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Constructing atomic layer $g-C_3N_4-CdS$ nanoheterojunctions with efficiently enhanced visible light photocatalytic activity[†]

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Ultrathin two dimensional (2D) materials have triggered extensive interest for their exceptional properties and potential applications. Herein, atomic layer graphitic carbon nitride $(g-C_3N_4)$ was obtained by a simple ultrasonic exfoliation approach, and cadmium sulfide (CdS) nanoparticles were successfully grown on these ultrathin $g-C_3N_4$ nanosheets (UCNNS) *via* a facile solvothermal method. The as-prepared UCNNS–CdS nanocomposite exhibits significantly enhanced photocatalytic activity for methyl orange (MO) degradation under visible light irradiation. The enhancement of the photocatalytic activity should be attributed to the well-matched band structure and intimate contact interfaces between the UCNNS and CdS, which lead to the effective transfer and separation of the photogenerated charge carriers. The mechanism for the photodegradation of MO by the composite was also investigated in this study. This study highlights the potential applications of atomic layer $g-C_3N_4$ based photocatalysts, and we hope our work may provide a new insight for the construction of photocatalysts with efficient visible light activity.

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1. Introduction

2D nanosheet materials, which consist of a monolayer or a few atomic layers, have aroused a broad interest in different research areas owing to their unique optical and electronic properties, as well as their large surface area.¹⁻⁵ These merits render 2D nanosheet materials promising candidates for catalysis, energy storage, environmental remediation and water splitting applications.⁴⁻⁸ Among various 2D materials, graphene, which exhibits superiority in properties such as its high carrier mobility, large specific surface area and quantum hall effect, is the most famous and widely investigated.^{2,3} In particular, graphene-based photocatalysts generally show remarkably enhanced photocatalytic performance due to the accelerated transfer and promoted separation of photo-generated carriers by graphene.9-11 However, pristine graphene is a zero bandgap material and does not show any photocatalytic activity, serving just as an electron acceptor or transport intermediate in a photocatalytic reaction.^{2,12} In addition, excess graphene blocks incident light and hampers the external quantum efficiency of a photocatalyst.^{13,14}

Recent years have witnessed a burst of research into g-C₃N₄. This novel metal-free photocatalyst possesses a proper band structure that is suitable for water splitting and photocatalytic degradation of organic pollutants under visible light.15-19 Nevertheless, the photocatalytic efficiency of bulk g-C₃N₄ is far from satisfactory due to its high recombination rate of photogenerated charge carriers and relatively small surface area.^{20,21} Noticeably, as a π -conjugated material, g-C₃N₄ has not really been viewed from the perspective of a 2D material.^{21,22} Actually, recent works have reported that ultrathin g-C₃N₄ nanosheets, obtained by peeling off the bulk counterpart, present fascinating prospects for improving the transfer and separation of photoexcited charge carriers.^{12,21-24} Compared to bulk g-C₃N₄, there are three main apparent advantages of ultrathin nanosheets: (1) the specific surface area is larger than the bulk one, and can provide abundant reactive sites.^{21,22} (2) The ultrathin nanosheet structure can remarkably reduce the distance to transfer the photoexcited carriers from one place to the interface.^{12,21-23} Therefore, there is an improvement in the transportation and separation of the photogenerated electron-hole pairs. (3) The shift-up conduction and shift-down valence bands of the ultrathin nanosheets can strengthen the reduction and oxidation abilities of the electrons and holes, respectively.²³ However, before practical applications can be considered, the light absorption capacity of g-C₃N₄ still needs further improvement as this material can only absorb light with a wavelength shorter than 460 nm, which accounts for a small part of the whole visible light region.^{16,25,26}

