Facile synthesis of 3D porous thermally exfoliated g-C₃N₄ nanosheet with enhanced photocatalytic degradation of organic dye

Xiaoya Yuan^{a,*}, Chou Zhou^a, Yanrong Jin^a, Qiuye Jing^a, Yaling Yang^a, Xu Shen^a, Qi Tang^a, Yuanhua Mu^a, An-Ke Du^b

*^aCollege of Materials Science and Engineering, Chongqing Jiaotong University,
Chongqing 400074, China*

^bChongqing Academy of Science and Technology, Chongqing 401123, China

Abstract: 3D porous framework composed of exfoliated ultrathin nanosheets is a hot topic in the field of energy storage and conversion. A facile method to prepare 3D mesoporous C₃N₄ with few-layered nanosheets interconnected in large quantity via H₂SO₄ intercalation and subsequent thermal treatment was described herein. The obtained thermally-exfoliated C₃N₄ (TE-C₃N₄) was thoroughly characterized by scanning electron microscopy (SEM), High-resolution transmission electron microscopy (HRTEM), powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) spectroscopy, Atomic force microscopy (AFM), UV-Vis diffuse reflectance spectroscopy (DRS) and Brunauer-Emmett-Teller (BET) measurements. The detailed analysis indicated that TE-C₃N₄ possessed enlarged inter-layer space, enhanced UV-light adsorption and high specific surface area with 3D interconnected structure composed of ultrathin 2D

* Corresponding author. Tel.: +86-23-62789154; Fax: +86-23-62789154.

E-mail address: yuanxy@cqjtu.edu.cn(X. Yuan)

nanosheets. Compared to bulk C_3N_4 , TE- C_3N_4 showed an enhanced photocatalytic activity for photodegradation of Rhodamine B under UV-light irradiation and exhibited no significant loss of photocatalytic activity after 11 recycled runs. The pseudo-first reaction rate constant for TE- C_3N_4 was about four times higher than that for pure bulk- C_3N_4 . The better photocatalytic performance could be attributed to more active catalytic sites, prolonged photo-excited carrier lifetime and shorted pathway of the carriers to the reaction sites.

Keywords: Photocatalytic degradation; C_3N_4 nanosheets; Mesoporous; Thermal exfoliation

1. Introduction

The increasingly awareness of serious energy crisis and environmental pollution has stimulated intensive research on solar energy conversion. Semiconductor photocatalysis as one of the most promising technologies is an alternative to the production of clean energy and environmental remediation because the use of the catalyst and solar energy is the most economical for practical applications [1, 2]. As a new fascinating photocatalyst, graphite-like carbon nitride (g- C_3N_4), a metal-free layered polymer semiconductor, has attracted plenty of attention due to its appropriate band structure and visible-light adsorption ability combined with excellent chemical and thermal stability, low cost and easy of large-scale preparation [3,4]. g- C_3N_4 has exhibited multifunctional potential applications in the fields of wastewater detoxification [5-9], CO_2 reduction [10, 11], hydrogen/oxygen evolution through

water splitting [12-14], electroactive materials for batteries [15-18], bioimaging [19] and sensor [20,21]. However, like other photocatalysts, bulk g-C₃N₄ prepared by direct thermal pyrolysis of suitable precursors usually suffers from low quantum efficiency, low surface area and poor photocatalytic activity [4].

Motivated by the two-dimensional (2D) crystal graphene, which presents a lot of intriguing physicochemical properties different from bulk graphite [23-25], great effort have been currently made to prepare nanosheets with single- or few-layer thickness. By exfoliating layered materials into nanosheets, exotic optoelectronic properties and high specific surface areas accompanied by remarkably enhancing the properties of the bulk counterparts have been obtained and show great potential in applications in electronics, energy storage and conversion, biotechnology, etc. [26-28]. In such a context, recent research about g-C₃N₄ ultrathin nanosheets shows that single layer or few-layer g-C₃N₄ nanosheets do exhibit many superior properties to its bulk analogy [29-35]. Xie et al. demonstrated ultrathin g-C₃N₄ nanosheets prepared by a green liquid exfoliation from bulk g-C₃N₄ in water showed enhanced intrinsic photoabsorption and photoresponse and was expected to be a promising candidate for bioimaging applications [19]. Zhu et al. prepared single atomic layer g-C₃N₄ by a simple chemical exfoliation method and confirmed that the photocatalytic H₂ production, pollutant decomposition activities and photocurrent generation of single layer g-C₃N₄ nanosheets were much higher than those of bulk g-C₃N₄ [29]. Wu et al. disclosed that the g-C₃N₄ nanosheets by a facile dicyandiamide-blowing method possessed higher specific area surface, improved electron transport ability and

