded to nitrogen atoms in an aromatic ring (N-C=N), respectively.³¹ Compared with bulk g- C_3N_4 , the peak intensity of the C-NH₂ group in the HCNNSs decreases, while the peak intensity of N-C=N increases. This result indicates that more CN hybridized aromatic rings have been built during the hard template assisted thermal condensation process, leading to the well-structured CN framework of carbon nitride hollow spheres.

The N 1s XPS spectra of the tested g-C₃N₄ samples are fitted into three peaks (Fig. 4d). For bulk g-C₃N₄, the peak at 398.2 eV is assigned to sp² hybridized aromatic nitrogen atoms bonded to carbon atoms (C-N=C), while the peak at 398.9 eV relates to the tertiary nitrogen $N-(C)_3$ groups linking the structural motif (C_6N_7). The last peak at 400.5 eV corresponds to the nitrogen atoms from the -NH₂ group.²⁷ As for the HCNNSs, the peaks of the C-N=C (398.6 eV), N-(C)₃ (399.9 eV) and -NH₂ (401.2 eV) groups slightly shift to higher binding energy regions, which is in accordance with the hollow porous carbon nitride prepared from cyanamide.¹⁶ Due to the restriction of mesopores in the SiO₂ templates, the thermal condensation of CY molecules undergoes a specific situation and results in the better structured CN framework of HCNNSs with less oxygen content than g-C₃N₄, which reduces the electron density around the nitrogen atom and thereby increasing the binding energy.³⁴

On the basis of the above discussion, hollow carbon nitride nanospheres with a well-structured CN framework have been fabricated. In the presence of multiple CN hybridized aromatic rings with less oxygen-containing groups, the hollow carbon nitride nanospheres are expected to facilitate the migration and separation of the photogenerated charge carriers.

3.1.3. Optical absorption properties. The light absorption property of the as-prepared photocatalysts is characterized by UV-vis/DRS (Fig. 5). As shown in Fig. 5a, $g-C_3N_4$ exhibits a semiconductor absorption in the region of 200 to 460 nm, originating from the charge transfer from the valence band (VB) populated by N 2p orbitals to the conduction band (CB) formed by C 2p orbitals.³⁵ Compared with the bulk g-C₃N₄,



Fig. 5 UV-vis/DRS (a), the corresponding band gap plots (b), Mott-Schottky plots (c), VB XPS spectra (d) and band structures (e) of $g-C_3N_4$ and the HCNNSs.

the HCNNSs show a slight blueshift of the absorption edge, i.e. the absorption band edges are 440 and 450 nm for HCNNS-200 and HCNNS-500, respectively, which might be due to the quantum size effect.^{13,21} In addition, the enhanced light absorption in the range of 440 to 800 nm for the HCNNSs compared to the bulk g-C3N4 is believed to reflect the ability of the hollow nanospheres to have multiple reflections within the structure, which increases the effective path length for light absorption,^{21,36} making these materials promising candidates for photocatalytic applications. For two hollow g-C₃N₄ nanospheres, HCNNS-200 with a smaller size and thinner shell exhibits a slightly stronger light absorption ability in the visible light region. The band gaps of the bulk g-C₃N₄ and HCNNSs are calculated by the formula $\alpha hv = A$ $(hv - E_g)^{1/2}$, where α , v, E_g and A are the absorption coefficient, the light frequency, the band gap and a constant, respectively. The $E_{\rm g}$ values are therefore estimated to be 2.74 (g-C₃N₄), 2.89 (HCNNS-200) and 2.85 eV (HCNNS-500), respectively (Fig. 5b and Table 1).

