Simple Synthesis of High Specific Surface Carbon Nitride for Adsorption-Enhanced Photocatalytic Performance

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Abstract
TMC-incorporated carbon nitride (CN) with hexagonal and quadrangle honeycomb-like structure and having periodic lattice defects linked by –CONH– bond was synthesized through combining the high calcination with the chemical condensation of melamine and 1,3,5-benzenetricarbonyl trichloride. The obtained CN has a tri-s-triazine ring and benzene ring skeleton, which makes it have excellent mechanical and thermal stability. The BET specific surface area was enhanced to about 125.6 m²/g, and the mean pore size is about 3.43 nm. This CN exhibited an excellent adsorption-enhanced photocatalytic performance.

Keywords: Carbon nitride materials, Melamine, Nanoparticles, Sintering

Background
Graphite carbon nitride (g-C₃N₄), possessing a two-dimensional (2D) nanosheet structure like graphene, has attracted much attention recently. The basic skeleton structure of g-C₃N₄ consists of tri-s-triazine units connected with tertiary amino groups, which owns regularly distributed triangular water-selective permeation nanopores throughout the entire laminar structure. Moreover, the spacers between the g-C₃N₄ nanosheets, which interact with each other through weak van der Waals forces, also provide nanochannels for water transport while bigger molecules are retained [1]. Due to this unique nanosheet structure, g-C₃N₄ exhibited many useful properties with applications in many fields, such as membrane separation materials [2, 3], photocatalysis [4–6], and electronic devices [7–9]. Up to now, the main method to prepare g-C₃N₄ was high-temperature calcination. However, the specific BET surfaces of these g-C₃N₄ materials were only 5–35 m²/g [2, 4, 10], which seriously limits the displaying of their unique properties in applications [4]. Then, the enhancement of specific BET surface for g-C₃N₄ was very important.

Inspired by the structures of covalent organic framework materials (COFs) [11–16] and their preparation methods [17], we try to combine the high calcination with the chemical condensation to prepare a new kind of porous TMC-incorporated carbon nitride (CN) linked by –CONH– bond and having periodic lattice defects as well [18]. This CN was synthesized by the condensation of melamine and 1,3,5-benzenetricarbonyl trichloride through the reaction of –NH₂ and –COCl. Besides, due to the further calcination and thermal oxidation “etching” using melamine as a precursor, this CN could possess large numbers of –NH and –NH₂ groups in the lattice structure, which could endow the CN with excellent performances.

Methods/Experimental
Materials
Melamine (99%), 1,3,5-benzenetricarbonyl trichloride (TMC, 98%), N,N-dimethylacetamide (DMAc, ≥ 99.8%), N,N-dimethylformamide (DMF, 99.5%), and triethyl phosphate (TEP, ≥ 99.5%) were purchased from Aladdin Chemistry Co., Ltd. (China). Ethanol (≥ 99.7 wt.%) and acetic acid (≥ 99.5 wt.%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Purified water was
purchased from Hangzhou Wahaha Group Co., Ltd. (Hangzhou, China). All the materials and reagents were of analytical grade and used without further purification.

**Synthesis of CN Material**

The synthesis procedure of CN material is illustrated in Scheme 1. At first, a white suspension was obtained by dissolving melamine (5 g) and TMC (1.75 g) in DMAc (93.25 g) with the stirring at 80 °C for 3 h under oil bath reflow (Additional file 1: Table S1–S3 and Figure S1–S3). Then, the suspension was transferred into roller ball mill to mill 12 h, using zirconia porcelain balls as the ball milling media. After that, the suspension was followed by ultrasonic treatment for 3 h. Secondly, the suspension was filtrated and washed with ethanol and deionized water for three times, respectively. In the end, the resulted white precipitate was dried at 80 °C in vacuum drying oven for about 24 h.

The above white powder was heated in two steps at 550 °C and 500 °C, respectively. Specifically, the procedure consisted in an initial heating from room temperature (25 °C) to 500 °C, which required 150 min, holding for 120 min. Then, the temperature was increased to 550 °C in 10 min and holding for 240 min. After that, the temperature was allowed to drop back to 25 °C, which took 100 min. The obtained bulk CN was milled into powder. Finally, the bulk CN was transferred into an open ceramic boat and heated to 500 °C in air for 4 h with a ramp rate of 10 °C/min. The yield is about 25%.