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CdS has long been one of the most attractive visible light active semiconductor photocatalysts due to its efficient absorption of visible light (up to 520 nm or even longer) and suitable band edge position.^{11,27,28} In light of this, CdS can act as an excellent photosensitizer in many wide bandgap photocatalyst systems like CdS-TiO₂^{29,30} and CdS-ZnO.^{31,32} Regrettably, there are still two large barriers that prevent the wide application of pure CdS. Firstly, the recombination rate of the photo-induced electron-holes is undesirably high.^{11,17} Worse still, S²⁻ in CdS tends to be oxidized by photoexcited holes upon strong irradiation, which is known as the photocorrosion phenomenon.^{27,33} Hence, numerous works focus on addressing the intrinsic disadvantages of CdS. Approaches such as using a sacrificial agent and the loading of a proper co-catalyst have been adopted and have proven to be effective.^{11,33-35} Promisingly, fabricating heterojunctions between two semiconductors is another strategy to tackle both of these barriers. Efficaciously transferring holes from the CdS domain can alleviate the accumulation of holes, thus inhibiting charge carrier recombination and simultaneously achieving photocorrosion.^{30,36} When reviewing the band alignment of CdS and g-C₃N₄, it is fortunate to find that their band edges match quite well to facilitate the separation of e-h pairs. Though some very recent works have demonstrated the validity of the above-mentioned strategy by synthesizing g-C₃N₄-CdS composites via different preparation methods,^{17,33,37,38} the unique properties of atomic layer g-C₃N₄ were, without exception, not taken into account or investigated in-depth in these works. However, the novel characteristics of these ultrathin g-C₃N₄ nanosheets (UCNNS) are probably extremely important for boosting the photocatalytic activity considering the great success of similar graphene coated photocatalysts. Hitherto, there is no report for the in situ growth of CdS nanoparticles on UCNNS.

In this study, UCNNS were obtained through thermal condensation of urea followed by a facile ultrasonic method. CdS nanoparticles were then grown in situ on the UCNNS to fabricate nano-heterojunctions via a solvothermal method, during which the UCNNS provided many binding sites for anchoring CdS nanoparticles. In addition, intimate contact interfaces between the UCNNS and CdS were also developed. Consequently, the composite exhibits significantly enhanced capability to degrade MO due to the dramatically promoted charge separation. It was observed that the optimal photocatalytic activity of the composite with 10 wt% UCNNS loading was about 6 and 50 times higher than pure the CdS and UCNNS, respectively, for the degradation of MO, and the photostability of CdS was also apparently reinforced. Moreover, the active species of the composite for the degradation reaction were investigated systematically. This study highlights the potential applications of atomic layer g-C₃N₄ based photocatalysts, and it is hoped that the present work may provide a new insight for the construction of stable photocatalysts with efficient visible light activity.

2. Experimental section

2.1 Materials

All reagents in this work were AR grade and used without further purification. Urea $((NH_2)_2CO)$, cadmium acetate dihydrate

 $(Cd(CH_3COO)_2 \cdot 2H_2O)$, thioacetamide (TAA), ethyl alcohol and scavengers isopropanol (IPA), ammonium formate (AF) and *p*-benzoquinone (PBQ) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). The deionized water used in this work was from local sources.

2.2 Synthesis of the photocatalysts

Metal-free g-C₃N₄ nanosheets were prepared according to a reported method.²⁰ In detail, 5 g of urea was put into an alumina combustion boat, then heated to 550 °C at a heating rate of 2 °C min⁻¹ and kept at 550 °C for 4 h, followed by cooling to room temperature. The whole process was performed under a helium (He) gas flow (100 mL min⁻¹). The product was ground to a powder and washed with deionized water. The as-prepared g-C₃N₄ was then collected in a beaker and 100 mL ethanol was added. After ultrasonication for 8 h, the as-prepared g-C₃N₄ was exfoliated into ultrathin g-C₃N₄ nanosheets (UCNNS). When the ethanol had completely evaporated the UCNNS were obtained.

Bulk g-C₃N₄ (BCN) was prepared according to a reported procedure with some modifications.²⁴ In detail, melamine was heated at 550 °C for 4 h in air at a ramp rate of 2 °C min⁻¹, and then cooled to room temperature.

UCNNS-CdS composites were synthesized via a one-step procedure. A measured amount of UCNNS was redispersed in 20 mL ethanol and ultrasonicated again for 1 h. The suspension with 5 mmol Cd(CH₃COO)₂·2H₂O was added to the 20 mL ethanol solution, and was then stirred for 5 h to form a homogeneous suspension. After that, a 20 mL ethanol solution with 5 mmol TAA was added to the above mixed suspension and stirred for another 30 min. The obtained suspension was autoclaved in a 100 mL Teflon-lined stainless steel vessel at 180 °C for 12 h. After cooling to room temperature, the as-prepared yellow product was washed with water and ethanol several times and collected by centrifugation. Finally, the obtained sample was dried in a vacuum oven at 80 °C. The UCNNS-CdS composites with weight ratios of the UCNNS to CdS of 3, 5, 10, 15 and 20 wt% were marked as 3CN, 5CN, 10CN, 15CN and 20CN, respectively. The 10 wt% BCN/CdS was synthesized by the same procedure without an ultrasonication step, and the obtained product marked as 10BCN.

