g-C₃N₄ Homophase Junction With High Crystallinity Using MoS₂ as Cocatalyst For Robust Visible-Light-Driven Photocatalytic Pollutant Degradation

Ying Liu

Shihezi University

Jun Han

Shihezi University

Xianpeng Zeng

Shihezi University

Zongju Tian

Shihezi University

Feifan Yu

Shihezi University

Xiyin Sun

Shihezi University

Wei Wang (✉ wangwei_group@sina.com)

School of Chemistry and Chemical Engineering <https://orcid.org/0000-0001-9952-6253>

Qinghua Liu

University of Science and Technology of China

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Abstract

g-C₃N₄ photocatalyst has attracted great attention in environmental pollution control, but how to further improve its photoactivity is still a huge challenge. Herein, we have developed a simple strategy, by simultaneously improving the photocatalytic performance of g-C₃N₄ itself by recrystallization method, introducing the promoter MoS₂ to form a g-C₃N₄/g-C₃N₄/MoS₂ composite photocatalyst. Various characterization results show that the homophase junction g-C₃N₄ prepared by the double-precursor recrystallization treatment improves the crystallinity of the catalyst, and the cocatalyst MoS₂ is introduced into the interlayer of g-C₃N₄ by the ultrasonic-assisted oil bath method to form a stable composite photocatalyst, and the closely contacting interface effectively promotes charge transfer. The optimized photocatalyst g-C₃N₄/g-C₃N₄/MoS₂ displayed excellent photodegradation performance for methyl orange ($k=0.08700 \text{ min}^{-1}$), it shows 6.03 times enhancement of photocatalytic activity for degradation rate compared to homophase junction g-C₃N₄. In order to test its superior photocatalytic performance, g-C₃N₄/g-C₃N₄/MoS₂ can be used to degrade other organic pollutants, all of which can show high photocatalytic degradation ability (rhodamine B ($k=0.38963 \text{ min}^{-1}$)). This research highlights a feasible strategy for the introduction of co-catalyst engineering to develop excellent photocatalysts.

Highlights

- The homophase junction g-C₃N₄ with high crystallinity was prepared by double precursor through recrystallization treatment.
- A g-C₃N₄/g-C₃N₄/MoS₂ composite catalysts was synthesized by the ultrasonic-assisted oil bath method.
- In g-C₃N₄/g-C₃N₄/MoS₂, cocatalyst MoS₂ is ultrasonically shattered and enters between the homophase junction g-C₃N₄ nanosheets, and then effective contact between the catalysts in the oil bath to form a stable composite photocatalyst.
- Under visible light irradiation ($\lambda > 420 \text{ nm}$), compared with the homophase junction g-C₃N₄, the degradation rate of g-C₃N₄/g-C₃N₄/MoS₂ to methyl orange is increased by 6.03 times.

Introduction

Water pollution caused by industrial development has caused great harm to the environment and human health. Therefore, organic pollution is a problem that we urgently need to face and solve today. Among the many strategies to solve water pollution, visible light-driven photocatalytic technology has the advantages of low cost, green, energy saving, and environmental protection, and has broad application prospects in organic wastewater treatment. (Pramoda et al. 2017, Yuan et al. 2019b). In recent few decades, various semiconductor photocatalysts have been researched, such as metal oxides (Jing et al. 2019, Wang et al. 2019b, Zarezadeh et al. 2019), metal sulfides (Liang et al. 2020, Lu et al. 2018), and so on (Dong et al. 2019, Song et al. 2018). Among the catalysts, graphitic carbon nitride (g-C₃N₄) has

attracted worldwide attention due to its appropriate band gap, visible light response, low cost, good thermal and chemical stability, and so on (Li et al. 2020b, Monga et al. 2020, Sun et al. 2016). However, the photogenerated electron-hole pair of the original g-C₃N₄ has low separation efficiency and high recombination rate, making its photocatalytic activity unsatisfactory (Li et al. 2017, Zhang et al. 2020). Numerous strategies have been probed to optimize the catalytic performance of g-C₃N₄, such as metal or nonmetal doping (Reddy et al. 2020, Tonda et al. 2014, Wang et al. 2019c), defect engineering (Han et al. 2021, Wang et al. 2020), nano engineering (Liu et al. 2020, Wu et al. 2019, Zhang et al. 2014), junction engineering (Ge et al. 2011, Li et al. 2020a, Meng et al. 2021), morphology designing (Dong et al. 2020, Wang et al. 2019a, Yuan et al. 2019a). Among these strategies, junction engineering is considered as the most noteworthy method. For example, TiO₂/g-C₃N₄ (Du et al. 2020), MoS₂/g-C₃N₄ (Hu et al. 2020, Wu et al. 2020), MoO₃/g-C₃N₄ (Xie et al. 2018), and so on (Shen et al. 2021, Vesali-Kermani et al. 2020).

