Environmental Science Nano





Cite this: Environ. Sci.: Nano, 2019, 6, 2565

Received 3rd May 2019, Accepted 19th June 2019

DOI: 10.1039/c9en00509a

rsc.li/es-nano

Environmental significance

Template-free synthesis of oxygen-containing ultrathin porous carbon quantum dots/g-C₃N₄ with superior photocatalytic activity for PPCPs remediation^{\dagger}

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The development of facile and environmentally compatible synthetic strategies for broad-spectrum response photocatalysts is a primary goal for researchers in this area. For this study, we report on a templatefree thermal treatment strategy for the synthesis of an oxygen-containing ultrathin porous carbon quantum dots/polymeric carbon nitride metal-free composites (CQD/OUPCN). Morphology characterization revealed that the thermal treatment induced bulk CQD/g-C₃N₄ (CQD/BCN) to transform to porous ultrathin 2D nanosheets with a high specific surface area. Chemical structure characterization revealed that O atoms were involved in the chemical composition of C_3N_4 following the introduction of CQD and subsequent thermal treatment. Optical and electrical characterization, as well as density functional theory (DFT) calculations, confirmed that the introduction of O atoms and CQD enabled the tuning of the intrinsic electronic state, and improved the charge transfer capacity of C_3N_4 . Together with the up-converted fluorescence properties of CQD, the CQD/OUPCN exhibited remarkable broad-spectrum activity toward the degradation of PPCPs. Under visible light irradiation, the CQD/OUPCN-0.5% showed an 18.5 fold higher indomethacin (IDM) degradation rate than did g-C₃N₄. Further kinetics studies, including reactive species (RS) and degradation intermediate detection, indicated that RS, particularly O₂⁻⁻, was generated during the photocatalytic process, which could lead to the decomposition, and finally mineralization of IDM.

Currently, water environment issues have attracted increasing concern. Efficient semiconductor photocatalysis is a promising and effective strategy for purifying water contaminated by various environmental pollutants. In this regard, the development of facile and environmentally compatible synthetic strategies for broad-spectrum response photocatalysts is a primary goal in this area. Herein, we report the fabrication of an oxygen-containing ultrathin porous carbon quantum dots/polymeric carbon nitrogen metal-free composites (CQD/OUPCN) for the degradation of pharmaceutical and personal care products (PPCPs) under broad spectrum light irradiation. The CQD/OUPCN hybrid demonstrated a remarkable photocatalytic activity for the degradation of IDM under UV, vis, and NIR irradiation due to the ultrathin and porous nanostructures, introduction of O atoms, as well as the supervisor properties of CQD. The present work may lead to an environmentally compatible strategy for the design of high performance photocatalysts with broad-spectrum response, while offering a promising system for the remediation of PPCPs.

1 Introduction

Solar-driven semiconductor photocatalysis is considered to be a promising strategy toward addressing current energy and environmental issues.^{1,2} Given that UV light accounts for only $\sim 4\%$ of the solar energy spectrum, the development and exploitation of novel and efficient photocatalysts that can harvest a broad portion of the solar spectrum (from UV to



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 $[\]dagger$ Electronic supplementary information (ESI) available. See DOI: 10.1039/ c9en00509a

near-infrared light (NIR)) remains a high-priority challenge.^{3,4} As a polymeric metal-free semiconductor with a suitable band gap of ca. 2.7 eV, graphitic carbon nitride (g-C₃N₄) has demonstrated immense capabilities for visible light-driven photocatalytic water splitting, CO2 reduction, and the environmental remediation of organic contaminants.⁵⁻⁷ While g-C₃N₄ has potential applications in various areas, its low specific surface area, rapid recombination of charge carriers, and inadequate visible-NIR photoabsorption seriously limit its photocatalytic performance.^{7,8} To remedy these drawbacks, various noble metals and transition metals have been integrated to optimize the photocatalytic activity of g-C₃N₄.^{9,10} However, high costs combined with the potential environmental pollution of these metals strongly hamper their practical application.¹¹ This situation has motivated the pursuit of low cost and environmentally compatible co-catalysts.¹² In this regard, carbon materials are promising candidates for solar based photocatalysis.