increased lifetime of photoexcited charge carriers and significantly enhanced photocatalytic H₂ activities than that of bulk g-C₃N₄ [30]. Unfortunately, most of the current methods to fabricate ultrathin g-C₃N₄ nanosheets, including liquid-phase exfoliation [21,31-32], thermal etching [33], modified thermal polycondensation [34] and ball milling [35], are usually low-yield, poor reproducibility and time-consuming [36]. In view of the fascinating properties of 2D ultrathin g-C₃N₄ nanosheets, a new alternative way to obtain ultrathin g-C₃N₄ nanosheets with high quality and large quantity is still highly desirable.

Additionally, 3D mesoporous architectures fabricated from nano-scale building block is a hot topic due to its special relevance for realistic development of the above-cited applications because the resulting materials would offer a desirable combination of high internal reactive surface area and straightforward molecular transport through broad “highways” leading to such a surface [37, 38]. Though some recent advances have been made to produce some assembly of g-C₃N₄ hybridized with graphene or carbon nanotubes [14,16, 39-40], regretfully, the construction of a 3D mesoporous g-C₃N₄ is still a big challenge. Consequently, it is of great urgency to develop a preparative method to produce high efficiency macroscopic 3D g-C₃N₄ photocatalyst for the industrial and practical applications [36].

Here, we report the facile synthesis of a macroscopic 3D porous g-C₃N₄ by a well-designed intercalation-thermal exfoliation method. The resulting TE-C₃N₄ possessed a 3D porous interconnected network composed of 2D ultrathin g-C₃N₄ nanosheets. Remarkably, compared to the classical method to prepare 3D porous g-

C₃N₄ based materials, this method described here was free of any templates and could be used for mass-production of 3D porous g-C₃N₄. The photocatalyst was thoroughly characterized by XRD, SEM, HRTEM, XPS, AFM, UV-DRS and BET measurements and its photocatalytic properties were evaluated by degradation of Rhodamine B (RhB) under UV-light irradiation.

2. Experimental

2.1 Synthesis of 3D porous TE-C₃N₄

The bulk g-C₃N₄ (B-C₃N₄) was prepared by direct pyrolysis thermal polycondensation of melamine in the semi-closed system. In a typical synthesis, 10 g of melamine was placed in an alumina crucible with a cover and then heated to 550 °C with a heating rate of 3 °C min⁻¹, and kept at this temperature for 4h in static air. The as-prepared yellow C₃N₄ powder (1.0g) was mixed with concentrated H₂SO₄ (10 mL) and stirred for 8h at room temperature for its intercalation, during which the solution color changed from yellow to light yellow. Then the mixture was slowly poured into deionized water (200 mL). The obtained light-grey suspension was filtrated, washed repeatedly with DI water to remove the residual acid and finally freeze-dried under vacuum to give the grey-white H₂SO₄-intercalated C₃N₄ (H₂SO₄-C₃N₄). Afterwards, the obtained intercalated-C₃N₄ was calcinated at 550 °C in N₂ for 2h, leading to light-yellow porous TE-C₃N₄.