However, be limited by the lattice mismatching between different semiconductors, the photocatalytic activity of g-C₃N₄ based heterojunction is still greatly suppressed (Fu et al. 2018). Therefore, isotype heterojunctions and homophase junctions composed of the same semiconductor have attracted widespread attention (Bai et al. 2019). Yu's work (Bai et al. 2019) showed that homophase junction provided smoother channel for charge transfer. Moreover, Wang (Cui et al. 2012), Dong (Dong et al. 2013), et al (Duan et al. 2019, Qiao et al. 2018, Yang et al. 2016), carried out researches about g-C₃N₄/g-C₃N₄ heterojunction. As the defects in the catalyst become the center of charge recombination, the photocatalytic performance of g-C₃N₄ based isotype heterojunction or homophase junction is not satisfactory. Researches have shown that crystallization treatment can effectively increase the crystallinity of the sample, thereby promoting the separation of photogenerated electrons and holes (Bai et al. 2021). In homophase junction, despite the charge separation is effectively boosted, the recombination of photogenerated electron-hole pairs is still not effectively inhibited. As an efficient and noble-metal-free cocatalyst, molybdenum disulfide (MoS₂) attracts more and more scientific focus (Bian et al. 2018, Li et al. 2018, Wei et al. 2014). In the composite photocatalyst, the cocatalyst MoS₂ serves as the electron convergence center to extract electrons from the main catalyst, then the charge separation is furtherly boosted and the charge recombination is effectively inhibited (Li et al. 2016a). Therefore, the coupling of MoS₂ and g-C₃N₄ is an ideal strategy for the preparation of high efficiency photocatalyst.

In this work, we firstly proposed that the homophase junction g-C₃N₄ prepared by the crystallization treatment of the double precursor improves the crystallinity of the catalyst, thereby providing an effective interface electron field for the photocatalytic process, and promoting the separation rate of photogenerated electrons and holes in the catalyst. Then MoS₂ is ultrasonically smashed and entered into the layer of exfoliated g-C₃N₄ nanosheets, and then g-C₃N₄ and MoS₂ effectively contact in the oil bath to form a stable composite photocatalyst. Under the driven of interfacial electric field, the photogenerated electron transfers from g-C₃N₄ to MoS₂ and this is verified by high resolution XPS and photoelectrochemical analysis. Therefore, in g-C₃N₄/g-C₃N₄/MoS₂, cocatalyst MoS₂ acts as electron

convergence center and electron transfer bridge, which significantly reduces the recombination rate of photogenerated electrons and holes of the composite photocatalyst. This indicates that the formation of g-C₃N₄/g-C₃N₄/MoS₂ composite catalyst is an attractive strategy for effectively improving the performance of the g-C₃N₄ based photocatalyst.

Experimental

All the reagents in this work were used directly without further purification. Dicyandiamide was purchased from Shanghai Titan Scientific Co., Ltd, urea was bought from Beijing Solarbio Science and Technology Co.,Ltd, thiourea and sodium molybdate dihydrate were bought from Shanghai Macklin Biochemical Co., Ltd. Sodium chloride and anhydrous sodium sulfate were purchased from Tianjin Shengao Chemical Reagent Co., Ltd. 2,2,6,6-Tetramethylpiperidine was bought from Shanghai Shaoyuan Technology Co., Ltd. Isopropanol was purchased from Tianjin Yongsheng Fine Chemical Co., Ltd. Triethanolamine was bought from Shanghai Aladdin Biochemical Technology Co., Ltd. Absolute ethanol was purchased from Tianjin Fuyu Fine Chemical Co., Ltd. Methyl orange (MO) and Rhodamine B (RhB) were purchased from Yuanye Bio-Technology (Shanghai). Deionized water is used for all experiments.

2.1 Synthesis of DCHCN

Ultrasonically dissolved dicyandiamide into distilled water to form saturated solution, then the solution was put into refrigerator until dicyandiamide was recrystallized. The recrystallized dicyandiamide was dried at 50°C overnight. According to the same method, the recrystallized urea was gotten. After that, the recrystallized dicyandiamide and urea were mixed and ground thoroughly according to specific mass ratio (mass ratio of dicyandiamide to urea is 1:1, 1:2, 1:3, 1:4, 1:5). The mixture was heated from room temperature to 550°C with a rate of 5°C•min⁻¹ under Ar ambience in a tube furnace. After being kept at 550°C for 4 h, the furnace was cooled down to room temperature naturally, then a series of g-C₃N₄/g-C₃N₄ homophase junction catalysts were obtained and marked as DCHCN-x (x=1, 2, 3, 4, 5).

2.2 Synthesis of HCN-4, CND and CNU

To reveal the influence of recrystallization on the structure and photocatalytic activity of g-C₃N₄, referential g-C₃N₄/g-C₃N₄ homojunction was prepared. In detail, 2 g dicyandiamide and 8 g urea (mass ratio of dicyandiamide to urea is 1:4) are mixed directly without excessive crystallization treatment, ground and heated under the same condition as that of DCHCN. The resulted sample was designed as HCN-4.