As a novel class of carbon nanomaterials, carbon quantum dots (CQD) have inspired great interest due to their unique properties, such as low toxicity, water solubility, superior optical properties, and electrical conductivity.^{13,14} Recently, CQD have been employed as efficient components in the design of C₃N₄ based photocatalysts. Kang et al.⁶ initially synthesized CQD/g-C₃N₄ (CQD/BCN) photocatalysts, and found that they demonstrated enhanced photocatalytic performance for water splitting. Subsequently, Fang et al.¹⁵ revealed that CQD could serve as an electron transfer mediator to facilitate charge separation. Our previous research showed that the photocatalytic performance of g-C₃N₄ for the environmental remediation of pharmaceutical and personal care products (PPCPs) could be significantly enhanced by N-doped carbon quantum dots (NCQD). Further mechanistic studies revealed that this augmentation may be attributed to the unique upconverted fluorescence properties and efficient charge separation of the NCQD.¹⁶ Although the CQD/BCN hybrid demonstrated high photocatalytic activity for visible light driven hydrogen production and environmental remediation, its catalytic performance under the broad-spectrum condition remained unsatisfactory due to its low specific surface area and number of active sites.¹⁷ To overcome these issues, the synthesis of CQD/ultrathin g-C₃N₄ nanosheets (CQD/UCN), or CQD/mesoporous g-C₃N₄ (CQD/mpg-C₃N₄) have been explored.¹⁸⁻²⁰ These porous and ultrathin nanostructures might serve to maximize the exposure of C₃N₄ active sites, thereby improving photocatalytic activity. However, the synthesis of porous and ultrathin nanostructures is timeconsuming and may result in undesirable environmental pollutants due to the use of soft- or hard-templates. Therefore, the development of a facile and environmentally compatible strategy for the synthesis of porous and ultrathin CQD/g-C₃N₄ composite nanostructures is a highly desired target toward the achievement of high performance broad-spectrum photocatalysts.

As an efficient optional strategy, heteroatom doping (O, S, P, and so on) has been typically applied to enhance the

photocatalytic activity of g-C₃N₄.²¹ For example, the boron atom-doped g-C₃N₄ that was prepared by Zou *et al.*⁷ showed improved photocatalytic degradation activities. Meng *et al.*²² revealed that the introduction of O atoms could significantly enhance the performance of C₃N₄ photocatalytic hydrogen generation and modify its electronic structure, while improving its charge transfer capabilities. Nevertheless, to the best of our knowledge the synthesis of oxygen-containing CQD/g-C₃N₄, which integrates both porous and ultrathin nanostructures, has not been reported to date. As a new type of emerging pollutant, PPCPs have recently attracted widespread attention due to their potential environmental hazards for aquatic organisms and human health.^{23,24} It is therefore imperative to develop cost-effective and environmentally compatible treatment methods for the remediation of PPCPs.

On the basis of these premises, we developed a facile twostep template-free thermal treatment strategy for the synthesis of an oxygen-containing ultrathin porous carbon quantum dots/polymeric carbon nitrogen metal-free composites (COD/ OUPCN). The characterization of the CQD/OUPCN hybrid verified that it was endowed with both ultrathin and porous nanostructures, as well as oxygen atoms. The ultrathin and porous nanostructures provided for a high population active sites, while the presence of CQD and oxygen atoms modified its electronic structure and improved charge separation. This synergistic modulation strategy resulted in remarkable broadspectrum activity for the photocatalytic degradation of PPCPs. The present work may lead to an environmentally compatible strategy for the design of high performance photocatalysts with broad-spectrum response, while offering a promising system for the remediation of PPCPs.

2 Experimental

2.1 Preparation of photocatalysts

2.1.1 Preparation of CQD. All chemicals were of analytical grade and used as received without further purification. The CQD were synthesized according to our previous work, with slight modifications.²⁵ In a typical experiment, 1.05 g of citric acid and 0.335 ml of ethylenediamine were dissolved in 10 ml of deionized (DI) water. Subsequently, the mixture was transferred to a Teflon-lined stainless steel autoclave where it underwent a hydrothermal reaction at 200 °C for 5 h. After cooling to room temperature, the resulting brown solution was centrifuged at 10 000 rpm for 30 min to remove any large particles. The solution was then dialyzed with a 10 kDa dialysis bag for 3 d to obtain a CQD aqueous solution.

2.1.2 Preparation of CQD/BCN photocatalyst. The CQD/ BCN photocatalyst was synthesized using a thermo polymerization method. Typically, 3.0 g of dicyandiamide and a predetermined volume of CQD solution were dispersed in 10 mL of DI water. Once the solution was evaporated at 70 °C, the obtained powder was heated to 550 °C for 3 h in N₂, with a ramp rate of 2.8 °C min⁻¹. The resultant CQD/BCN powder was collected through fine grinding and filtration. The CQD/ BCN samples with CQD contents of 0, 0.25, 0.5, 1.0, 2.0, and

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4.0 wt% were marked as CQD/BCN-0%, CQD/BCN-0.25%, CQD/BCN-0.5%, CQD/BCN-1.0%, CQD/BCN-2.0%, and CQD/BCN-4.0%, respectively. For comparison, bulk g-C₃N₄ (BCN) was prepared by directly heating dicyandiamide without the addition of the BCN solution.

2.1.3 Preparation of CQD/OUPCN photocatalyst. The CQD/ OUPCN was prepared *via* a facile thermal treatment process. Briefly, 0.5 g of CQD/BCN was placed in a porcelain boat, which was then transferred to a tube furnace and heated at 550 °C for 12 h, with a ramp rate of 1.0 °C min⁻¹ under flowing O₂/Ar. After cooling to room temperature, the final CQD/OUPCN product was obtained, which were marked as CQD/OUPCN-0%, CQD/OUPCN-0.25%, CQD/OPUCN-0.5%, CQD/OPUCN-1.0%, CQD/OPUCN-2.0%, and CQD/OPUCN-4.0%, respectively. Similarly, the OUPCN was prepared using the identical route with BCN as the precursor.