Besides a suitable band gap, the suitable CB and VB edge potentials of the semiconductor are also important for the photocatalytic reaction. Herein, Mott–Schottky plots are applied to verify the flat-band of g-C₃N₄ and the HCNNSs, which can be used to estimate the CB level.³⁷ As shown in Fig. 5c, all samples exhibit a positive slope in the linear region, implying their n-type semiconductor structure. The estimated flat band potentials are -1.09, -1.12 and -1.13 V vs. NHE for g-C₃N₄, HCNNS-500 and HCNNS-200, respectively, indicating the enhanced reduction capability of photogenerated electrons (e_{CB}) generated on the HCNNSs. The relative positions of the VB for the samples are determined using the XPS valence spectra. As shown in Fig. 5d, HCNNS-200 exhibits the most positive location (1.76 V), which is 0.03 V and 0.11 V higher than that of HCNNS-500 (1.73 V) and $g-C_3N_4$ (1.65 V), respectively, indicating the strongest oxidizing ability for the photogenerated holes (h⁺_{VB}) generated on HCNNS-200. Additionally, such values of VB are consistent with the valence bands calculated by combining the result of band gaps and flat band potentials. Therefore, the band structure of g-C₃N₄ and the HCNNSs are well resolved as illustrated in Fig. 5e. The most negative CB and positive VB positions of HCNNS-200 is attributed to the strongest quantum size effect induced by the smallest nanoparticle size of HCNNS-200, leading to the largest bandgap energy of HCNNS-200.

3.1.4. Charge separation and transfer property. The photogenerated charge carrier separation and transfer property is evaluated by electrochemical impedance spectroscopy (EIS), photoelectrochemistry tests and time-resolved fluorescence spectroscopy. As shown in Fig. 6a, the Nyquist semicircles of the HCNNSs show a smaller diameter compared with that of the bulk g-C₃N₄; moreover, the Nyquist semicircle diameter of HCNNS-200 is smaller than that of HCNNS-500. Therefore, HCNNS-200 exhibits the fastest electronic conductivity and the most efficient charge separation. This result is further supplemented by the photocurrent measurements shown in Fig. 6b. All samples show a stable and reproducible photocurrent response, and the photocurrent intensity follows the order: HCNNS-200 > HCNNS-500 > bulk g-C₃N₄, which reflects the fastest separation and transfer efficiency of the photogenerated charge carriers within HCNNS-200. In addition, the fluorescence decay spectra also illustrate the longer calculated average life-time of HCNNS-200 compared with HCNNS-500 and g- C_3N_4 (Fig. S2[†]). For example, the calculated average life-time values are 3.601 ns for HCNNS-200, 3.188 ns for HCNNS-500 and 2.938 ns for the bulk g-C₃N₄.

Based on the above results, the fast charge separation and transfer property of HCNNS-200 is due to its perfect small and hollow spherical nanostructures with micro- and



Fig. 6 EIS Nyquist plots (a) and photocurrent responses (b) of $g-C_3N_4$ and the HCNNSs electrodes.

mesopores in the shell. At first, the hollow nanostructure can improve the light-harvesting efficiency *via* the multiple reflections within it, increasing the probability of electron transition and the population of photogenerated electrons and holes. Secondly, the well-structured CN framework facilitates the charge transfer to the surface without trapping at defect sites. Finally, plentiful micro- and mesopores in the thin shell can shorten the migration distance of the photogenerated charge carriers to the surface of the photocatalyst. Therefore, it is worth anticipating that HCNNS-200 will give excellent photocatalytic activity.

3.2. Photocatalytic studies

3.2.1. Visible-light photocatalytic activity. The visible-light photocatalytic activity of HCNNSs is firstly evaluated by the degradation of levofloxacin (LEVO). LEVO is a well-known fluoroquinolone (FQ) antibiotic that is extensively used in human and veterinary medicine, and it has strong recalcitrance to microbial degradation and photolysis.³⁸ For comparison, bulk g-C₃N₄ and Degussa P25 TiO₂ are also tested under the same conditions. Before light irradiation, the adsorption behaviors of the tested photocatalysts are studied (Fig. 7a). The adsorption-desorption equilibrium between LEVO molecules and the photocatalyst was reached after stirring the suspension for 30 min, and the adsorption capacity of P25 TiO₂, bulk g-C₃N₄, HCNNS-500 and HCNN-200 towards LEVO molecules is 6%, 8%, 18% and 19%, respectively. The stronger adsorption ability of the HCNNSs than the bulk g-C₃N₄ is closely related to their perfect hollow nanosphere structure and large BET surface area. Considering that the photocatalytic reaction takes place on the surface of the catalyst, the stronger adsorption ability of the photocatalyst toward the substrate is beneficial to improving its photocatalytic activity.³⁹ Under visible-light irradiation, the direct photolysis of LEVO can be negligible, however, significant degradation of LEVO occurs in the presence of both the photocatalyst and visible-light irradiation. The photocatalytic activity of the HCNNSs obviously outperforms P25 TiO2 and bulk g-C3N4. Only 10-15 min was needed to finish the photodegradation