In order to highlight the superior photocatalytic activity of homophase junction, referential single-precursor g-C₃N₄ was prepared. Detailly, under the same synthesis condition as that of HCN-4, urea or dicyandiamide was used as single precursor to synthesize g-C₃N₄ which was marked as CNU and CND, respectively.

2.3 Synthesis of MoS₂

Ultrasonically dissolved 1.7108 g Na₂MoO₄·2H₂O and 2.1529 g CH₄N₂S into 60 mL distilled water to form uniform suspension, then the suspension was hydrothermally treated at 200°C for 24 h. Next, the obtained powder was washed with water and ethyl alcohol for three times, respectively. The sample was vacuum dried at 45°C for 12 h and MoS₂ was obtained. To improve the performance of MoS₂, MoS₂ was mixed with sodium chloride in a mass ratio of 1:100 and ball milled for 6 h at 500 rpm, the mixture was washed with water to remove NaCl and vacuum dried at 45°C overnight. The final MoS₂ powder was gained.

2.4 Synthesis of UOMSHCN

25 mg MoS₂ was ultrasonically dispersed into 45 mL distilled water to form solution A. 100 mg DCHCN powder was ultrasonically dispersed into 45 mL distilled water to form solution B. Next, solution A was ultrasonically mixed with solution B for 45 min. Then the mixed solution was oil bathed at 70°C for 5 h. After be cooled down and centrifuged, the obtained sample was vacuum dried at 55°C overnight and flagged as UOMSHCN-25.

Change the quality of MoS₂, a series of UOMSHCNs were synthesized and marked as UOMSHCN-5 (5 mg), UOMSHCN-15 (15 mg), UOMSHCN-20 (20 mg) and UOMSHCN-35 (35 mg), respectively. The pictorial representation for synthesis of UOMSHCN is showed in Scheme 1.

2.5 Synthesis of OMSHCN-25 and UMSHCN-25

In order to investigate the effect of ultrasonic or oil bath on the structure and photocatalytic performance of UOMSHCN, referential OMSHCN-25 (with oil bath without ultrasonic treatment) and UMSHCN (with ultrasonic without oil bath treatment) were synthesized according to the same method as UOMSHCN except ultrasonic or oil bath treatment. In detail, 25 mg MoS₂ was stirring dispersed into 45 mL distilled water to form solution C. 100 mg DCHCN powder was stirring dispersed into 45 mL distilled water to form solution D. Then solution C and solution D were stirring mixed and oil bathed at 70°C for 5 h. After be cooled down and centrifuged, the obtained sample was vacuum dried at 55°C overnight and flagged as OMSHCN-25.

Additionally, solution A and solution B were ultrasonically mixed for 45 minutes and without oil bath treatment. The obtained sample was centrifuged and vacuum dried at 55°C overnight and marked as UMSHCN-25.

2.6 Characterization

The crystal phase was characterized by powder X-ray diffraction (XRD) pattern which was recorded on a D8-Advance X-ray diffractometer using Cu K α irradiation ($\lambda=1.5406$ Å) with a scan rate of 10° min⁻¹ at 40 kV and 40 mA. The chemical composition and the functional groups information of catalyst were

analyzed by Fourier transform infrared spectroscopy (FTIR) on a FTIR spectrometer (Bruker Vertex 70V) and X-ray photoelectron spectroscopy (XPS) on a Thermo Scientific K-Alpha X-ray photoelectron spectrometer with a standard Al K α X-ray source. The morphology was obtained by scanning electron microscopy (SEM, ZEISS, Gemini SEM 300), transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM, JEM-2100F). The recombination rate of photogenerated carriers was explored by photoluminescence spectroscopy (PL) on JASCO FP-8500 fluorescence spectrometer. Ultraviolet-Visible diffuse-reflectance spectrum (UV-Vis DRS) was used to estimate the optical response and the band gaps of all samples on a Shimadzu UV-3600 UV-vis spectrometer, BaSO₄ base was used as the reflection standard. Finally, The Brunauer-Emmett-Teller (BET) surface area and pore volume were picked up via nitrogen adsorption-desorption isotherm methods at 77 K (Micromeritics ASAP 2020).

2.7 Photoelectrochemical test

Transient photocurrent response, electrochemical impedance spectroscopy (EIS) and Mott-Schottky (M-S) curves were conducted on a standard three-electrode electrochemical workstation (CHI760E, Shanghai Chenhua Ltd, China) with a platinum sheet and Ag/AgCl served as the counter and reference electrodes, respectively. The photoelectrode was prepared by quantitative dripping plate method. In detail, 1.0 mg photocatalyst was ultrasonically dispersed into 1 mL mixed solvent (volume ratio of ethyl alcohol to water is 2:1) to form uniform suspension. Next, the suspension was dropped onto a fluorine doped tin oxide glass electrode with a cover area of 1 cm² and dried in air. Then a Na₂SO₄ solution (0.2 mol/L, pH=7.0) was used as the work electrolyte solution. After that, A Xenon lamp (PLS-SXE 300C (BF), ceallight, Beijing, 300 W, equipped with a 420 nm filter) was served as the light source to test the photoelectrochemical characteristics of catalysts.