2.3 Characterization

The crystal structures of the as-prepared samples was identified by X-ray diffraction using a Bruker D8 ADVANCE X-ray diffractometer with Cu K_{α} radiation ($\lambda = 0.15418$ nm) which operated at 40 kV and 40 mA. The scan rate was $0.05^{\circ} 2\theta \text{ s}^{-1}$. Scanning electron microscopy (SEM) images were obtained using a HITACHI SU8000 field-emission scanning electron microscope. Atomic force microscopy (AFM, Nanoscope Multimode IIIa microscope, Veeco Instruments) was used to observe the thickness of the 2D g-C₃N₄ nanosheets. Transmission electron microscopy (TEM, Tecnai G2 F20 S-TWIN, FEI company), using a field emission gun which operated at 200 kV, was used to investigate the morphologies of the samples. Infrared spectroscopy (IR) analysis was performed on a Nicolet Nexus 670 FT-IR spectrometer. X-ray photoelectron spectroscopy (XPS) analysis

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was done on an ESCALAB 250 photoelectron spectrometer (Thermo Fisher Scientific) with an Al K_{α} X-ray beam (1486.6 eV). Total organic carbon (TOC) measurements of the degradation solution after 16 min of irradiation were conducted on a TOC analyzer (TOC-VCPH, Shimadzu). A Varian Cary-500 spectrophotometer with BaSO₄ as a reference was employed to obtain diffuse reflectance spectra of the samples. Photoluminescence (PL) spectra were recorded on a Varian Cary-Eclipse 500 with an excitation wavelength of 325 nm. Nitrogen adsorption and desorption isotherms were recorded on a Micrometrics ASAP 2020 analyzer. During the degassing process, the samples were held at 180 °C for 5 h. Electrochemical analysis was conducted using a ZEN-NIUM electrochemical workstation (Zahner, Germany) with a conventional three-electrode system. The reference and counter electrodes were Ag/AgCl and Pt plate, respectively, and 0.2 M Na_2SO_4 (pH = 6.8) aqueous solution served as the electrolyte. 5 mg of the as-prepared sample was dispersed in 0.5 mL N,N-dimethyl formamide (DMF) solution by sonication, and the slurry was then evenly spread onto a indium tin oxide (ITO) conductor glass substrate to serve as a working electrode. A 300 W xenon lamp was used to provide a visible light source equipped with a UV cut off filter ($\lambda \ge 420$ nm). For electrochemical impedance spectrscopy (EIS) measurements, the amplitude of the sinusoidal wave was 10 mV, and the frequency ranged from 4 MHz to 0.01 Hz.

2.4 Photocatalytic activity test

The photocatalytic activity of the as-prepared samples was evaluated by the photodegradation of MO with a concentration of 5 mg L⁻¹ under visible light. A PLS-SXE 300 lamp (Beijing Perfectlight Co., Ltd.), with a UV cut-off filter ($\lambda \ge 420$ nm), served as the light source. 30 mg of the photocatalyst was added to a quartz vial with 80 mL MO solution (5 mg L⁻¹). Before irradiation, the suspension was stirred for 30 min in the dark to establish an adsorption–desorption equilibrium. During the irradiation period, 3 mL of the solution was quickly extracted at a definite time interval. After that, the solution was centrifuged at 12 000 rpm to remove the catalyst completely and analyzed on a UV-vis spectrometer (Cary-50, Varian Co.).

The recycling photocatalytic activity test was performed as follows. After the 1st run of the reaction, the catalyst was cleaned and collected for the next run. Similarly, 3rd and 4th runs were carried out. Controlled activity experiments were performed in a similar way to the above photocatalytic activity experiment with different radical scavengers added to the reaction system.

3. Results and discussion

Fig. 1 shows the XRD patterns of pure CdS, pure UCNNS and their composites with different amounts of the UCNNS. For pure g- C_3N_4 , the distinct diffraction peak at 27.4°, corresponding to the (002) peak in JPCDS 87-1526, represents the interlayer stacking of the conjugated aromatic groups. The weak peak, corresponding to the (100) plane at about 13°, is attributed to the in-plane structure of tri-*s*-triazine units^{20,22,39}



Fig. 1 XRD patterns of pure CdS, pure UCNNS, and UCNNS-CdS composites.