Fig. 7 Adsorption property and photocatalytic activity of the HCNNSs towards the degradation of LEVO (a) and TMP (b) under visible-light irradiation. The UV-vis absorption spectra of LEVO (insert of a) solution as a function of irradiation time during the HCNNS-200-photocatalyzed degradation process (catalyst amount 50 mg; $c_0 = 20$ mg L⁻¹; volume 50 mL; 400 nm $< \lambda < 680$ nm).

of 99% LEVO over the HCNNSs, which is at least two times faster than that of P25 TiO₂ or bulk g-C₃N₄. In the cases of the two HCNNSs, HCNNS-200 exhibits a much higher visiblelight photocatalytic activity than HCNNS-500. For example, after visible-light irradiation for 10 min, the degradation of LEVO reaches 99% and 90%, respectively, over HCNNS-200 and HCNNS-500. The variations of the UV-vis absorption spectra of LEVO under visible-light irradiation of HCNNS-200 show that the characteristic UV-vis absorption peaks at 227, 290 and 326 nm of LEVO reduced gradually with prolongation of the irradiation time (insert of Fig. 7a). The result is consistent with those shown in Fig. 7a. HCNNS-200 still exhibits the highest photocatalytic activity in the degradation of TMP (Fig. 7b), and it takes less than 60 min to degrade TMP completely.

3.2.2. Mineralization of LEVO. Mineralization of organic pollutants reflects the deep oxidation of the photocatalysts. Here, the mineralization ability of the HCNNSs is evaluated by monitoring the concentration changes of the yielded organic acids and inorganic anions during the HCNNS-200photocatalyzed LEVO degradation process. As shown in Fig. S3,† both citric acid and acetic acid are found by IC analysis. The concentration of the yield citric acid increases to 4 mg L^{-1} after 4 h of visible-light irradiation and was kept at this level for the next 12 h (Fig. 8a). While the concentration of the yield acetic acid increases gradually to 16 mg L^{-1} with visible-light irradiation for 16 h, suggesting the continuous mineralization of LEVO. Additionally, F⁻ and NO₃⁻ ions are also detected by IC (Fig. 8b). The concentration of F⁻ increases rapidly to 0.75 mg L⁻¹ after 4 h of irradiation, and then slowly increases to 0.85 mg L⁻¹ after the next 12 h, finishing at 85% conversion of LEVO into the final product F⁻. Differently, the concentration of NO₃⁻ increases gradually to 4.3 mg L⁻¹ with light irradiation for 16 h, which is only 43% of the expected concentration of NO₃⁻. The above results confirm that the as-prepared HCNNSs can efficiently mineralize the pollutants under visible-light irradiation, working as the robust photocatalysts to decompose organic pollutants in water.

3.2.3. Regeneration and reusability. Taking HCNNS-200 as the representative photocatalyst, the regeneration and reusability of the as-prepared hollow $g-C_3N_4$ nanospheres are



Fig. 8 Concentration changes of the yielded citric acid and acetic acid (a), and F^- and NO_3^- ions (b) in the HCNNS-200-photocatalyzed LEVO degradation system (catalyst amount 50 mg; $c_0 = 20$ mg L^{-1} ; volume 50 mL; 400 nm $< \lambda < 680$ nm).

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investigated by selecting LEVO as the target compound. For each recycling run, HCNNS-200 is collected by centrifugation, and then it is washed with ethanol at 60 °C three times. As shown in Fig. 9a, no apparent deactivation of the photocatalyst is observed after six consecutive runs. The XRD measurements (Fig. 9b) and TEM observations (Fig. 9c and d) confirm that the crystal structure and the morphology of the used HCNNS-200 have scarcely changed after the photocatalytic reaction. These results suggest that the HCNNSs can work as recoverable visible-light-driven photocatalysts for the decomposition of aqueous organic pollutants.