2.2 Characterization of photocatalysts

Scanning electronic microscopy (SEM, Hitachi S4800), transmission electron microscopy (TEM, JEM-2100HR), and atomic force microscopy (AFM, Bruker Dimension Edge) were employed to investigate the morphologies of the samples. The crystalline phases of the samples were characterized using an X-ray diffractometer with Cu Ka radiation (XRD, BRUKER D8 ADVANCE). The optical properties of asprepared photocatalysts were investigated through a UV-vis DRS spectrophotometer (UV-2450, Shimadzu) and FluoroMax-4 photoluminescence spectroscopy (HORIBA Jobin Yvon). The Fourier transform infrared spectroscopy (FT-IR) spectra was recorded using a Nicolet FTIR 6700 spectrophotometer (Thermo Electron Corporation) with KBr as the reference sample. X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo VG ESCALAB 250. Electron spin resonance (ESR) signals were obtained with a Bruker JES FA200.

2.3 Photocatalytic activity tests

The photocatalytic activity of the CQD/OUPCN was evaluated by decomposing IDM under broad-spectrum irradiation, in which a 500 W mercury lamp (Nanjing Xujiang electromechanical plant) and 350 W xenon lamp (Nanjing Xujiang electromechanical plant) were coupled with a 420 nm cutoff filter. A 350 W xenon lamp with a 290 nm cut-off filter, and a 9 W monochromatic light lamp (850 nm wavelength) (Shenzhen Lamplic Tech. Co., LTD.) were employed as the UV, visible, simulated sunlight, and near-infrared light irradiation sources, respectively. During the photocatalytic process, the catalysts (0.5 g L^{-1}) were introduced into quartz test tubes, followed by the addition of 50 mL of an aqueous 10 mg L⁻¹ IDM solution. Subsequently, the mixture was stirred for 30 min in darkness to attain adsorption equilibrium prior to light irradiation. At predetermined time intervals, aliquots of the samples were extracted and filtered through 0.22 µm Millipore filters to remove the photocatalyst. The concentrations of IDM in solution were analyzed by LC-20A high performance liquid chromatography (HPLC) (Shimadzu, Japan). Moreover, the photocatalytic degradation intermediates of the IDM were identified by Thermo Scientific Ultimate 3000 RSLC high resolution liquid chromatography, coupled with Q Exactive Orbitrap accurate mass spectrometry (HRAM LC-MS/MS). The detailed analytical method of HPLC and HRAM LC-MS/MS are depicted in Text S1 to S2 and Tables S1 to S3 in the ESI.[†]

2.4 Electrochemical analysis

A CHI660E electrochemical analyzer (CHI Shanghai, Inc.) was applied to obtain transient photocurrent measurements, electrochemical impedance spectroscopy (EIS), and Mott–Schottky plots of the samples, where Ag/AgCl were used as the reference electrode. The working electrodes were prepared by dip-coating method. 5 mg of the sample was suspended in 2 mL of anhydrous ethanol to produce suspension, which was then spin-coated onto a FTO glass electrode. The electrolyte was 0.1 M Na₂SO₄ aqueous solution. A 50 W xenon lamp (PLS-SXE300, Beijing Perfectlight Co. Ltd) with a 420 nm cut-off filter (100 mW cm⁻²) was used as the visible light source.

2.5 Calculation details

Spin polarized calculations were carried out with the Vienna *ab initio* simulation package (VASP) version 5.4.1, which is a plane wave density functional code.^{26,27} The detailed calculation method, as well as the model structure of the BCN, CQD/BCN, and CQD/OUPCN may be found in Text S3 and Fig. S1 in the ESI.[†]

The frontier electron densities (FEDs) of the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO), and point charge of IDM were calculated in Gaussian 09. The hybrid density functional B3LYP method with the 6-311G(d,p) basis set (B3LYP/6-311G+(d,p)) was applied.

3 Results and discussion

3.1 Characterization of as-prepared materials

As shown in Fig. 1A, the CQD/OUPCN was synthesized via a simple thermal treatment process, which involved the copolymerized synthesis of CQD/BCN, with the subsequent direct oxidation-etching of the CQD/BCN in ambient air. The carbon quantum dots were first synthesized according to the hydrothermal method, using citric acid and ethylenediamine as the precursors. TEM imagery revealed the rounded shape of the CQD with a mean size of ~ 4 nm (Fig. S2A in the ESI[†]). High resolution (HRTEM) images clearly revealed lattice fringes with spacings of 0.195 nm in the CQD, which corresponded to the (101) spacing of graphitic carbon (insert of Fig. S2A in the ESI[†]).⁶ Subsequently, the CQD was mixed with dicyandiamide and heated at 550 °C for 3 h to obtain the CQD/BCN composites. Finally, the oxygen-containing ultrathin porous CQD/OUPCN hybrids were obtained through the direct oxidation-etching of the CQD/BCN composites under O₂/Ar atmosphere at 550 °C for 12 h. Scanning electron