2.8 photocatalytic activity of organic pollutant degradation

Organic pollutant photodegradation experiment was adopted to evaluate the photocatalytic activity of catalyst. Detailed, 25 mg catalyst was uniformly dispersed into 50 mL methyl orange (MO) solution with a concentration of 10 mg•L⁻¹ and stirred in dark for 30 min to reach adsorption-desorption equilibrium. Then the solution was irradiated with a Xenon lamp (300 W, equipped with a 420 nm filter) under uninterrupted stirring at a constant temperature of 25°C. 3 mL suspension solution was taken out every 10 min and centrifuged to remove the catalyst (a rotate rate of 10000 rpm for 10 min) for degradation efficiency test. Furthermore, Rhodamine B was also used to estimate the photocatalytic activity of UOMSHCN-25.

2.9 Photodegradation mechanism

A radical trapping experiment was carried out to explore the photodegradation mechanism and the major active species during photodegradation process. A certain of trapping agent was added into the photodegradation system before light irradiation, other reaction conditions were identical with the

photodegradation experiment. Detailed, 2,2,6,6-Tetramethylpiperidine (HTMP), triethanolamine (TEOA) and isopropanol (IPA) were chosen as the scavengers for $\cdot\text{O}_2^-$, h^+ and $\cdot\text{OH}$, respectively.

According to the radical trapping experiments, a reasonable mechanism was proposed.

Results And Discussion

3.1 Characterization of photocatalyst

SEM, TEM and HRTEM images are collected to investigate the morphology, the phase structure and the influence of ultrasonic and thermal treatment on the structure of catalyst (Fig.1, Fig.S1, Fig.S2). SEM images show that DCHCN-4 (Fig.1a) is ultrasonic exfoliated to “egg roll” structure and MoS_2 (Fig.1b) is ultrasonic smashed to nano particles and the nano particles loosely coalesce to form “raspberry” particles. When the “egg roll” and “raspberry” are ultrasonic mixed and oil bathed, the loosely MoS_2 “raspberry” particles are smashed and jolted into the $\text{g-C}_3\text{N}_4$ “egg roll” to form well-knit composite photocatalyst (UOMSHCN-25, Fig.1c). According to the comparison between Fig.1a and Fig.1c, the layer spacing of UOMSHCN-25 is obviously enlarged, which indicates that MoS_2 has a good interlayer dissection effect on $\text{g-C}_3\text{N}_4$ and efficient hetero/homojunction is formed. As a result, for UOMSHCN composite photocatalyst, the interface electronic transmission resistance is reduced and the photocatalytic activity is enhanced (Li et al. 2019, Yuan et al. 2019b). In contrast, SEM images of OMSHCN-25 (Fig.S1) show that without ultrasonic assistance, MoS_2 is simply physical mixed with DCHCN-4. When the catalyst is treated only by ultrasonic while without oil bath, part MoS_2 was smashed and located on DCHCN surface, but resultful composite photocatalyst was not constructed (Fig.S2).

To obtain incontrovertible evidence for UOMSHCN composite photocatalyst, TEM and HRTEM images of DCHCN-4 and UOMSHCN-25 are pictured and displayed in Fig.S3, Fig.S4 and Fig.1d. Fig.S3 confirms the homophase junction structure in DCHCN-4. The left low density region is CNU and the right high density region is CND. When MoS_2 particles are ultrasonically mixed and oil bathed with DCHCN sheets, MoS_2 fully enters the DCHCN layer to form a stable composite photocatalyst (Fig.S4, Fig.1d). Fig.S5 displays TEM, HRTEM and elements distribution of C, N, Mo, S and O in UOMSHCN-25 sample. The elements mappings confirm that UOMSHCN composite photocatalyst is successful constructed.

XRD patterns are collected to appraise the influence of recrystallization, ultrasonic, oil bath and MoS_2 doping on the crystal texture of HCN catalyst. The XRD curves of HCN-4, DCHCN-4, UOMSHCN-x, OMSHCN-25, UMSHCN-25 and MoS_2 are exhibited in Fig.2. As shown in Fig.2a, all samples demonstrate two characteristic peaks at around 12.8° and 27.6° except MoS_2 , which corresponding to (100) and (002) crystal planes of $\text{g-C}_3\text{N}_4$ (He et al. 2020, Li et al. 2016b). The peak at 12.8° is assigned to the repeated cycle of aromatic rings in-plane. Compare to HCN-4, this peak does not change obviously for DCHCN-4. This means that recrystallization does not influence the crosslinking structure in-plane. Ultrasonically composite MoS_2 with DCHCN-4 and with the increase of MoS_2 concentration, the (100) peak does not