3.3. Mechanism consideration

In order to understand the mechanism underlying the photocatalytic degradation of aqueous pollutants over the HCNNSs, the reactive species generated during the process of the HCNNS-200-photocatalyzed aqueous LEVO degradation are identified by ESR measurements as well as free radical and hole trapping experiments.

In order to detect the formation of O_2^- and 'OH radicals in the HCNNS-200 photocatalytic system, 5,5-dimethyl-1pyrroline-*N*-oxide (DMPO) spin-trapping EPR measurements are carried out. As shown in Fig. 10a, the signals corresponding to the DMPO- O_2^- and DMPO-OH adducts are hardly observed in the dark. After visible-light irradiation, the signal of the DMPO-OH adduct is still not found in this system, which suggests that the 'OH radical is not the active species for the photodegradation of organic pollutants. However, an obvious quartet signal with an intensity ratio of 1:1:1:1 is observed in this system under visible-light irradiation, which is assigned to the characteristic signal of the DMPO- O_2^- ad-



Fig. 9 Recycling experiments of the visible-light photocatalytic degradation of LEVO over HCNNS-200 (a). XRD patterns of HCNNS-200 before and after the reaction (b). TEM images of HCNNS-200 before (c) and after (d) the reaction.



Fig. 10 EPR spectra of DMPO- $'O_2^-$ in methanol dispersion and DMPO-'OH in aqueous dispersion with irradiation for 120 s in the presence of HCNNS-200 (a), and influence of various scavengers on the visible-light photocatalytic activity of the HCNNS-200 toward the degradation of LEVO (b).

duct. This result evidences the generation of O_2^- radicals in the HCNNS-200 photocatalytic system.

Free radical and hole trapping experiments obtain the same results with those of the ESR measurements. As shown in Fig. 10b, compared with the scavenger-free HCNNS-200 photocatalytic system, the degradation rate of LEVO is decelerated obviously in the presence of 1 mmol L^{-1} of EDTA-2Na (hole scavenger), while the degradation of LEVO is almost inhibited after the addition of 1 mmol L^{-1} of 1,4-benzoquinone (BQ, scavenger of 'O₂⁻ radicals). However, in the presence of *tert*-butyl alcohol (*t*-BuOH, 1 mmol L^{-1} , scavenger of 'OH radicals), the degradation rate of LEVO is hardly inhibited. This result indicates that h_{VB}^+ , especially 'O₂⁻, is the main active species that is responsible for the oxidization of LEVO completely under the visible-light irradiation.

The combination of the physicochemical properties, photoelectrochemical properties and the identified active species confirms that the enhanced visible-light photocatalytic activity of nanopore enriched hollow g-C₃N₄ nanospheres with a smaller particle size (HCNNS-200) originated from the contribution of its perfect morphological characteristics. On the one hand, the hollow nanostructure of HCNNS-200 can improve the light-harvesting efficiency via multiple reflections within the nanostructure; meanwhile, the smaller size and thinner shell of HCNNS-200 are beneficial for the light penetrating and reflecting within their void space. Both factors give rise to higher electron transition probability and thereby higher population of the photogenerated electrons and holes. On the other hand, the rapid separation and transfer of these photogenerated charge carriers within HCNNS-200 is another important reason for its excellent photocatalytic activity. The well-structured CN framework with lower oxygen-content has been built during the synthesis of HCNNS-200, which can promote the separation and transfer of the photogenerated charge carriers owing to the reduced defect sites. Additionally, the thinner shell of HCNNS-200 with plentiful pore channels within it efficiently shortens the migration distance of the photogenerated charge carriers to the surface and thereby minimizes the recombination of e_{CB}^- and h_{VB}^+ . Additionally, owing to the quantum size effect, HCNNS-200 exhibits an enlarged bandgap



Scheme 2 Mechanism of the visible-light photocatalytic degradation of aqueous LEVO over HCNNS-200.

with the improved oxidation ability of h_{VB}^+ for deep oxidation of organic pollutants. Finally, uniform pore channels combined with thin shell as well as monodispersed spherical nanostructures render HCNNS-200 with a large BET surface area, which can facilitate the adsorption of the reactants and increase the population of active sites. Consequently, the accessibility of the reactants to the active sites is improved significantly, promoting the efficiency of photocatalytic degradation.