Fig. 1 (A) The synthesis process of the CQD/OUPCN; SEM images of (B) CQD/BCN-0.5%, (C) OUPCN, and (D) CQD/OUPCN-0.5%; TEM images of (E) CQD/BCN-0.5%, (F) OUPCN, and (G) CQD/OUPCN-0.5%; (H) HRTEM image, (I) AFM of CQD/OUPCN-0.5%; (J) nitrogen adsorption-desorption isotherms (insert: pore-size distribution) of BCN, CQD/BCN-0.5%, and CQD/OUPCN-0.5%.

microscopy (SEM) and transmission electron microscopy (TEM) images (Fig. S3 in the ESI⁺) show that the BCN morphology consisted of layer-like structures with smooth surfaces. The SEM and TEM images (Fig. 1B and E) of the CQD/ BCN-0.5% depict the attachment of CQD on the BCN surface with the average diameters of 3.8 nm. HRTEM image also clearly revealed lattice fringes with spacings of 0.194 nm COD, which corresponded well to the (101) spacing of graphitic carbon. Following the thermal treatment, the OUPCN and CQD/OUPCN-0.5% composites exhibited soft and loose tremella-like nanosheet morphologies with an abundance of pores (Fig. 1C, D, F and G). HRTEM images clearly indicated the presence of the CQD on the surfaces of the OUPCN, with a lattice fringe spacing of with the average diameters of 3.5 nm and a lattice fringe spacing of 0.197 nm (Fig. 1H, S4A-C in the ESI[†]). These results indicated that the thermal treatment process did not alter the CQD structure, which might have been due to the π - π stacking interactions between CQDs and OUPCN.^{28,29} Atomic force microscopy (AFM) images and associated height profiles in (Fig. 1I) revealed the average thickness of the CQD/OUPCN-0.5% to be ~6.9 nm, which was far thinner than that of the CQD/BCN-0.5% (55.3 nm, Fig. S5 in the ESI[†]). The Brunauer-Emmett-Teller (BET) surface area of the CQD/OUPCN-0.5% was determined to be 69.9 m^2 g⁻¹, which was much larger than that of the BCN (10.5 $m^2 g^{-1}$) and CQD/BCN-0.5% (7.6 $m^2 g^{-1}$) (Fig. 1J). Further, the pore size distributions of the samples in the insert of Fig. 1J reveal both the microporous and mesoporous structures of the CQD/OUPCN-0.5%.

FT-IR spectra (Fig. 2A) of the BCN show typical absorption peaks at 808.9 cm⁻¹, 1200–1700 cm⁻¹, and 3160 cm⁻¹, which

correspond to the vibration modes of s-triazine units, CN stretching vibrations, and N-H or O-H stretching vibrations, respectively.³⁰ No obvious change was observed following the loading of CQD, which might have been due to the small quantity of CQD. As anticipated, following the thermal treatment, the COD/OUPCN-0.5% showed an enhancement of the C-O stretching at 1211 cm⁻¹, revealing the incorporation of oxygen atoms.31 The chemical compositions and states of samples were further investigated by XPS. Fig. S6A in the ESI[†] reveals the presence of C, N, and O in all of the samples. The O 1s spectrum (Fig. 2B) of the BCN exhibited a broad peak at 532 eV, which corresponded to the chemisorbed oxygen of surface hydroxyls.^{32,33} A new peak appeared at 533.5 eV, assigned to the 1s-p* transition in the epoxide structure (C=O) was observed following the introduction of CQD, which was due to CQD resident carboxyl groups.¹⁶ A significant enhancement in the intensity of the peak at 533.5 eV could be observed subsequent to the thermal treatment process, indicating that oxygen atoms were involved in the C₃N₄ chemical composition. In addition, an obvious enhancement in the intensity of the peak at 533.5 eV could also be observed in the O1s of OUPCN, indicating that oxygen atoms mainly derived from the thermal treatment process of C₃N₄. The C1s of BCN (Fig. 2C) could be divided into three peaks centered at 284.9, 286.9, and 288.5 eV, which corresponded to graphitic carbon, C-OH, and N-C=N, respectively.²⁵ Significantly, the intensity of the C-OH peak increased from BCN to CQD/BCN-0.5% due to the presence of oxygencontaining functional groups in the CQD. The intensity of this feature further increased from CQD/BCN-0.5% to CQD/ OUPCN-0.5% following the sequence of calcination



Fig. 2 (A) FT-IR spectra, (B) high-resolution XPS spectra of O1s and (C) C1s, (D) XRD spectra of BCN, CQD/BCN-0.5%, and CQD/OUPCN-0.5%.

treatments, which was well consistent with the FTIR results. The N1s of all the samples showed four peaks centered at 398.9, 400.1, 401.4, and 404.9 eV, which were ascribed to the N species of C=N-C, C₃-N, N-H, and graphitic species (Fig. S6B in the ESI†).³⁴