**Characterizations**

The size and morphology were analyzed by scanning electron microscopy (SEM, QUANTA FEG450) and transmission electron microscopy (TEM, Tecnai G2 F30 S-TWIN). The crystalline structure was confirmed by

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**Scheme 1** Proposed reaction mechanism of melamine and 1,3,5-benzenetricarbonyl trichloride for the synthesis of the TMC-incorporated carbon nitride
X-ray diffraction (XRD, Switzerland ARL/X, TRA). Fourier transform infrared spectrometry (FT-IR, Nicolet is50) was used to study the chemical structure. Thermal stability was inspected using thermal gravimetric analysis and differential scanning calorimetry (TG-DSC, STA449F3). X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250) signals were recorded with a monochromatic Al Kα source and a change neutralizer (hv = 1486.6 eV). Conventional method for measurement of the BET specific surface and average pore sizes were carried out by a B40-SA3100PLUS specific surface area and void meter (BECKMAN Coulter). The particle size distribution was analyzed by ZETSIZER NANO (ZSE, Malvern Instruments Ltd., UK).

Photodecomposition of 20 mg/L and 10 mg/L methyl orange (MO) were chosen as the model system to investigate the photoactivity of products using XPA photocatalytic reactor under visible-light irradiation of a 500-W Xe lamp with a 420-nm cutoff filter. A certain amount known concentration of H₂O₂ was then added into the reactor after 30 min dark adsorption, and the lamp was turned on to run 120 min continuously. Five milliliters of samples were withdrawn at regular intervals (20 min) with centrifugation to separate solids for measure. Furthermore, the CN suspension was filtered by a filter membrane and washing three times by deionized water and absolute ethanol, respectively. Then, the CN was dried in an oven at 80 °C for 3 h. The obtained CN was used to degrade MO again according to the above steps. The recycling experiments were carried out three times.

In order to prove the structure of the synthesized CN material, the XRD patterns of the CN molecular structure was simulated by Material Studio software (MS 2017, ver. 17.1). The lattice models (e.g., cell parameters, orientation standard, atomic positions, and total energies) were then fully optimized using MS Forcite and Reflex modules method (Additional file 1: Figure S9).

**Results and Discussion**

**Chemical Structure of CN Material**

Figure 1a depicts the chemical structure of CN. The sharp peak at 810 cm⁻¹ was assigned to the s-triazine ring mode. The characteristic peaks appearing at 1239 cm⁻¹, 1324 cm⁻¹, 1470 cm⁻¹, 1569 cm⁻¹, and 1645 cm⁻¹ were related to the C–NH–C and N–(C)₃ stretching vibration modes [19]. The peak at 1753 cm⁻¹ was belonged to –CONH– vibration,

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**Fig. 1** a FT-IR spectra, b XPS survey spectrum, the high-resolution scan of c C1s and d N1s of CN material.
which was often called amide I band. A broad absorption
around 3170 cm\(^{-1}\) was attributable to stretching modes of
primary and secondary amines at the defect sites and their
intermolecular hydrogen bonding interactions.\(^2\)

XPS was further employed to investigate the surface
c hemical composition and chemical states of the CN. As
shown in Fig. 1b, the C/N ratio of CN was about 1:1,
which was far beyond the traditional carbon-rich g-C\(_3\)N\(_4\)
[2, 20–22] (C/N ratio, about 3:1). Thus, this prepared
material is the type of nitrogen-rich g-C\(_3\)N\(_4\) [22] and we
marked it as CN, the same phenomenon was obtained
from the EDX element analysis in Additional file 1:
Figure S5, 6, wherein only carbon, nitrogen, and oxygen
species were detected (Fig. 1b). Besides, the O1s peak at
531.9 eV was likely due to the surface adsorbed H\(_2\)O or
hydroxyl group. As can be seen, the four same peaks in
Fig. 1c at 288.59 eV, 288.20 eV, 285.42 eV, and 284.75 eV
were ascribed to C–N–C, C–(N)\(_3\), O = C–N, and C–C
groups, respectively. From the high-resolution scan of
N1s (Fig. 1d), four typical peaks are ascribed to the
nitrogen in C–N–C (398.81 eV), N–(C)\(_3\) (399.99 eV),
N–H (400.80 eV), and pi-excitations groups (404.75 eV)
[3], respectively. Furthermore, from the -resolution scan
of O1s (Additional file 1: Figure S7), the two peaks at
533.12 eV and 531.82 eV were ascribed to C–O and
C=O groups, respectively. The C=O was mainly ascribed
to the C=O–N and C=O–C groups in the TMC and the
generated –CONH–. The C–O peak may be due to the
surface oxygen cavity or hydroxyl group. In all, from
above analysis results, the possible detailed monomer
structure is shown in Fig. 2a, and the CN material was
prepared in a brief process successfully.