(see Fig. S1, ESI[†]). Compared with BCN, both the (002) and (100) peaks of the UCNNS display a markedly reduced intensity and are broader. This indicates that the interlayer structure of the UCNNS was destroyed. This is in agreement with the g-C₃N₄ nanosheets reported in the literature.^{20,22,39-41} In addition, the layer number of the g-C₃N₄ nanosheets can be evaluated from the (002) diffraction peak using the Scherrer formula.42,43 According to the Scherrer formula, the average thickness of the UCNNS is estimated to be 1.0 nm. Therefore, the layer number of the UCNNS is about 2-3, 24,44 and this can be further confirmed by TEM and AFM, which will be discussed later. The XRD pattern of pure CdS possesses three discernible diffraction peaks at 26.6°, 43.9° and 52.0°, which can be attributed to the (111), (220) and (311) peaks of the face-centered cubic structure of CdS (JCPDS 89-0440), respectively. The XRD patterns of the UCNNS-CdS composites show no difference to pure CdS due to the low X-ray diffraction intensity of the g-C₃N₄ nanosheets and have characteristic peaks overlapping with CdS. Nevertheless, the presence of g-C₃N₄ nanosheets in the composites can be confirmed by SEM, TEM, FTIR and XPS analyses.

The detailed morphologies and crystal structures of the UCNNS, CdS and as-prepared composites were directly analyzed by SEM and TEM/HRTEM. As shown in Fig. 2a, pure $g-C_3N_4$ is composed of nanosheets with a laminar structure. In the TEM images (Fig. 2b and Fig. S2, ESI[†]), the UCNNS look like a silk veil, similar to graphene or graphene oxide that have been reported,^{3,45} and look transparent due to their thin nature. The thickness of the g-C3N4 nanosheets can be further determined by atomic force microscopy (AFM). Fig. 2c and d reveal that the average thickness of the obtained g-C₃N₄ nanosheets is approximately 0.8 nm, which indicates that the g-C₃N₄ nanosheets are composed of only about two C-N layers.24,44 Compared with the as-prepared bulk g-C₃N₄, which consists of an irregular thick block-like material (Fig. S3, ESI†), it is apparent that the as-prepared UCNNS possess a larger specific surface area (see Table S1, ESI⁺). The morphological features of the bare CdS nanoparticles were investigated by SEM. As shown in Fig. 2e, the CdS nanoparticles are significantly aggregated together to form clusters. As shown in Fig. 2f, after introducing CdS through the solvothermal approach, the CdS nanoparticles are dispersed



Fig. 2 (a) SEM image and (b) TEM image of pure UCNNS. (c) AFM image and (d) corresponding thickness analysis of pure UCNNS. (e) SEM image of pure CdS, (f) SEM image of the 10CN sample. (g) TEM image and (h) HRTEM image of the circle in (g) for the 10CN sample.

on the UCNNS. The TEM and HRTEM images (Fig. 2g and h, respectively) intuitively show that the UCNNS are decorated with CdS nanoparticles, and a lattice spacing of 0.337 nm can be assigned to the (111) crystal face of CdS (JCPDS 89-0440). These results indicate that the CdS nanoparticles spread onto the UCNNS to form nanoheterojunctions. The 2D g-C₃N₄ nanosheets can provide anchor sites to immobilize the CdS, which can partially prevent aggregation of the CdS nanoparticles.¹¹ After formation of the nano-heterojunctions, the specific surface area of the composites increases to some extent compared with CdS (see Fig. S7 and Table S1, ESI†). Based on the above results, a mechanism for the fabrication of UCNNS–CdS composites can be proposed and is illustrated in Scheme 1.

To investigate the interaction between CdS and the UCNNS, FTIR spectroscopy was carried out. FTIR spectra of pure CdS, pure UCNNS, and UCNNS–CdS composites are compared in Fig. 3. For CdS, the peaks between 1100 and 1650 cm⁻¹ are ascribed to the Cd–S bond and the band at 1618 cm⁻¹ is



Scheme 1 Mechanism for the formation of the UCNNS-CdS nanocomposites.



