Crystallinity Modulation of Layered Carbon Nitride for Enhanced Photocatalytic Activities

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Abstract: As an emerging metal-free semiconductor, covalently bonded carbon nitride (CN) has attracted much attention in photocatalysis. However, drawbacks such as a high recombination rate of excited electrons and holes hinder its potential applications. Tailoring the crystallinity of semiconductors is an important way to suppress unwanted charge recombination, but has rarely been applied to CN so far. Herein, a simple method to synthesize CN of high crystallinity by protonation of specific intermediate species during conventional polymerization is reported. Interestingly, the as-obtained CN exhibited improved photocatalytic activities of up to seven times those of the conventional bulk CN. This approach, with only a slight change to the conventional method, provides a facile way to effectively regulate the crystallinity of bulk CN to improve its photocatalytic activities and sheds light on large-scale industrial applications of CN with high efficiency for sustainable energy.

Introduction

Due to the rapid depletion of limited fossil fuels and increasingly worse environmental pollution, renewable solar energy has been widely investigated in recent years to address these global problems. In these processes, a photocatalyst is essential for solar energy conversion. Among them, as a new kind of semiconductor that combines the merits of both organic and inorganic counterparts, such as easy functionalization and high thermal stability, covalently bonded carbon nitride (de-noted as CN; $E_{g}$ = 2.7 eV) has emerged as a competitive candidate for photocatalytic fields, such as photocatalytic water splitting, CO$_2$ photoreduction, photocatalytic degradation of pollutants, and photoelectrochemistry. However, bulk CN suffers from a low specific surface area, low visible-light absorption and quantum yield, a high recombination rate of photogenerated electron–hole pairs, and low crystallinity; these hinder its potential practical applications. Thus, many strategies, such as utilization of chemical doping to tailor the electronic structure of CN, nanoarchitectonics to engineer the porosity and morphology, and photoelectrochemical activity by a factor of up to seven times, compared with that of conventional bulk CN. It was also developed to improve the crystallinity; nevertheless, the high cost (ca. $200 g^{-1}$) hindered its large-scale applications. Herein, we report that the polymerization kinetics for CN in an anodic aluminum oxide (AAO) membrane template resulted in CN with high efficiency for sustainable energy.

Polymerization

The most common way to prepare CN is based on a solid-state thermal condensation process. However, the inherent limitation in diffusion of intermediate species during solid-state polymerization results in poor crystallinity of as-prepared CN. By using molten salts as the solvent, the crystallinity was largely improved, but the resulting product was virtually inactive in photocatalytic reactions because of the occurrence of a secondary change of CN into poly(triazine imide), or was inapplicable for large-scale applications in photocatalysis due to extremely low synthetic yields. The confined growth of CN in an anodic aluminum oxide (AAO) membrane template was also developed to improve the crystallinity; nevertheless, the high cost (ca. $200 g^{-1}$) hindered its large-scale applications. Herein, we report that the polymerization kinetics for CN could be greatly improved merely by protonating specific intermediate species during thermal condensation. Interestingly, such a slight modification to the conventional method (Scheme 1) resulted in CN with a high crystallinity and preferred orientation. Consequently, as-prepared CN exhibited not only significant enhancements in photocatalytic dye degradation, but also photoelectrochemical activity by a factor of up to seven times, compared with that of conventional bulk CN. It should be noted that, although protonation of precursors such as DCDA and melamine was used to engineer the morpholo-
gy of CN with improved photocatalytic activity, no improvement of the crystallinity has been achieved so far, and low crystallinity has limited potential applications of CN, such as exfoliation of high-quality nanosheets for solid-state photoelectric conversion devices.\(^{[20]}\)