XRD patterns of the as-synthesized BCN, COD/BCN-0.5%, and CQD/OUPCN-0.5% are shown in Fig. 2D. The distinct diffraction peaks of CQD/BCN-0.5% were well indexed to BCN (JCPDS Card No. 87-1526), which signified that the presence of CQD did not alter the BCN crystal structure. The diffraction peaks at 27.43° and 13.12°, indexed as (002) and (100) crystal facets, corresponded to the interlayer stacking of aromatic segments and the in-plane structural packing motif of tri-s-triazine units, respectively.³⁵ Compared with the CQD/ BCN, both the (100) and (002) peak of CQD/OUPCN become weaker. This is mainly attributed to the damage in the inplane repeated packing and the interlayer stacking after heat treatment. In addition, the (002) peak shifted from 27.43° to 27.62° following the thermal treatment process, which corresponded to the reduction of the interlayer distance of aromatic segments, from 0.325 nm for BCN, to 0.322 nm for CQD/OUPCN-0.5%. This was primarily attributed to the fact that the introduction of oxygen can strengthen the interactions between the adjacent layers.²² Previous studies have demonstrated that the introduction of COD and oxygen atoms can significantly impact the electronic band structure

of C₃N₄.^{16,25,36,37} Density functional theory (DFT) calculations was first performed to glean insights into the roles of the CQD and oxygen atoms. The total density of states (TDOS), projected density of states (PDOS), as well as the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the BCN, COD/BCN, and COD/ OUPCN are presented in Fig. 3. The band gap of BCN was theoretically calculated to be 1.2 eV, in which the HOMO and LUMO were dominated N and C atoms, respectively. It was found that the band gap of BCN was narrowed following the introduction of CQD. A further decrease in the CQD/BCN band gap was observed after the introduction of O atoms. These theoretical calculation results were consistent with previous theoretical results.^{36,37} Further, the electron density distribution and PDOS showed that the HOMO of CQD/BCN was predominantly distributed on the CQD, while the LUMO was located on the C₃N₄. In the CQD/OUPCN system, the HOMO was located on the C₃N₄, particularly on O atoms, while the LUMO was distributed on the CQD. Significantly, the HOMO and LUMO in both CQD/BCN and CQD/OUPCN systems were segregated, revealing the effective separation of photogenerated electron-hole pairs.

UV-vis reflectance spectroscopy was subsequently performed to investigate the optical properties of the asprepared samples. As shown in Fig. 4A, BCN revealed an adsorption edge at \sim 477 nm. Compared with the BCN, the



Fig. 3 The band structures and the corresponding DOS of (A) BCN, (B) CQD/BCN, and (C) CQD/OUPCN (the energy levels of CQD are distinguished by red line); the HOMO and LUMO of (D) BCN, (E) CQD/BCN, and (F) CQD/OUPCN (atom colour code: carbon (brown), nitrogen (grey), hydrogen (white)).



Fig. 4 (A) UV-vis absorption spectra of BCN, CQD/BCN-0.5%, OUPCN, and CQD/OUPCN-0.5%; (B) up-converted photoluminescence spectra of CQD; (C) Mott–Schottky plots, (D) band gaps, (E) schematic band structure evolution, (F) photoluminescence spectra, (G) ESR spectra, (H) transient photocurrent response, and (I) electrochemical impedance spectroscopy of BCN, CQD/BCN-0.5%, OUPCN, and CQD/OUPCN-0.5%.

COD/BCN-0.5% exhibited a remarkable red-shift of the absorption edge, from 477 nm to 607 nm and showed intense absorption in the visible light to near-infrared region. The optical properties of the CQD were further investigated by photoluminescence spectrometry. As shown in Fig. 4B, the CQD emitted shorter (350-650 nm) wavelengths, and upconverted photoluminescence under longer (500-900 nm) light wavelength excitation. The enhancement of CQD/BCN-0.5% light absorption, as well as the up-converted PL properties of the CQD revealed that the solar spectrum harvesting capability of the BCN could be significantly promoted following the introduction of the CQD. Interestingly, the adsorption edge of the CQD/OUPCN-0.5% exhibited a slight and unexpected blue-shift in contrast to the CQD/BCN-0.5%, which appeared to be inconsistent with the theoretical results. This blue-shift might have been due to the quantum confinement effects of the ultrathin structure of the CQD/OUPCN-0.5%.³⁸