2.2 Characterization

FTIR was measured on Nicolet 6700 Fourier Transform Infrared instrument with scanning from 400 cm⁻¹ to 4000 cm⁻¹ by using KBr disks. Scanning electron

microscopy (SEM) images were obtained with a Hitachi SU8020 scanning electron microscope with acceleration voltage of 20 kV. High-resolution transmission electron microscopy (HRTEM) were performed on a FEI Tecnai G2 F20 field-emission transmission electron microscopy at an accelerating voltage of 200 kV. The powder X-ray diffraction (XRD) patterns were recorded on a PANalytical X'pert Pro powder diffractometer with Cu-K α radiation ($\lambda=1.5418\text{\AA}$) with a scan step of 0.013° . X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Fisher ESCALAB 250Xi photoelectron spectrometer using monochromatic Al K α X-ray source ($h\nu=1486.6\text{ eV}$). Atomic force microscopy (AFM) was performed using a Veeco Nanoscope IIIa Multimode atomic force microscope (the samples were prepared by drop-casting the dissolved dilute aqueous solution onto freshly cleaved silicon surface). The Brunauer-Emmett-Teller (BET) surface area was obtained with a Micromeritics AutoChem II 2920 system and pore size distribution was obtained by BJH method. UV-Vis diffuse reflectance spectroscopy (DRS) was carried out on a Shimadzu UV-2450 UV-vis spectrophotometer using BaSO₄ as the reference sample. The photoluminescence spectra (PL) were measured with a fluorescence spectrophotometer (F-7000, Japan) using a Xe lamp as excitation source with optical filters.

2.3 Photocatalytic experiments

The photocatalytic activities of the sample were evaluated via degradation of RhB under UV light ($\lambda=200\sim400\text{ nm}$). The UV-light source was provided by a 500W UV lamp with maximum wavelength emission at 365 nm (Shanghai Jiguang Special

Lighting factory, China). The lamp source was laid in the empty chamber of the annular quartz condensing tube with a cooling water jacket outside to immediately remove the heat released from the lamp. In a typical photocatalytic experiment, 50 mg of the catalyst was dispersed in 50mL of RhB aqueous solutions of different concentrations. The distance between the light source and the tube containing the reaction mixture was 15cm. Prior to irradiation, the mixture solution was magnetically stirred for 60 min in the dark to establish the adsorption-desorption equilibrium. During the irradiation, 4 mL of the reaction solution was withdrawn at certain time intervals and centrifuged to remove the photocatalyst from the solution. The concentration of RhB ($\lambda_{\max}=554$) was analyzed by recording the absorbance for the characteristic peak of RhB at 554 using the Evolution 600 UV-Vis spectrophotometer (Thermo Fisher Scientific Inc.).

3. Results and discussions

3.1. Characterization of B-C₃N₄, H₂SO₄-C₃N₄ and TE-C₃N₄

The synthetic routine to the 3D porous TE-C₃N₄ is illustrated in Figure 1. Firstly, the B-C₃N₄ was mixed with H₂SO₄ (98 wt%) to allow the intercalation of H₂SO₄ in the interlayer space of graphitic B-C₃N₄. Secondly, higher temperature treatment of the H₂SO₄-C₃N₄ expanded the interlayer of lamellar g-C₃N₄ due to the released SO₂ gas from the thermal decomposition of the H₂SO₄ embedded in the C₃N₄ gallery, leading to the formation of 3D porous TE-C₃N₄ composed of few-layered ultrathin 2D nanosheets. Intercalation of H₂SO₄ into B-C₃N₄ was also found in recent reports [29,41,42] and the whole process described herein was considerably similar to the

preparation of expandable graphite via the widely reported H_2SO_4 intercalation [43]. XRD was used to characterize the phase structure of $\text{B-C}_3\text{N}_4$, $\text{H}_2\text{SO}_4\text{-C}_3\text{N}_4$ and $\text{TE-C}_3\text{N}_4$ (Figure 2). Two typical diffraction peaks at around 13.0° and 27.0° were found in all the XRD patterns of these three samples, implying the basic graphitic C_3N_4 atomic crystal structure were largely retained during the H_2SO_4 intercalation and subsequent thermal decomposition of H_2SO_4 . These two peaks at 13.0° and 27.0° matched well with the (100) and (002) crystal planes of $\text{g-C}_3\text{N}_4$. The strongest peak (002) at about 27.0° was attributable to the inter-planar stacking peak of aromatic systems and the low-angle reflection peak at 13.0° was derived from the in-plane structural packing motif. When compared with that at 27.8° of $\text{B-C}_3\text{N}_4$, the (002) peak in the XRD pattern of $\text{H}_2\text{SO}_4\text{-C}_3\text{N}_4$ shifted down to 27.4° and the corresponding interlayer space increased from 0.310 to 0.325 nm, which confirmed that successful intercalation of H_2SO_4 into the lamellar $\text{g-C}_3\text{N}_4$ gallery. Upon thermal treatment of $\text{H}_2\text{SO}_4\text{-C}_3\text{N}_4$ at high temperature, this interlayer space of $\text{TE-C}_3\text{N}_4$ was further increased to 0.33 nm calculated from its (002) peak at 27.0° in the XRD pattern, indicating the thermal decomposition of H_2SO_4 indeed expanded the gallery distance between the layers of $\text{g-C}_3\text{N}_4$ and thus $\text{TE-C}_3\text{N}_4$ was successfully prepared as expected as shown in Figure 1. Combined with the ultrathin nature of the C_3N_4 nanosheets (3~4 layers of 2D nanosheets from the TEM and AFM measurements below), this method described herein to obtain 3D porous C_3N_4 composed of 2D nanosheets in large quantity was facile and more cost-efficient than other methods reported elsewhere [19-21, 29-35].