change remarkably. The steady inside structure in-plane signifies that MoS₂ does not fuse into g-C₃N₄ plane. The peak at 27.6° is ascribed to interplanar stacking structure of conjugated aromatic rings (Lu et al. 2018, Yuan et al. 2019b). The intensity of the (002) peak of DCHCN-4 is stronger than that of HCN-4. This peak upshift from 27.62° (HCN-4) to 27.73° (DCHCN-4) (Fig.2b). The upshift for (002) peak reveals a decreasing layer spacing of g-C₃N₄ (Tab.S1). Higher crystallinity and smaller layer spacing are favour of higher separation efficiency and transfer ability of photogenerated carriers. So, recrystallization is beneficial for photocatalytic performance of g-C₃N₄ catalyst. When MoS₂ was ultrasonically mixed with DCHCN, MoS₂ performed good interlaminar separation on g-C₃N₄, and MoS₂ particles are smashed and jolted into the slits of DCHCN layers. As a result, the layer spacing is expanded, the separation efficiency and transfer ability of photogenerated carriers are decreased. With the increase of MoS₂ concentration, the layer spacing is increase gradually. So, the separation efficiency and transfer ability of photogenerated carriers will be decreased gradually. While, to our notice, the MoS₂ nanoparticles in the slits will boost the separation and transfer of photogenerated carriers as a medium for charges beside adsorption site for organic molecule. Therefore, the final separation efficiency and transfer ability of photogenerated carriers will be enhanced with the increase of MoS₂ concentration. But, excessive MoS₂ is not conducive to the separation and transfer of photogenerated carriers (UOMSHCN-35). The shift of the (002) peak verifies the formation of UOMSHCN composite photocatalyst. In contrast, without ultrasonic treatment or thermal treatment, MoS₂ cannot effectively contact with DCHCN. As a result, the photocatalytic acitivity of OMSHCN-25 and UMSHCN-25 will not be enhanced efficiently.

The FTIR spectra of all samples are exhibited in Fig.3. As shown in Fig.3a, the FTIR peaks at 2890 cm⁻¹ and 1083 cm⁻¹ of MoS₂ can be observed in the FTIR spectra of UOMSHCN-x, which illustrates that MoS₂ is successfully doped into DCHCN-4 and the composite photocatalyst is fabricated. Along with the increase of MoS₂ amounts, the intensity of MoS₂ peaks in FTIR spectra of UOMSHCN-x catalysts is gradually enhanced. The moderate peak at 812 cm⁻¹ and the weak peak at 891 cm⁻¹ are rooted in the out-of-plane bending vibration of aromatic C-N hybrid cyclic units (Jiao et al. 2019, Yuan et al. 2019b). It should be noted that as the concentration of MoS₂ increases, the two peaks at 812 cm⁻¹ and 891 cm⁻¹ are weakened. This suggests that MoS₂ is tightly contacted with DCHCN-4 by chemical bonding instead of physical mixing. The region between 1000-1750 cm⁻¹ is assigned to the stretching vibration of the aromatic cyclic units. The peaks between 1000-1750 cm⁻¹ show no discernible difference for all samples. The enlarged FTIR spectra (Fig.3b) display enhanced shoulder peaks and satellite peaks at 1142 cm⁻¹, 1277 cm⁻¹, 1248 cm⁻¹, 1553 cm⁻¹ and 1685 cm⁻¹, which confirmed the close interaction between MoS₂ and DCHCN-4.

XPS patterns are used to characterize the surface chemical composition and chemical states of MoS₂, DCHCN-4 and UOMSHCN-25 (Fig.4). The survey spectra (Fig.4a) suggest that UOMSHCN-25 is composed by C, N, Mo, S and O. High-resolution XPS spectra reveal the exquisite surface chemical states of all elements. C1s spectrum (Fig.4b) of DCHCN-4 is deconvoluted into three peaks at 284.80 eV, 288.08 eV and 293.52 eV, which are belong to C-C of adventitious reference carbon, sp² bonded C in N=C-N unit and