On the basis of the above discussion, a reasonable mechanism of the visible-light photocatalytic degradation of LEVO over the nanopore enriched hollow carbon nitride nanospheres is revealed and illustrated in Scheme 2. Under visible-light irradiation, an increased amount of photogenerated charges carriers are generated in HCNNS-200 because of the multiple light reflections within the hollow spherical nanostructures. Due to the well-structured CN framework and shortened photogenerated charge carrier migration distance, e_{CB}^- and h_{VB}^+ rapidly separate from each other and then transfer/migrate to the inner and external surfaces of the catalyst. Subsequently, e_{CB}^- reacts with the dissolved dioxygen to produce 'O₂⁻ radicals. Under the attack of both the 'O₂⁻ radicals and h_{VB}^+ , LEVO is finally degraded to NO₃⁻, F⁻, H₂O and CO₂.

The proposed degradation pathway of LEVO over visiblelight irradiated HCNNS-200 can support the above mechanism considered. As displayed in Fig. S4,† ESI-MS identifies eleven intermediates generated during the process of the photocatalytic degradation of LEVO; additionally, the IC technique finds two aliphatic acids (citric acid and acetic acid, Fig. S3^{\dagger}) as well as inorganic anions (NO₃⁻ and Cl⁻, Fig. 8) in the catalytic system. On the basis of these results, the pathway of the visible-light photocatalytic degradation of aqueous LEVO over HCNNS-200 is tentatively put forward (Scheme 3). Under the attack of O_2^- and h_{VB}^+ , LEVO is firstly decomposed to compound 2 via the cleavage of the piperazinyl ring. Subsequently, compound 2 suffers from a series of decarbonylations to produce compounds 3, 4 and 5. Further photooxidation of compound 5 generates compound 6, and then compound 6 suffers decarboxylation to produce compound 7. After the leakage of the C-F bond from compound 7, compound 9 is vielded, accompanied by the release of a F anion into the reaction media. In addition, the leakage of the C-F bond also occurs in compound 5, which gives rise to compound 8 and a F⁻ anion. Continuous photooxidation of compound 8 leads to compound 9. Subsequently, simultaneous photooxidation and decarboxylation from compound 9



Scheme 3 Pathway of the visible-light photocatalytic degradation of aqueous LEVO over HCNNS-200.

results in compound 10. Further photooxidation and deamination from compound 10 produces compound 11, and the process is accompanied by the production of a NO₃⁻ anion. Continuous photooxidation of compound 11 leads to the opening of the aromatic ring, together with the formation of citric acid and acetic acid. Under the continuous attack by $'O_2^-$ radicals and h_{VB}^+ , citric acid and acetic acid are eventually decomposed into CO₂ and H₂O.

4. Conclusions

Nanopore enriched hollow carbon nitride nanospheres are successfully synthesized by using silica templates composed of a solid core and a polyporous shell. HCNNS-200 with a small particle size of 200 nm and a thin shell thickness of 40 nm exhibits extremely high visible-light photocatalytic ability toward the degradation of aqueous contaminants of emerging concern. It takes less than 10 and 60 min for HCNNS-200 to finish the decomposition of LEVO and TMP, respectively, which outperforms bulk g-C₃N₄ and HCNNS-500. Moreover, HCNNS-200 can be reused six times without obvious activity loss. Such an excellent photocatalytic ability of HCNNS-200 is attributed to its unique hollow nanostructure which endows HCNNS-200 with enhanced lightharvesting ability, faster charge separation and transfer efficiency, easier accessibility of the reactants to the active sites and stronger oxidation ability of h_{VB}^+ . The active species including O_2^- radicals and h_{VB}^+ produced in the HCNNS-200 system are responsible for the photooxidization and mineralization of LEVO and TMP. Additionally, a more systematic photocatalytic degradation pathway of LEVO is proposed based on IC and HPLC-MS analysis. It is expected that HCNNS-200 can be used as a genuine heterogeneous visiblelight-driven photocatalyst that may find wide applications in environmental remediation.

Conflicts of interest

There are no conflicts to declare.

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