Fig. 3 FTIR spectra of CdS, UCNNS, and UCNNS-CdS nanocomposites.

attributed to the O-H bending vibration of surface-absorbed water molecules. For pure UCNNS, the characteristic peaks that appear around 1246, 1316, 1422, 1569 and 1641 cm^{-1} can be assigned to the typical stretching modes of CN heterocycles in g-C₃N₄.^{12,41} The representative breathing mode of the triazine units in pure g-C₃N₄ nanosheets can be observed at 813 cm⁻¹.^{12,17,41} After constructing nanojunctions between CdS and the UCNNS, all of the characteristic bands of CdS are present in the composites because of its high percentage. Additionally, the characteristic peaks for the g-C₃N₄ nanosheets can also be observed in the composites. The characteristic bands of g-C₃N₄ gradually increase with the increase in the g-C₃N₄ nanosheet ratio in the composites. As shown in Fig. S8 (ESI[†]), the corresponding peaks for the C-N stretching vibration mode and triazine units for the mixed-10CN sample show no discrepancies with the pure UCNNS. The mixed-10CN sample is simply formed by mechanical mixing of the UCNNS with CdS. For 10CN, a 10 cm⁻¹ red shift occurs at 813 cm⁻¹, and the relevant FTIR band for the C-N stretching vibration is also weaker than the mixed-10CN. This indicates that an interaction may have developed between UCNNS and CdS, which weakens the force between the C and N atoms. The FTIR results of the



Fig. 4 X-ray photoelectron spectra of (a) C 1s, (b) N 1s, (c) Cd 3d and (d) S 2p in the samples.

as-prepared samples are well in accordance with the SEM and TEM/HRTEM images, and all indicate that the UCNNS-CdS composites are successfully obtained.

To further confirm the existence of g-C₃N₄ in the composites and study their surface chemical state, XPS measurements were conducted. Fig. 4a-d indicate that the 10CN sample contains C, N, Cd and S elements. For the UCNNS sample, the C 1s spectrum can be fitted with three peaks at 284.6 eV, 285.8 eV and 288.2 eV (Fig. 4a, top). The peak at 284.6 eV is related to surface adventitious carbon.³⁹ The peak centered at 288.2 eV can be attributed to sp² C bonded to N-containing aromatic rings (N-C=N), which represents the carbon species in g-C₃N₄.^{33,38} The small peak (285.8 eV) is ascribed to the sp³-bonded carbon species from defects on the g-C₃N₄ surface.^{33,38} Three peaks at 399.0 eV, 400.3 eV and 401.5 eV, can be identified in the N 1s spectrum for the UCNNS (Fig. 4b, top). The binding energy of 399.0 eV is derived from the sp²-bonded N in the triazine units (C–N=C) in g-C₃N₄. The weak peaks at 400.3 and 401.5 eV originate from tertiary nitrogen N-(C)3 units and amino groups (C-N-H), respectively.33,37,38,46 From Fig. 4a and b, we can see that the peak for C 1s (285.8 eV) shifts to a higher binding energy when UCNNS are combined with CdS, and the two peaks at 400.3 and 401.5 eV for N 1s shift to lower binding energies. The shift in binding energy suggests an electronic interaction between the UCNNS and CdS,47 which is consistent with the IR results. In Fig. 4c and d, the XPS peaks at 405.1 and 411.9 eV, and the peaks at 161.1 and 162.2 eV, are ascribed to Cd 3d and S 2p in the 10CN and bare CdS samples, respectively.33,37,38

The optical performances of the as-prepared samples were investigated by UV-vis diffuse reflectance spectroscopy (DRS). As shown in Fig. 5, the absorption edge for pure UCNNS is about 420 nm, which is shorter than the 450 nm of the as-prepared BCN. This blue-shift is caused by the quantum size confinement effect when reducing the dimensionality of the material.²⁵ The absorption band edge of pure CdS is 520 nm,



Fig. 5 UV-vis spectra of the as-prepared samples.

which sensitizes the UCNNS to strengthen the optical response.¹⁷ All the as-prepared nanocomposites show broader absorption in the visible region compared to the UCNNS, and slightly narrower absorption than CdS. These observations for the composites are attributed to the interaction between CdS and the UCNNS.³⁷ The interaction probably plays a significant role in improving the separation of the photogenerated electron-hole pairs to enhance the photocatalytic activity. As a result, the composites may have a higher photocatalytic activity than pure UCNNS and CdS.