The XRD characterization in Additional file 1:
Figure S4a–c was indicated that the crystal structure
of CNs were not destroyed by different solvents,
temperature, and addition amount of TMC. From
Fig. 2b–d, we know that the strong peak located at
26.96° corresponded to the stacking of conjugated
aromatic planes (002 planes) and the relatively weak
peak at 12.45° was assigned to in-plane structural
packing motif of tri-s-triazine units (100 planes), re-
spectively. When different space groups were used to
build CN to obtain XRD patterns, typical characteris-
tic peaks of XRD patterns, typical characteristic
peaks of CN were perfectly displayed in the

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**Fig. 2** a Energy-optimized structural monomer representation and b–d the comparison of XRD patterns for CN material
simulated XRD patterns. Thus, the CN structure predicted in this work is reasonable.

Physical Structure of CN Material

The permanent porosity of CN was demonstrated by N\textsubscript{2} adsorption-desorption analysis at $-195.671$ °C (Fig. 3a). The isotherm shows a sharp uptake below P/P\textsubscript{0} = 1.0, and the Brunauer-Emmett-Teller (BET) surface area was calculated to be 125.6 $\text{m}^2/\text{g}$. Compared with traditional g-C\textsubscript{3}N\textsubscript{4} materials (5–35 $\text{m}^2/\text{g}$ \cite{2, 20, 21}, Fig. 3b and Additional file 1: Table S4), the BET surface of this new CN was enhanced greatly. From Scheme 1, through the reactions between $–\text{NH}_2$ and $–\text{COCl}$ in melamine and TMC, melamine could graft to TMC strongly and regularly, thereby dispersing uniformly in DMAc solution.

![Fig. 3](image)

Fig. 3 Pore size distribution of a CN and b g-C\textsubscript{3}N\textsubscript{4}. Inset: N\textsubscript{2} adsorption and desorption isotherm measured at $-195.671$ °C and the particle size of c CN and d g-C\textsubscript{3}N\textsubscript{4}

![Fig. 4](image)

Fig. 4 a SEM and b TEM images of CN material
Then, this process may provide more grafting sites for the subsequent calcination of melamine and improved the BET specific surface area greatly. As shown in Fig. 3c, d, the average particle size of CN was 467.1 nm, which was smaller than the 955.5 nm of g-C$_3$N$_4$. It is also proved that the CN material owned a large BET surface.

It was seen that the CN showed a uniformly distributed and loose block morphology from Fig. 4a. From the Additional file 1: Figure S8, the different CN layer structures were arranged orderly, and there was no obvious agglomeration. Besides, there were many pores in this CN due to the introduction of TMC. Moreover, as clearly observed in TEM (Fig. 4b), the CN owned many wrinkles and grooves. These are just the main reasons for that the CN has a high BET surface.

Adsorption-Enhanced Photoactivity of CN Material

The results of TGA curves are shown in Fig. 5. From Fig. 5, as the most stable allotrope of carbon nitride, the prepared CN material and g-C$_3$N$_4$ showed a unique temperature resistance up to 721 °C and 710 °C, respectively. From the result, it can be concluded that the CN is thermally stable in oxygen condition under 530 °C.

The photoactivity of 20 mg/L and 10 mg/L methyl orange (MO) was investigated by XPA photochemical reactor, which is shown in Fig. 6 (the $C_0$ is the absorbance of MO in initial concentration (20 mg/L and 10 mg/L), the $C$ is the absorbance of MO at different time) [20].