Mott–Schottky plots at various frequencies were conducted to further study the electronic band structures of the asprepared samples (Fig. 4C). The flat potentials of BCN, CQD/ BCN-0.5%, and COD/OUPCN-0.5% were determined to be -1.65, -1.11, and -1.43 V versus the Ag/AgCl electrode, respectively, which corresponded to -1.43, -0.89, and -1.21 V versus the normal hydrogen electrode (NHE).³⁹ Generally, the conduction band (CB) position of n-type semiconductors is located near to the flat-band potential. Therefore, the CB of the BCN, CQD/BCN-0.5%, and CQD/OUPCN-0.5% were estimated to be -1.43, -0.89, and -1.21 eV, respectively. According to the Tauc approach, the band gap energy (Eg) of the BCN, CQD/BCN, and CQD/OUPCN were estimated to be 2.55, 2.05 and 2.17 eV, respectively (Fig. 4D).40 Therefore, the valence band (VB) positions of the BCN, CQD/BCN-0.5%, and CQD/ OUPCN-0.5% were calculated to be 1.12, 1.16, and 0.96 eV, respectively, based on their Eg and CB (VB = Eg + CB). The schematic diagrams of the energy band structures of the BCN, CQD/BCN-0.5%, and CQD/OUPCN-0.5% are conveyed in Fig. 4E. Accordingly, the positive shift of CB in the CQD/BCN-0.5% might have been due to the electron accumulation effect caused by the CQD. Simultaneously, the up-shift of CB and slight negative shift of VB in the CQD/OUPCN-0.5%

represented the combined influences of O-doping and the quantum confinement effects of the ultrathin structure. Note-worthily, the up-shift of the CB position in the CQD/OUPCN-0.5% was considered to be favorable for the generation of photoelectrons due to the high reducing capacity of CB photoelectrons.⁴¹

In order to explore the charge separation and recombination behaviors of the obtained samples, the photoluminescence (PL) spectra was recorded at an excitation wavelength of 325 nm, as depicted in Fig. 4F. It can be seen that the CQD/BCN-0.5% exhibited an obviously weaker PL emission peak compared with BCN, which indicated that the introduction of CQD facilitated electron transfer and inhibited the recombination of photogenerated electron-hole pairs. The intensity of the emission peak for the CQD/ OUPCN-0.5% decreased significantly compared with that of the CQD/BCN-0.5%, implying that the charge separation could be efficiently improved following the thermal treatment process. The electronic band structures of the as-prepared samples were subsequently investigated by room temperature electron paramagnetic resonance (EPR) technology. As shown in Fig. 4G, single Lorentzian lines were observed in all the samples, which corresponded to the unpaired electrons of carbon atoms in the aromatic rings.²⁰ The signal intensity was amplified subsequent to CQD loading, which further increased significantly following the sequence of calcination treatments. This certifies that the electron mobility is promoted in the π -conjugation system of carbon nitride, potentially due to the extended delocalization of the π -conjugated system and mobility of spins following the introduction of CQD, and the subsequent thermal treatments.⁴²⁻⁴⁴ Such this

delocalization of the π -conjugated system would lead to the increase of charge carrier densities, which was well consistent with the results of the electron density distribution and PDOS analyses. The photoinduced charge transfer behaviors were then confirmed by electrochemical experiments Fig. 4H. As expected, the COD/OUPCN-0.5% demonstrated much higher photocurrent intensity than did BCN and CQD/BCN-0.5% under visible light irradiation, which suggested higher separation and transfer efficiencies of photo-induced charges for the CQD/OUPCN-0.5%. EIS measurements in Fig. 4I revealed that the arc radii of the Nyquist plots of the CQD/ OUPCN-0.5% were much smaller than that of the BCN and CQD/BCN-0.5%, which indicated that the CQD/OUPCN-0.5% possessed lower interfacial charge-transfer resistance that allowed for faster charge transfer. In summary, the incorporation of CQD effectively enhanced the optical and electrical properties of the BCN. Subsequent to simple thermal treatment, the generation of O atoms and ultrathin structures provided additional active sites and optimized the electronic band structure of the CQD/BCN-0.5%, which might enhance the photocatalytic activities of the CQD/OUPCN-0.5%.

3.2 Photocatalytic performance

The photocatalytic performance of the as-prepared samples was evaluated through the photocatalytic degradation of IDM. As shown in Fig. 5A there was no obvious change in the concentration of IDM when exposed to visible light, which implied the photochemical stability of the IDM. The BCN exhibited a degradation efficiency of only 23.4% in under 18 min of visible light irradiation. In contrast, the CQD/BCN-



Fig. 5 (A) Photocatalytic activity of the photocatalysts based on the photocatalytic degradation of IDM under visible light irradiation; kinetic rate constant of IDM over different (B) loading amount of CQD, (C) light source irradiation; (D) recycling runs of the photocatalytic activity of the CQD/ OUPCN-0.5% toward IDM photodegradation under visible light irradiation.