The photocatalytic performances of the CdS–UCNNS composites were evaluated *via* MO photodegradation tests under visible light ($\lambda \ge 420$ nm) illumination. Each of the photodegradation reactions was carried out after 30 min adsorption equilibrium in the absence of light. The photocatalytic activity for each photocatalyst is demonstrated in Fig. 6a. As we can see from the figure,



Fig. 6 (a) Photocatalytic degradation of MO over the as-prepared samples under visible light illumination ($\lambda \ge 420$ nm). (b) The corresponding rate constant *k* of the different as-prepared samples.

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the activity for BCN is the weakest as almost no MO has decomposed after 16 min visible light irradiation. The photoactivity for the UCNNS is a little better than BCN due to the larger specific surface area, but its photocatalytic ability to decompose organic pollution is still weak due to its limited light absorption capacity. The composite photocatalysts reveal notably enhanced photoactivity for MO degradation compared to the bare UCNNS and CdS. In our research system, the optimal activity was achieved with the 10CN sample, which almost completely eliminated MO after 16 min irradiation (see Fig. S3 and S6, ESI⁺). As depicted in Fig. 6b, the photoactivity of the 10CN sample is about 6 and 50 times higher compared to CdS and the UCNNS, respectively. The specific surface area is always a crucial factor in photocatalysis. To describe the photocatalytic performance more exactly, the reaction rate for photocatalytic degradation before and after normalization with the surface area is compared (see Fig. S12, ESI[†]). After normalization with the surface area, 10CN still exhibits a remarkably higher photocatalytic activity compared to 10BCN, which convincingly demonstrates the advantage of the 2D g-C₃N₄ nanosheet hybrid photocatalysts to the bulk one. These results suggest that the synergic effect between the CdS and UCNNS probably plays a pivotal role for accelerating the transfer and separation of the charge carriers to improve the photocatalytic activity. This can be certified through further research.

The stability of the as-prepared samples was evaluated *via* a recycling test under visible light illumination. From Fig. 7, the photocatalytic activity of CdS decreases gradually during the cycling test due to photocorrosion under irradiation. Meanwhile, 10BCN also exhibits a slower decrease in photocatalytic performance. There is no noticeable decrease in the photocatalytic activity for 10CN after four successive cycles of the reaction. In addition, as shown in Fig. S9 and S10 (ESI†), neither the structure or the morphology of the 10CN sample changed after the recycling test, which indicates that the 10CN sample is stable during the photocatalytic reaction. These results indicate that the UCNNS–CdS composite not only significantly enhances the photocatalytic activity, but can also effectively prevent photocorrosion of the CdS. The 10CN sample is more stable than 10BCN, which also suggests that the 2D



Fig. 7 Cycling photocatalytic degradation of MO over UCNNS-CdS composites under visible light irradiation ($\lambda \ge 420$ nm).

g- C_3N_4 nanosheets are superior to the bulk sample to stabilize the CdS particles.

Based on the aforementioned experimental results, we believe that the enhancement of the photocatalytic activity for the UCNNS-CdS composite is accredited to the efficient interfacial transfer and separation of photogenerated carriers between the g-C₃N₄ nanosheets and CdS particles. This assumption can be verified by photoelectrochemical measurements. Fig. 8a shows the transient photocurrent response of 10CN, CdS, UCNNS, and BCN under visible light irradiation for several on-off cycles. From Fig. 8a we can clearly see that the photocurrent response of BCN is lower than that of the UCNNS and 10CN is significantly higher than that of the UCNNS and CdS under the same visible light illumination. The generation of the photocurrent is mainly the result of photoinduced electrons diffusing to the ITO.⁴⁸ Therefore, the enhanced photocurrent implies that more effective charge transfer and separation are achieved after constructing the heterojunctions. The strength of the photocurrent is in line with the order of the photocatalytic activity. To further confirm the above results, electrochemical impedance spectroscopy (EIS), a useful measurement to characterize charge carrier transportation, was also performed. Fig. 8b displays that the impedance radius of the UCNNS is smaller than BCN, which indicates a smaller charge transfer resistance for the ultrathin g-C₃N₄. 10CN is much smaller than the bare CdS and g-C3N4 nanosheets, which reflects a decreased charge transfer resistance across the interface49,50 between CdS and the UCNNS. Therefore, the remarkably improved life-time and more efficient separation of the photoexcited carriers induce a notable enhancement of the photocatalytic activity in MO degradation.