The textural structures and morphologies of the samples were examined by SEM. As shown in Figure 3a, B-C₃N₄ was composed of a large number of irregular aggregated particles about several micrometers in size. Figure 3b revealed that some small pores could be detected in the flat B-C₃N₄ particles, coming from the impact of gas discharged from the melamine decomposition, which contributed to the intercalation of concentrated H₂SO₄. After acid treatment, the H₂SO₄-C₃N₄ sample exhibited smaller, quite uniform and surface-smooth particles (figure 3(c,d)), which was quite different from loose structure of the B-C₃N₄. Upon thermal treatment, the H₂SO₄ embedded in the C₃N₄ interlayer decomposed and released SO₂ gas, which generated abundant pores in the final product with much higher surface area. As shown in Figure 3(e,d), TE-C₃N₄ exhibited three-dimensional sponge-like framework with an interconnected porous structure, which could enhance the light scattering under irradiation and provide more interfacial contact between the aqueous solution and the solid catalyst.

Figure 4 shows the typical TEM images of the aqueous dispersion obtained after ultrasonication treatment of H₂SO₄-C₃N₄ and TE-C₃N₄. The obtained H₂SO₄-C₃N₄ solution could be very stable for several months without the observations of any floating or precipitated nanoparticles. As shown in Figure 4a, the Tyndall effect of H₂SO₄-C₃N₄ solution was clearly observed, indicating its colloidal nature of the aqueous dispersion. The almost transparent morphology of the exfoliated H₂SO₄-C₃N₄ nanosheets implied that the obtained lamellar C₃N₄ nanosheets were made of few atomic layers after H₂SO₄ intercalation (Figure 4b), which was favorable for the

fabrication of 3D framework with the inner interconnected walls of nano-scale thickness. The ultrathin 2D-nanosheets of C_3N_4 as the building block for 3D porous TE- C_3N_4 were also observed in Figure 4(c,d). The obvious transparency of the 2D-nanosheets obtained from the ultrasonicated TE- C_3N_4 aqueous solution indicated its ultrathin nature. Meanwhile, the slight curling of this 2D C_3N_4 nanosheets to lessen surface energy was also an evidence of the ultrathin thickness, very similar to graphene [23-25]. The typical AFM measurements for TE- C_3N_4 in Figure 5 gave the height profiles about 0.8~1.4 nm, corresponding to 3~4 layers of 2D C_3N_4 nanosheets. These topographic morphological results clearly demonstrated that 3D mesoporous TE- C_3N_4 framework prepared herein was indeed composed of ultrathin 2D g- C_3N_4 nanosheets, which were formed via gas shock resulting from the thermal decomposition of the H_2SO_4 embedded in the intercalated- C_3N_4 gallery.