0.5% exhibited considerably improved photocatalytic activity, with a degradation efficiency of 62.6%. Significantly, the photocatalytic performance was further enhanced following the thermal treatment. Almost 10 mg L⁻¹ of IDM could be completely degraded after 18 min of visible light irradiation in the presence of CQD/OUPCN-0.5%. Notably, the degradation of IDM followed the pseudo-first order reaction kinetics model. Concretely, the photocatalytic activity increased from 0.035 to 0.263 min⁻¹ with higher CQD loadings (0 to 0.5 wt%). The CQD/OUPCN with 0.5% CQD exhibited the highest photocatalytic performance, which had 5.1 and 18.5-fold higher efficiency than CQD/BCN and BCN, respectively (Fig. 5B). However, further increasing the amount of CQD, from 0.5 to 4.0 wt% led to a decreased degradation efficiency, from 0.0263 to 0.0922 min⁻¹. This inhibition of photocatalytic activity might have been attributed to the optical shielding effect of the CQD, which could reduce the number of photons required for C₃N₄. The photocatalytic performance was then tested under UV light, visible light, NIR light, and simulated sunlight irradiation to evaluate the broad-spectrum response properties of CQD/OUPCN-0.5%. As shown in Fig. 5C, the BCN and OUCN showed poor photocatalytic performance under UV light, visible light, and simulated sunlight irradiation. Further, no IDM degradation could be observed when they were exposed to longer wavelengths (>550 nm). On the contrary, CQD/BCN-0.5% and CQD/OUPCN-0.5% exhibited superior photocatalytic performance under broad-spectrum irradiation. This excellent activity might have been due to the superior up-conversion photoluminescence and efficient charge transfer properties of the CQD. Particularly, CQD/ OUPCN-0.5% revealed optimal photocatalytic performance toward the degradation of IDM, which indicated that synergis-

tic effects between the CQD, O atoms, and ultrathin porous structures would be generated in the CQD/OUPCN-0.5%. In order to further investigated the significant roles of oxygen atoms and ultrathin porous nanostructures during the photocatalytic process, an ultrathin porous carbon quantum dots/ polymeric carbon nitrogen without oxygen atoms (COD/ UPCN-0.5%) was prepared according to the previous work.²⁰ As shown in Fig. S7 in the ESI,† CQD/UPCN-0.5% existed a BET surface area of 60.3 m² g⁻¹, which was quite close to CQD/OUPCN (69.9 m² g⁻¹). It can be found that 80% of IDM could be degraded by CQD/UPCN-0.5% after 18 min of visible light irradiation, which was lower than by CQD/OUPCN-0.5% $(\sim 100\%)$. This results further revealed the significant role of oxygen atoms in enhancing photoactivity of CQD/OUPCN. In addition, a 97.8% IDM removal rate could be obtained after a five cycles experiment (Fig. 5D). No distinct change of XRD patterns is found for the recycled samples, indicating the high stability of the CQD/OUPCN-0.5% (Fig. S8 in the ESI†).

3.3 Photocatalytic mechanism

3.3.1 Predominant reactive species. In order to investigate the photocatalytic mechanism of the CQD/OUPCN-0.5%, the ESR spin-trap technique was employed by using DMPO as a radical trapper. As shown in Fig. 6A and B, the characteristic four-line ESR signals for DMPO-'OH and DMPO-O₂⁻⁻ could be observed in the CQD/OUPCN-0.5% photocatalytic system, which indicated the generation of 'OH and O₂⁻⁻. Furthermore, the CQD/OUPCN-0.5% showed much stronger ESR signals for both DMPO-'OH and DMPO-O₂⁻⁻ than that of the CQD/BCN-0.5%, which demonstrated that the introduction of O atoms and the ultrathin porous structure would improve the



Fig. 6 ESR spectra of the (A) DMPO- O_2^- adducts and (B) DMPO- $-O_1$ recorded with the CQD/BCN-0.5% and CQD/OUPCN-0.5% under visible light irradiation; (C) kinetic rate constant of IDM over different scavengers; (D) the mineralization of IDM during CQD/OUPCN-0.5% photocatalytic degradation process.

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generation of additional OH and O_2^{-} ; thus, enhancing photocatalytic activity. To further identify the contribution of the reactive species (RS) involved in the IDM degradation process over the CQD/OUPCN-0.5% photocatalytic system, a scavenger-quenching experiment was performed using isopropanol (IPA), p-benzoquinone (BQ), K₂Cr₂O₃, and Na₂C₂O₄ as the 'OH, O2', photoelectron (e), and photohole (h), scavengers, respectively.45 It can be observed in Fig. 6C that with IPA and Na₂C₂O₄ incorporated into the photocatalytic system, the degradation kinetic constant of IDM over CQD/OUPCN-0.5% showed a slight inhibition. However, with the addition of BQ to scavenge the O_2^{-} , the degradation rate of IDM exhibited an obviously decrease, suggesting the key role of O2' during the CQD/OUPCN-0.5% photocatalytic process. In addition, it was observed that the IDM photodegradation process was almost restricted when K₂Cr₂O₃ was applied, revealing that e⁻ played a critical role in the IDM photocatalytic process. Notably, previous works have confirmed that O2may be generated by photoelectrons through the trapping of dissolved oxygen.

3.3.2 Mineralization and transformation pathways. Generally, the RS generated in the photocatalytic process attacked organic contaminants, leading to the formation of intermediate and mineralized products. To obtain a further elucidation into the kinetics of the CQD/OUPCN-0.5% photocatalytic process, HRAM LC-MS/MS was performed to identify the IDM degradation intermediates. As revealed in Fig. 7 and S9 and S10 in the ESI,† six products could be identified based on mass spectrum analysis. Further, the extent of mineralization of the IDM in Fig. 6D revealed that 51.4% of the TOC was removed following 18 min of visible light irradiation. This result confirmed that IDM and its transformation intermediates were decomposed to CO_2 and H_2O by RS during the CQD/OUPCN-0.5% photocatalytic process.