Fig. 8 Photoelectrochemical properties of the as-prepared CdS, UCNNS, BCN and 10CN samples. (a) Transient photocurrent response under visible light irradiation ($\lambda \ge 420$ nm) and (b) EIS Nyquist plots of the samples; the inset image is a comparison between the BCN and UCNNS.



Fig. 9 Comparison of the PL spectra for the BCN, UCNNS, and 10CN samples excited at 325 nm.

Both the images of the composites and the above results suggest that the enhanced photocatalytic activity is attributed to the interfacial transfer of the photogenerated charges between the UCNNS and CdS. This transfer is also investigated by photoluminescence (PL) measurements. Fig. 9 presents the PL spectra for the BCN, UCNNS, and the 10CN samples. The BCN sample shows a strong emission peak centered at about 465 nm, which can be assigned to the recombination of electrons and holes in g-C₃N₄. In comparison, the emission intensity of the UCNNS clearly decreases, which reveals that ultrathin g-C₃N₄ undergoes more rapid charge transfer than the bulk sample. When the CdS nanoparticles are added, the PL drops remarkably. The reduction of the PL can be interpreted as the efficient transfer of photoinduced electrons and holes between the UCNNS and CdS particles.

In order to understand the role of the photoexcited active species in the degradation of the MO dye, a succession of control experiments were performed. Different scavengers aiming for the hydroxyl radicals (•OH), holes (h⁺) and superoxide radicals (•O₂⁻) were added during the degradation process. Herein, isopropanol (IPA)^{51,52} was used to scavenge •OH, ammonium formate (AF) was for h⁺,³⁵ and *p*-benzoquinone (PBQ) was for •O₂⁻.^{53,54} Fig. 10 presents the photocatalytic activity of the 10CN sample with the addition of the different scavengers. It is clear that when PBQ was added to the reaction system, the degradation of MO almost terminated and when AF was added, the degradation was apparently inhibited. Thus, it can be concluded that the superoxide radicals play the most pivotal role in the degradation of the MO dye and •O₂⁻ and h⁺ are the main active species affecting the degradation rate.

On the basis of the above experiments and results, a tentative mechanism for the degradation of MO on the UCNNS–CdS nanocomposite is illustrated in Fig. 11. Both the UCNNS and CdS can generate photoexcited holes and electrons under visible light irradiation. It is reported that the conduction band (CB) and valance band (VB) of CdS are lower than that of g- C_3N_4 . After constructing the nanoheterostructure, the photoinduced electrons in the CB of the UCNNS can directly migrate to CdS, while the holes in the VB of CdS can transfer to



Fig. 10 Effects of the addition of different scavengers on the photocatalyzed degradation of MO for the 10CN sample.



Fig. 11 Schematic diagram of the photogenerated electrons and holes transfer in the UCNNS-CdS composite and photocatalytic degradation of MO under visible light irradiation ($\lambda \ge 420$ nm).

the VB in the UCNNS. Thus, the separation efficiency of the electron-hole pairs is improved to a large extent, and the photocorrosion of CdS by holes is greatly alleviated, leading to a remarkable enhancement of the photocatalytic activity.

4. Conclusions

In summary, atomic layer $g-C_3N_4$ can be obtained through thermal condensation of urea and a simple ultrasonic method. UCNNS–CdS nanocomposites were successfully synthesized by a simple solvothermal method. The photoactivity of MO degradation under visible light irradiation is significantly enhanced after constructing a heterostructure between the UCNNS and CdS. The result also indicates that such 2D UCNNS can provide more binding sites than the bulk sample to anchor CdS nanoparticles, resulting in an improved photoactivity. In addition, the as-prepared composites are stable during the photocatalytic reaction. Both the photostability and enhanced photocatalytic activity of the composites can be explained by the effective transfer and separation of photogenerated charge carriers between the CdS and UCNNS. Furthermore, superoxide radicals play the most pivotal role in the degradation of the MO dye. This study highlights the potential application of ultrathin $g-C_3N_4$ nanosheet hybrid photocatalysts, and we hope that it may provide a new insight for the construction of stable photocatalysts with efficient visible light activity.

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