The functional groups of all the C_3N_4 samples were monitored by FTIR spectroscopy. As shown in Figure 6, the FTIR spectrum of TE- C_3N_4 was similar to that of B- C_3N_4 , indicating that the few-layer TE- C_3N_4 nanosheets maintained the same chemical structure as that in the bulk g- C_3N_4 . In detail, the broad peaks between 3600 and 3000 cm^{-1} was clearly observed which were caused by uncondensed terminal amino groups. The absorption bands near 1543 and 1636 cm^{-1} were attributed to C=N stretching, while the three bands at 1237, 1316 and 1420 cm^{-1} corresponded to the characteristic stretching mode of aromatic CN heterocycles [29]. In addition, the sharp absorption band at 806 cm^{-1} was assigned to the breathing mode of triazine units [31]. Moreover, no absorption bands related to carbonyl bonds were

observed, demonstrating that no oxidative reactions took place within the lamellar C_3N_4 during the H_2SO_4 intercalation process, which was consistent with the following XPS observation.

XPS was used to investigate the chemical compositions of the products (Figure 7). As can be observed from survey XPS spectra (Figure 7a), $B-C_3N_4$, $H_2SO_4-C_3N_4$ and $TE-C_3N_4$ were mainly composed of carbon and nitrogen elements, while a small amount of sulfur element was detected in $H_2SO_4-C_3N_4$, indicating that concentrated H_2SO_4 didn't destroy the chemical structure of $g-C_3N_4$ and no side reactions happened in the process, which was in good agreement with the results reported elsewhere [29, 41,42]. The S_{2p} peak at 168.63 eV in the XPS spectrum of $H_2SO_4-C_3N_4$ was observed, which could be considered the binding energy characteristic of SO_4^{2-} [42], indicating H_2SO_4 was indeed successfully intercalated in $B-C_3N_4$ interlayers. However, compared to that of $H_2SO_4-C_3N_4$, the S_{2p} peak was not observed in the survey spectra of $TE-C_3N_4$, which demonstrated that H_2SO_4 embedded in the C_3N_4 inter-layer was totally removed by thermal treatment. The peaks at around 532 eV for O1s atom were attributable to the trace of water in the samples. No O1s peaks related to the functional groups (carbonyl, carboxylic groups, etc.) and the O atomic% was 1.91, 6.53 and 1.95 for $B-C_3N_4$, $H_2SO_4-C_3N_4$ and $TE-C_3N_4$, further indicating no unexpected reactions in the process described herein. All the samples showed similar C1s and N1s peaks (Figure 7b~c), further indicating that the chemical composition and structure of the graphitic C_3N_4 phase was untouched via acidic treatment and thermal annealing and this was crucial for the highly-effective photocatalysis

TE-C₃N₄ toward organic pollutants. The C1s spectra showed two peaks located at about 284.6 eV and 288.3eV, ascribed to the signal of the standard reference carbon and the sp²-hybridized carbon bonded to N inside the triazine rings [19, 44]. Meanwhile, the peak at 398.8 eV in N1s spectra was also deconvoluted into three different peaks at around 398.7 eV, 399.7 eV and 401.3 eV. The main peaks at 398.7 and 399.7 eV could be assigned to the sp² bonded N atoms involved in the triazine rings and the tertiary bridging N atom (N-(C)₃) [45,46]. In addition, the peaks at around 401.2 eV and 404.2eV could be ascribed to the amino functional groups carrying hydrogen (C-N-H). Notably, probably due to the charging effect, the peak at 404.2 in the N1s spectrum of H₂SO₄-C₃N₄ was more prominent in comparison with those of B-C₃N₄ and TE-C₃N₄ [41].

The nitrogen adsorption-desorption isotherms and Barret-Joyner-Halenda (BJH) pore size distribution curves of the B-C₃N₄ and TE-C₃N₄ samples revealed that the two samples possessed type III adsorption-desorption isotherms (Figure 8), which was usually caused by the weak adsorption interaction and the existence of porous structures in the sample. There were type H3 hysteresis loops at 0.80<P/P₀<1.00 in the isotherms of these two samples and this was often observed on the aggregates of plate-like particles, confirming the porousification effect of H₂SO₄ upon higher temperature treatment of H₂SO₄-C₃N₄. The Brunauer-Emmett-Teller (BET) specific surface areas of B-C₃N₄ and TE-C₃N₄ were calculated to be 12.0 and 54.3 m²/g, respectively. The BET surface area of TE-C₃N₄ was nearly 4.5 times higher than that of B-C₃N₄, indicating high temperature treatment of H₂SO₄-C₃N₄ significantly

increased the surface area of TE-C₃N₄ owing to the porousification of H₂SO₄. However, the surface area of porous TE-C₃N₄ is somewhat low, indicating the low H₂SO₄ intercalation content between the layers. Meanwhile, the pore size distribution of B-C₃N₄ and TE-C₃N₄ were centered at 3.8 and 29.9 nm, respectively (Figure 8b), further suggesting that H₂SO₄ decomposition at high temperature enlarged the interlayer distance between nanosheets and mesoporous TE-C₃N₄ was successfully prepared.