the shakeup peak (Cao et al. 2017, Yuan et al. 2019b), respectively. Compare to the C1s XPS spectrum of DCHCN-4, the C1s peaks of sp^2 bonded C in N=C-N unit and the shakeup peak in UOMSHCN-25 upshift to 288.20 eV and 293.61 eV, respectively. N1s spectrum (Fig.4c) of DCHCN-4 is deconvoluted into four peaks at 398.25 eV, 398.93 eV, 400.73 eV and 404.13 eV, which are ascribed to sp^2 bonded N atom (C=N-C), tertiary nitrogen group in a form of N-(C)₃, amino functions (C-N(H)₂ or C-N-H) and charging effects or positive charge localization (Wang et al. 2017). For UOMSHCN-25, N1s XPS peaks upshift to 398.54 eV, 399.24 eV, 401.02 eV and 404.42 eV, respectively. The upshift results of C1s and N1s propose that C and N atoms of DCHCN-4 are bonded with MoS₂ to form junction structure. To further verify the tight interaction between MoS₂ and DCHCN-4, Mo3d and S2p high resolution XPS are illustrated in Fig.4d and Fig.4e. Fig.4d shows that the four peaks in the region between 227 eV and 233 eV are ascribed to Mo⁴⁺ 3d_{5/2} and Mo⁴⁺ 3d_{3/2}. For MoS₂, the peaks at 229.1 eV and 232.5 eV are ascribed to 1T MoS₂, the peaks at 229.5 eV and 232.2 eV are ascribed to 2H MoS₂. For UOMSHCN-25, the peaks of 1T and 2H MoS₂ are downshift to 228.5 eV, 231.8 eV and 229.1 eV, 231.7 eV, respectively. Moreover, the peaks at 226.31 eV and 235.20 eV in MoS₂ are assigned to S2s and Mo⁶⁺. While in UOMSHCN-25, the two peaks downshift to 225.70 eV and 234.72 eV, respectively. S2p spectrum (Fig.4e) is deconvoluted into four peaks of S2p_{3/2} (162 eV and 162.3 eV) and S2p_{1/2} (163.2 eV and 163.7 eV) in MoS₂. While for UOMSHCN-25, the peaks downshift to 161.3 eV, 162.5 eV, 163 eV and 164.3 eV, respectively. The peaks of 162 eV and 163.2 eV (161.3 eV and 163 eV in UOMSHCN) are assigned to 1T phase MoS₂, and the peaks of 162.3 eV and 163.7 eV (162.5 eV and 164.3 eV in UOMSHCN-25) are assigned to 2H phase MoS₂. The upshift of C1s and N1s peaks and the downshift of Mo3d and S2p peaks show that the electrons are extracted and transferred from DCHCN-4 to MoS₂. An efficient composite photocatalyst is constructed. The O1s (Fig.4f) peak around 532 eV is assigned to adsorbed CO₂ and H₂O. The binding energy of O1s in adsorbed CO₂ and H₂O reflects the type of surface-active-site in catalyst. O1s peak of DCHCN-4 states that there is only one type active site on catalyst surface. However, the O1s peak of UOMSHCN-25 is divided into two peaks at 532.63 eV and 531.29 eV, which corresponding to adsorbed CO₂ and H₂O on DCHCN-4 and MoS₂ in UOMSHCN-25. The double-active-site enhances the adsorption capacity of CO₂ and H₂O on DCHCN-4 and MoS₂ in UOMSHCN-25.

The optical response and the band gaps of HCN-4, DCHCN-4, UOMSHCN-25, OMSHCN-25 and UMSHCN-25 are displayed in Fig.5a and Fig.S6. As shown in Fig.5a, HCN-4 is of an absorption edge at 484 nm. When the recrystallized urea and dicyandiamide are used as double precursors, the resulted DCHCN-4 possesses an absorption edge of 494 nm, the visible light response of DCHCN-4 is enhanced compare to HCN-4. Excitingly, combine MoS₂ with DCHCN-4 to form UOMSHCN-25 composite photocatalyst, the absorption edge substantially redshift to 574 nm, and that the visible light response characteristic is boosted obviously. In contrast, the absorption edge of OMSHCN-25 and UMSHCN are located at 558 nm and 549 nm. The visible light response ability of UOMSHCN-25 overmatch that of OMSHCN-25 and UMSHCN-25. At the same time, the visible light absorption intensities of UOMSHCN, OMSHCN and UMSHCN are both strengthened. From Fig.S6, the band gaps of HCN-4, DCHCN-4, UOMSHCN-25,

OMSHCN-25 and UMSHCN-25 are 2.56 eV, 2.51 eV, 2.16 eV, 2.22 eV and 2.26 eV, respectively, which corresponds to the optical response properties UV-Vis DRS spectra. The conduction band positions are investigated by Mott-Schottky curves (Fig.S7). The conduction bands of HCN-4, DCHCN-4, UOMSHCN-25, OMSHCN-25 and UMSHCN-25 are -0.733 eV, -0.753 eV, -0.873 eV, -0.793 eV and -0.773 eV, respectively. According to the band gaps and the conduction band positions, the valence bands of HCN-4, DCHCN-4, UOMSHCN-25, OMSHCN-25 and UMSHCN-25 are calculated as 1.827 eV, 1.757 eV, 1.287 eV, 1.427 eV and 1.487 eV following the equation of $E_{VB}=E_g+E_{CB}$. The band structures are exhibited in Fig.5b.