From Fig. 6a, this new CN had a high MO adsorption performance due to the large BET surface. After 120 min, the photoactivity was reached 60% far beyond the photoactivity of g-C$_3$N$_4$ [2], which was about 20%. The CN exhibited an excellent adsorption-enhanced photoactivity, even after 4 cycles under identical conditions (Fig. 6b). As we know, photo induced electron-hole pairs were generated on the surface of CN after absorption visible-light photons which were equal or higher than its band gap. During the photocatalytic process, while the photoelectron of CN reacted with oxygen to generate $\cdot$O$_2^-$ and $\cdot$OH. Subsequently, $\cdot$O$_2^-$ and $\cdot$OH combined with MO to further decompose into CO$_2$ and H$_2$O. However, the periodic lattice defects in the CN and g-C$_3$N$_4$ would capture photo-generated electrons, thereby reducing the photocatalytic efficiency [20]. Thus, the photoactivities of single CN and g-C$_3$N$_4$ materials were not high, which should be combined with other materials.

Conclusions

A new –CONH– bond linked CN material with hexagonal and quadrangle honeycomb-like structure was...
constructed by combining the high calcination with the chemical condensation of melamine and 1,3,5-benzenetri carbonyl trichloride. This material has a tri-s-triazine ring and benzene skeleton structure. The BET specific surface area of CN was about 125.6 m²/g, and the mean pore size is about 3.43 nm. This CN exhibited an excellent adsorption-enhanced photocatalytic performance.

**Additional file**

**Additional file 1:** Table S1 BET surface areas and average pore sizes of CNs prepared at 80 °C with the addition amount of 1.0 g TMC under different solvents. **Table S2** BET surface areas and average pore sizes of CNs prepared at different temperature with the addition amount of 1.0 g TMC under the solvent of DMAc. **Table S3** BET surface areas and average pore sizes of CNs prepared with different addition amount of TMC under the solvent of DMAc at 80 °C. **Figure S1.** Pore size distribution of CNs at 80 °C with the addition amount of 1.0 g TMC under different solvents. (a) H₂O, (b) CH₃COOH, (c) DMAc, (d) TEP, (e) DMF. Inset: N₂ adsorption and desorption isotherm for CNs measured at −195.671 °C. **Figure S2.** Pore size distribution of CNs at different temperature with the addition amount of 1.0 g TMC under the solvent of DMAc. (a) 50 °C, (b) 60 °C, (c) 70 °C, (d) 90 °C, (e) 100 °C. Inset: N₂ adsorption and desorption isotherm for CNs measured at −195.671 °C. **Figure S3.** Pore size distribution of CNs with different addition amount of TMC under the solvent of DMAc. (a) 50 °C, (b) 60 °C, (c) 70 °C, (d) 90 °C, (e) 100 °C. **Table S4.** The comparison of BET surface areas of CNs. **Figure S4.** XRD of different CNs (a) different solvents, (b) different temperature and (c) different addition amount of TMC. **Figure S5.** EDX spectra of (a) H₂O, (b) CH₃COOH, (c) DMAc, (d) TEP, (e) DMF. **Figure S6.** The element analysis of EDX. **Figure S7.** The high resolution scan of O1s of CN material. **Figure S8.** SEM images of CNs under different solvents. (a) H₂O, (b) CH₃COOH, (c) TEP, (d) DMF. **Figure S9.** Flow chart of simulation calculation of CN material. (DOC 8323 kb)

**Acknowledgements**

The authors are grateful for the financial support of Jiangsu Province Natural Science Foundation (BK20171260), the National Natural Science Foundation of China (21878118, 21476094), the Major Projects of Natural Science Foundation of Jiangsu Higher Education Institutions of China (18KJA530003), the Program for Science and Technology Development of Huaian (HAG201609), and Jiangsu province Ordinary Higher Education Institutions of China (18KJA530003), the Program for Science Foundation (BK20171268), the National Natural Science Foundation of China.

**Availability of Data and Materials**

The datasets supporting the conclusions of this article are included within the article and in additional file 1.

**Authors’ Contributions**

JW, Prof. ML, and Prof. YZ gave the idea and designed and performed the experiment, data processing, and manuscript drafting. Prof. ML modified the manuscript writing. All authors read and approved the final manuscript.

**Competing Interests**

The authors declare that they have no competing interests.

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Received: 30 May 2018 Accepted: 3 August 2018

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