Figure 9a shows the UV-vis DRS spectra of B-C₃N₄, H₂SO₄-C₃N₄ and TE-C₃N₄. The pure B-C₃N₄ showed an adsorption edge of 500 nm, signifying its photocatalytic activity under visible-light irradiation and a significant blue-shift was observed for H₂SO₄-C₃N₄, which was in agreement with the HCl-protonated C₃N₄ [47]. Compared to B-C₃N₄, TE-C₃N₄ exhibited a slight blue-shift and an increased adsorption within the UV-light range. The bandgaps of the bulk B-C₃N₄ and TE-C₃N₄ were about 2.65 eV and 2.79 eV, respectively. The blue-shift adsorption and narrower bandgap for ultrathin C₃N₄ nanosheets were also observed in recent reports, due to the smaller crystalline C₃N₄ size [16, 18] and the strong quantum confinement effect due to the ultrathin structure of TE-C₃N₄ [48]. Figure 9b shows the PL spectra of B-C₃N₄ and TE-C₃N₄. Compared to that of B-C₃N₄, the drastic decrease in the emission intensity was observed for the PL spectrum of TE-C₃N₄. Considering that the PL emission results from the free charge carrier recombination, the decreased peak intensity indicated that ultrathin TE-C₃N₄ was helpful for the separation of photogenerated electron-hole pairs [49], which favored an enhanced photocatalytic activity of

TE-C₃N₄.

3.2. Photocatalytic tests of TE-C₃N₄

The photocatalytic activities of B-C₃N₄ and TE-C₃N₄ were studied via RhB photodegradation experiments under visible- and UV-light irradiation (Figure 10). Prior to light irradiation, the solution was stirred in the dark for 1 h to ensure the establishment of adsorption-desorption equilibrium between the solid photocatalysts and RhB solution. Under visible-light irradiation, TE-C₃N₄ showed photocatalytic degradation behavior identical to B-C₃N₄ and thus its photocatalysis towards RhB was not further investigated. As depicted in Figure 10, the self-degradation of RhB under UV-light irradiation was negligible within 200 min's light irradiation in the absence of catalyst, demonstrating that RhB was very stable under the conditions. 100% degradation of RhB over TE-C₃N₄ was observed within 200min's UV-light irradiation while 68% over B-C₃N₄ when the initial concentration of RhB was 20 mg/L, indicating that TE-C₃N₄ showed better photocatalytic activity than B-C₃N₄. Furthermore, for higher RhB concentration (30mg/L), TE-C₃N₄ also degraded RhB completely within 4h, which was very appealing for practical environmental remediation.

A pseudo first-order linear relationship was revealed by the plots of $\ln(C/C_0)=-kt$, where k was the rate constant (min^{-1}), C_0 and C were the initial concentration and at the given time t of RhB dye. The determined reaction-rate constants k were 0.0087 and 0.0358 min^{-1} for bulk B-C₃N₄ and TE-C₃N₄, respectively. The photocatalytic RhB decomposition rate over TE-C₃N₄ was more than four times as fast as B-C₃N₄. In