N_2 adsorption-desorption isotherms are carried out to investigate the specific surface area, the pore volume and the pore type of catalysts. Fig.6a shows that MoS_2 , DCHCN-4 and UOMSHCN-25 possess IV-type isotherm with a H_3 -type hysteresis loop. The isotherm means that MoS_2 owns particle packing pore and DCHCN-4 has lamellar stacking pore. When ultrasonically smash and jolt MoS_2 into the slits of DCHCN, DCHCN is further exfoliated and expanded to generate more and larger slits. As a result, the specific surface area (Fig.6a), the pore diameter (Fig.6b) and the pore volume (Tab.S2) are enlarged significantly, it indicates that MoS_2 effectively strips DCHCN by ultrasonic treatment, and MoS_2 sufficient contacts with DCHCN to form UOMSHCN composite photocatalyst by oil bath. Fund of mesoporous and macroporous provide abundant active sites to enhance the photocatalytic activity of photocatalyst.

Electrochemical tests are used to uncover the separation efficiency and the transfer ability of photogenerated carriers of all catalysts. The transient photocurrent responses (Fig.7a) show that recrystallization, ultrasonic, oil bath and MoS_2 doping are beneficial for the separation of photogenerated carriers. Combine MoS_2 with DCHCN-4, MoS_2 dramatically facilitates the charge separation and the photocurrent is reached the highest value for UOMSHCN-25. Relatively, without ultrasonic treatment or thermal treatment, MoS_2 can't effectively perform interlaminar dissection for DCHCN-4 (OMSHCN-25) or form efficient hetero/homojunction (UMSHCN-25). As present in Fig.7b, recrystallization, ultrasonic, oil bath and MoS_2 doping are helpful for charge transfer. Reducing the recombination rate of photogenerated carriers is distinctly important for photocatalytic activity. In this work, PL spectra were used to characterize the charges recombination rate in catalysts. Fig.7c shows that compared with the CND and CNU photocatalyst prepared by a single precursor, the DCHCN photocatalyst prepared by crystallization of the double precursor significantly inhibits the recombination of photogenerated electrons and holes. Fig.7d reveals that combine MoS_2 with DCHCN-4, the recombination path and mechanism are changed. The emitted light at around 459 nm is come from the recombination of photogenerated electron-hole pairs in DCHCN-4. For UOMSHCN-25, MoS_2 changes the band structure of DCHCN-4, so the emitted light blueshifts to about 439 nm. At the same time, a stronger emitted light peak appears at 442 nm, which originates from the recombination of photogenerated electron-hole pairs between MoS_2 and DCHCN-4, means that the primary charge carriers recombination pattern is converted from photogenerated electron-hole pairs recombination in DCHCN-4 to charge carriers recombination between MoS_2 and DCHCN-4. Due to the electrons are extracted and transferred from DCHCN-4 to MoS_2 , electrons and holes are separated efficiently, and recombination rate between electrons and holes are

inhibited. With increase of MoS₂ content, the charge carriers recombination rate is decreased gradually to reach the lowest value for UOMSHCN-25. In summary, As the stripping substance, the electron convergence center and transfer bridge, MoS₂ accelerates the separation, collecting and transfer of electron, suppresses the recombination of photogenerated carriers(Jin et al. 2020).

3.2 Photodegradation Activity

The photocatalytic activities of all samples were evaluated by MO, RhB. Fig.S8 shows that DCHCNs exhibit higher photodegradation activity than HCN-4, CND, and CNU. DCHCN-4 gives the highest photocatalytic activity. So, DCHCN-4 is chosen as the main catalyst to combine with MoS₂ to synthesize UOMSHCN-x photocatalysts. Fig.8a demonstrates that the photocatalytic activities of UOMSHCN-x are higher than that of DCHCN-4. UOMSHCN-25 gives the highest degradation efficiency of 96.3% within 40 min for MO. To survey the influence of ultrasonic and oil bath on the photocatalytic activity of catalyst, the photodegradation efficiency of MO for OMSHCN-25 and UMSHCN-25 are tested and shown in Fig.S9. The results show that ultrasonic-oil bath treatment is far effective than ultrasonic treatment or oil bath treatment for photocatalytic performance.

The catalytic stability is another important factor for practical application of photocatalysis. To evaluate the influence of ultrasonic and thermal treatment on the stability of catalysts, we implement a four-cycle photocatalytic test for UOMSHCN-25 (Fig.8b), OMSHCN-25 (Fig.S10) and UMSHCN-25 (Fig.S11). UOMSHCN-25 displays very stable photocatalytic activity. The results confirm that ultrasonic-oil bath can enhance the interaction between MoS₂ and DCHCN. Meanwhile, the XRD patterns of UOMSHCN-25 before and after the photocatalytic experiment show no apparent difference in the crystal texture (Fig.S12).

The reaction kinetics for MO photodegradation are calculated according to the following formula and displays in Fig.8c, Fig.S13 and Tab.S3.

$$\ln \frac{C_0}{C} = kt$$

Where C_0 is the initial concentration of MO, C is the final concentration of MO at time of t , k is the apparent kinetic rate constant, t is the degradation time.

The kinetic rate constant of UOMSHCN-25 is 0.08700 min⁻¹, which outclass the kinetic rate constants of other catalysts.