Theoretical calculations, including the highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), as well as the Mulliken charge distribution of the IDM were performed to qualitatively predict the primary reactive sites for RS attack.⁴⁶ According to the frontier orbital theory, RS likely attacked positions with a high electron



Fig. 7 (A) The optimize structure, (B) HOMO, (C) LUMO, and (D) the charge distribution of IDM; (E) possible transformation pathways of IDM during CQD/OUPCN photocatalytic degradation process.



Fig. 8 Schematic photocatalytic mechanism for the CQD/OUPCN under broad-spectrum light irradiation.

density in HOMO and LUMO. Particularly, O2⁻ typically attacked the positions with a more positive point charge. It can be observed in Fig. 7A-D that 41O, 18C, 15N, 17C, and 16C showed high electron density for both HOMO and LUMO. Among them, 18C also demonstrated the most positive point charge, indicating that these positions would be preferentially attacked by RS. Based on the detection of photodegradation intermediates and DFT calculations, potential photocatalytic degradation pathways of IDM through the CQD/OUPCN photocatalytic process were proposed. In summary, four major pathways were involved in the photocatalytic process (Fig. 7E). The first pathway began with the cleavage of a C-N bond, leading to the formation of m/z 115 and m/z 218, which could be further oxidized into m/z 209. Pathway 2 was initiated by the cleavage of the carboxylic group, giving rise to a methyl radical,⁴⁷ and m/z 343 would be generated through the subsequent oxidation of this methyl radical. In terms of pathway 3, the IDM would undergo an addition reaction of the 16C=17C double bond and the hydroxylation reaction of the chlorobenzene ring, resulting in the generation of m/z 391. Pathway 4 was initiated by a RS attack on the 16C=17C and 2C-16C, giving rise to m/z 305. All of these intermediates and IDM would be further oxidized by RS, finally leading to mineralization.

3.3.3 Proposed mechanism. On the basis of the above results, a broad-spectrum photocatalytic mechanism for the CQD/OUPCN was proposed, as shown in Fig. 8. Under broadspectrum solar light irradiation, the UV light and a portion of visible light could be absorbed directly by the OUCN. Other visible light and NIR with long wavelengths could be converted to short wavelength light for OUCN adsorption due to the up-converting PL property of CQD. These photon absorptions would lead to the generation of e⁻ and h⁺ that remained in the CB and VB of the CQD/OUPCN, respectively. The presence of CQDs and O atoms could change the electron density distribution of the OUPCN, thereby restricting the recombination of e^{-}/h^{+} pairs. On the other hand, the ultrathin porous structure of the CQD/OUPCN allowed e⁻ to transfer from the interior to the surface of the photocatalyst. Subsequently, the e⁻ in CQD/OUPCN would

readily combine with the oxygen in solution to yield O_2^{-} . As the standard redox potential of VB is more negative than that of 'OH/H₂O (+2.27 eV vs. NHE) and 'OH/OH⁻ (+1.99 eV vs. NHE) OH⁻/'OH, the h⁺ in CQD/OUPCN were opposed to oxidizing OH⁻ or H₂O into 'OH.⁴⁸ Therefore, the 'OH appearing in the CQD/OUPCN system might be generated through O_2^{-} via the following reactions.⁴⁹

$$O_2^{-} + H_2O \rightarrow OOH + OH^{-}$$

 $\rm H_2O + 'OOH + e^- \rightarrow 'OH + OH^-$

Finally, the IDM could be easily absorbed to the surface of the CQD/OUPCN due to the large number of active sites of ultrathin porous structure. In turn, the IDM were attacked by the RS, leading to decomposition and complete mineralization.

4 Conclusions

In summary, we demonstrated a facile and environmentally compatible template-free thermal treatment strategy, to synthesize an oxygen-containing ultrathin porous CQD/OUPCN composite for the enhanced broad-spectrum photocatalytic degradation of PPCPs. The ultrathin porous structure had the capacity to provide additional active sites, while the CQD and O atoms could optimize the electronic band structure, and thus improve the charge transfer of the COD/OUPCN. In addition, the up-converted PL properties of the CQD endowed the CQD/OUPCN with a broad-spectrum response. Therefore, the as-prepared CQD/OUPCN demonstrated remarkable photocatalytic activity for the degradation of IDM under UV, Vis, and NIR irradiation. The ESR and RS quenching results revealed that O2⁻ played a key role during the CQD/OUPCN photocatalytic process. The identification of transformation intermediates and DFT calculations indicated that IDM could be attacked by RS, leading to its decomposition and final mineralization.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 21377031 and 21677040), Science and Technology Planning Project of Guangdong Province (No. 2017A050506052).

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