addition, the stability of 3D mesoporous TE-C₃N₄ was further evaluated under UV-light irradiation and the cyclic photocatalytic experiments were carried out by 50 mg TE-C₃N₄ in 50 mL RhB solution with the initial concentration of 10 mg L⁻¹. Furthermore, it was found that the photocatalytic activity only very slightly decreased after 11 successive cycles of photocatalysis (Figure 10b), indicating the 3D mesoporous TE-C₃N₄ composed of 2D nanosheets was fairly stable under the studied conditions. The enhanced photocatalytic activity of 3D mesoporous TE-C₃N₄ than B-C₃N₄ in RhB degradation could be attributed to several reasons: (1) firstly, the greatly increased surface area, the measured surface area of TE-C₃N₄, was 4.5 times larger than that of B-C₃N₄, suggesting more active sites within TE-C₃N₄ for photocatalytic reactions. (2) Secondly, the improved photogenerated charge carrier transportation and separation due to nanosheet-based structure [43], which was also discussed in PL spectra. Similar to graphene [50, 51], the mono-layered or few-layered nanosheet structure could significantly reduce the distance for the charge carriers to transfer from the place generated to the solid-liquid interface due to the ultrathin structure. (3) Finally, the negatively shifted conduction band due to the quantum size effect could increase the activity of photogenerated electrons [29].

4. Conclusion

In summary, 3D porous C₃N₄ composed of few-layered 2D nanosheets interconnected in large quantity via H₂SO₄ intercalation and subsequent thermal treatment was successfully prepared. The obtained thermally-exfoliated C₃N₄ as the photocatalyst showed better photocatalytic activity towards RhB than pure g-C₃N₄

under UV-light irradiation and its pseudo-first-order reaction rate constant was about four times higher than that of pure bulk-C₃N₄. The 3D porous C₃N₄ exhibited very high stability and could be reused for over 10 times without any significant loss of activity. The 3D porous photocatalyst prepared herein is being further evaluated by degrading other organic pollutants and has great potential in water remediation.

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Figure captions:

Figure 1. Schematic Illustration of synthetic strategy. (a) Intercalation of concentrated H_2SO_4 into the interplanar space of $\text{B-C}_3\text{N}_4$. (b) exfoliation of $\text{H}_2\text{SO}_4\text{-C}_3\text{N}_4$ via thermal shock at high temperature

Figure 2. XRD patterns of $\text{B-C}_3\text{N}_4$, $\text{H}_2\text{SO}_4\text{-C}_3\text{N}_4$ and $\text{TE-C}_3\text{N}_4$

Figure 3. SEM images of (a, b) $\text{B-C}_3\text{N}_4$, (c, d) $\text{H}_2\text{SO}_4\text{-C}_3\text{N}_4$ and (d, e) $\text{TE-C}_3\text{N}_4$

Figure 4. (a) Tyndall effect exhibited by exfoliated $\text{H}_2\text{SO}_4\text{-C}_3\text{N}_4$ nanosheets dispersion passed through with red laserlight. (b) HRTEM images of exfoliated $\text{H}_2\text{SO}_4\text{-C}_3\text{N}_4$. (c, d) HRTEM images of exfoliated $\text{TE-C}_3\text{N}_4$ nanosheets

Figure 5. Typical AFM images of 2D nanosheets obtained from the ultrasonicated $\text{TE-C}_3\text{N}_4$ dispersion and (b) the corresponding height profiles

Figure 6. FTIR spectra of $\text{B-C}_3\text{N}_4$ and $\text{TE-C}_3\text{N}_4$

Figure 7. (a) XPS survey spectra , (b) C1s and (c) N1s XPS high-resolution spectra of $\text{B-C}_3\text{N}_4$, $\text{H}_2\text{SO}_4\text{-C}_3\text{N}_4$ and $\text{TE-C}_3\text{N}_4$.

Figure 8. (a) Nitrogen adsorption-desorption isotherms and (b) Barret-Joyner-Halenda (BJH) pore size distribution plots for $\text{B-C}_3\text{N}_4$ and $\text{TE-C}_3\text{N}_4$ samples.

Figure 9. (a) UV-vis DRS spectra of $\text{B-C}_3\text{N}_4$, $\text{H}_2\text{SO}_4\text{-C}_3\text{N}_4$ and $\text{TE-C}_3\text{N}_4$. (b) PL spectra of $\text{B-C}_3\text{N}_4$ and $\text{TE-C}_3\text{N}_4$.

Figure 10. The photocatalytic degradation of RhB over $\text{B-C}_3\text{N}_4$ and $\text{TE-C}_3\text{N}_4$ and (b) recycled runs for photocatalytic degradation of RhB by $\text{TE-C}_3\text{N}_4$.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8a

Figure 8b

Figure 9a

Figure 9b

Figure 10a

Figure 10b