Furthermore, the photocatalytic activity of UOMSHCN-25 is also evaluated by RhB degradation. UOMSHCN-25 gives a surprising degradation efficiency of 98.7% within 10 min (Fig.S14) and a kinetic rate constant of 0.38963 min⁻¹ (Fig.S15) for Rh B. After a four-cycle test, the degradation efficiency of Rh B is hardly reduced (Fig.S16).

3.3 Photocatalytic Mechanism

As is well-known, during photocatalytic process, various active species will be produced under light irradiation. The oxidizing active radical will participate in and promote the degradation of organic molecule. To further unmask the reaction mechanism, HTMP, TEOA and IPA are chosen as the scavengers for $\cdot\text{O}_2^-$, h^+ and $\cdot\text{OH}^-$ (Jin et al. 2020), respectively. According to the photodegradation efficiency of MO, the most important radical for organic pollutant photodegradation will be filtered out. As shown in Fig.8d, the photodegradation rate of MO is nearly invariable by adding IPA. After adding HTMP or TEOA into reaction system, the photodegradation rate is substantially declined. The results reveal that the photodegradation process is controlled by $\cdot\text{O}_2^-$ and h^+ .

Based on the characteristic results, the photodegradation rate of MO and the radical trapping experiments, a reasonable photodegradation mechanism for UOMSHCN is proposed and illustrated in Fig.9. Driven by the interfacial electric field in UOMSHCN composite photocatalyst, the photogenerated electron-hole pairs are efficiently separated, then the electrons are extracted and transferred from DCHCN to MoS_2 . h^+ , which is retained in DCHCN, plays a pivotal role for MO degradation. On the other hand, e^- , which transfers from DCHCN to the surface of MoS_2 , reacts with the adsorbed O_2 to form $\cdot\text{O}_2^-$. $\cdot\text{O}_2^-$ represents super oxidation capacity for organic photodegradation. Then, a double-oxidation-site of h^+ and $\cdot\text{O}_2^-$ is proposed.

Conclusion

In summary, UOMSHCN composite photocatalyst are synthesized by recrystallization-ultrasonic-oil bath method using urea and dicyandiamide as double precursors. Design the homophase junction structure to provide a smoother channel for rapid charge transfer and recrystallization of the dual precursor can effectively increase the crystallinity of the photocatalyst, thereby promoting the separation of photogenerated electrons and holes. MoS_2 and DCHCN are respectively smashed into “raspberry” nano particles and exfoliated into “egg roll” nano sheets under ultrasonic treatment. During ultrasonic mixing process, MoS_2 performs effective interlaminar dissection for DCHCN, the smashed MoS_2 particles are ultrasonically jolted into the slits of DCHCN to form UOMSHCN composite photocatalyst. Oil bath enhances the interaction between MoS_2 particles and DCHCN sheets, this enhanced interaction furtherly boosts the separation of photogenerated carriers. On the other hand, MoS_2 plays a critical role of electron convergence center and transfer bridge. As a result, under visible light irradiation ($\lambda > 420 \text{ nm}$), UOMSHCN-25 presents the best photocatalytic activity for organic pollutant degradation. This work explores an efficient strategy for high activity g- C_3N_4 based photocatalyst.

Declarations

Ethics approval and consent to participate

Our manuscript does not report on or involve the use of any animal or human data or tissue, and our manuscript does not contain data from any individual person.

Consent for publication

The work described has not been published before, it is not under consideration for publication anywhere else, and its publication has been approved by all co-authors.

Availability of data and materials

All data generated or analysed during this study are included in this published article and its supplementary information files.

Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Authors' contributions

All authors contributed to the concept and design of the research. Material preparation, processing, data collection and analysis were completed by Liu Ying, Han Jun, Zeng Xianpeng, literature research was done by Tian Zongju and Yu Feifan, and also thank Sun Xiyin for the graphical abstract. The first draft of the manuscript was written by Liu Ying, all authors commented on previous versions of the manuscript, and they read and approve the final manuscript.

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Figures

Figure 1

SEM of DCHCN-4 (a), MoS₂ (b), UOMSHCN-25 (c) and HRTEM of UOMSHCN-25 (d)

Figure 2

XRD patterns of all samples(a) and its partial enlarged view(b)

Figure 3

FTIR of all samples(a) and its partial enlarged view(b)

Figure 4

XPS of MoS₂, DCHCN-4 and UOMSHCN-25

Figure 5

Uv-Vis DRS(a) and band structures of photocatalysts(b)

Figure 6

N₂ adsorption-desorption isotherms(a) and the pore size distribution of DCHCN-4, MoS₂ and UOMSHCN-25(b)

Figure 7

Transient photocurrent response(a), EIS Nyquist plots(b) and PL spectra of catalysts(c-d)

Figure 8

Photocatalytic performance of all samples in degradation of MO (a-c) and Radical capture experiment(d)

Figure 9

Schematic illustration of mechanism for organic pollutant photodegradation

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