**Results and Discussion**

It was reported that bulk CN could be reversibly protonated by HCl due to the presence of unpaired electrons of nitrogen atoms in the framework of CN, and the stacked lamellar texture of CN could be partially opened from the edges.\(^{[24]}\) This interesting phenomenon implied that protonation of the open edges with disrupted interfacial hydrogen bonding would result in more freedom to polymerize with each other in solid-state condensation. Thus, to obtain highly crystalline CN, a slight modification of the general method (Scheme 1), that is, additional protonation of the intermediates during thermal condensation, was investigated. In the first set of experiments, the intermediate species obtained by thermally condensing DCDA at 400 °C in \(\text{N}_2\) was protonated, as verified by the new appearance of the counteranion of the acid that could be detected by X-ray photoelectron spectroscopy (XPS; see Figure S1a and more discussion in the Supporting Information). After further condensation in \(\text{N}_2\), the final CN was obtained and denoted as CN-T-C, in which \(T\) is the polymerization temperature of the intermediate species from DCDA, and C is the concentration of HCl solution used for protonation. The FTIR spectra in Figure S1b in the Supporting Information suggested that the activation step did not alter the pristine conjugated structure of CN. Moreover, elemental analysis showed that, with protonation activation, the C/N atomic ratio of CN was almost unchanged. The structure of as-prepared CN was further characterized by powder X-ray diffraction (PXRD) curves in Figure 1 and Figure S2 in the Supporting Information. Compared to conventional bulk CN, the activated CN had a similar characteristic (100) diffraction peak, which indicated that the graphite-like structure of CN was retained after the activation step. However, it was observed that the FWHM of the (002) peak for CN with protonation activation was reduced in comparison with that of bulk CN prepared in the traditional way. For instance, the FWHM of CN-400-1 \(\mu\) m was much smaller (0.687) than that of CN (0.840). It was also observed that a higher concentration of HCl resulted in a moderate decrease in crystallinity, but this was still superior to that of conventional bulk CN (Figure S2 in the Supporting Information). Considering that a high concentration of HCl opened up more edges of the lamellar texture and caused an irreversible structural change to CN, the concentration of HCl needed to be optimized for high crystallinity. In addition, other mineral acids, such as HBr, were also applicable for such protonation activation. For a more comprehensive comparison, CN prepared by a traditional one-step polymerization in \(\text{N}_2\) atmosphere (CN-N\(_2\)) and that synthesized by the same two-step polymerization but without protonation (CN-400-0 \(\mu\) m) were also investigated as controls to exclusively verify that, instead of the condensation atmosphere and two-step polymerization, protonation activation itself played the primary role in enhancing the crystallinity of CN (Figure S3 in the Supporting Information).

Figure 1. The PXRD and capillary XRD (CXRD) patterns of CN (a) and CN-400-1 \(\mu\) m (b). Insets show the full-width at half-maximum (FWHM) values and the ratio of the (002) to (100) peak intensity.

CXRD was further used to exclude preferential orientation effects. Compared with that in the PXRD pattern, the \(I_{002}/I_{100}\) ratio of bulk CN in the CXRD pattern increased (Figure 1a), which indicated that bulk CN had a preferred orientation in the 002 direction. In contrast to bulk CN, the \(I_{002}/I_{100}\) ratio in the CXRD pattern of CN-400-1 \(\mu\) m decreased in comparison with that in the PXRD pattern (Figure 1b). The results essentially showed a preferred orientation in the 100 direction for CN-400-1 \(\mu\) m, that is, it gave higher priority to polymerization of CN with a larger lateral size. Nevertheless, with increased concentration of acid, such a trend for preferred orientation weakened (Figure S4 in the Supporting Information).

To obtain detailed information of the formation process of CN with improved crystallinity, the morphology of various CNs was characterized by SEM. As shown in Figure 2a and b, conventional bulk CN was composed of solid agglomerates with sizes of several micrometers and some stacked lamellar textures at the edges. The intermediate species, obtained by condensing DCDA at 400 °C (Figure S5a in the Supporting Information), was composed of randomly oriented particles with a larger size than that of conventional bulk CN because of shrinkage during further condensation (Figure 2a b). After protonation with a 1 \(\mu\) m solution of HCl, the large particles were partially transformed into finer particles with smaller sizes and a more evident stacked lamellar texture at the edges (Figure S5b in the Supporting Information). One possible reason was that the acid treatment process might disrupt hydrogen...
bonding between individual strands of (and aggregates) of melon (i.e., poly(melalem)) and form a more ordered structure simultaneously. Interestingly, after further condensation at 550 °C, the final product exhibited an individual sheet-like structure with unswerving edges (Figure 2d,e), TEM images of CN without (Figure 2c) and with (Figure 2f) protonation activation also showed distinct differences in edge structures, similar to those observed by SEM. Moreover, in contrast to the diffraction ring in the electron diffraction pattern for conventional bulk CN (Figure 2c, inset), hexagonal diffraction spots were observed for CN with protonation activation (Figure 2f, inset); this further verified higher crystallinity for the latter. The unswerving edge of CN gradually disappeared upon further optimizing the concentration of HCl used for protonation (Figure S5c in the Supporting Information); this was consistent with the XRD results shown in Figure 1 and Figures S2 and S4 in the Supporting Information.

The photocatalytic degradation of rhodamine B (RhB), which is an example of an organic pollutant, was first investigated to evaluate the photocatalytic activity of as-prepared CN with improved crystallinity. As shown in Figure 3a and Figure S6 in the Supporting Information, compared with CN, the photocatalytic degradation ability of CN-400-C (C = 1, 3, 6, 12 μm) was improved, whereas no degradation was observed without catalysts under identical illumination conditions, which showed that the catalytic activity was derived from the CN photocatalysts. With the respect to that of bulk CN, the first-order rate constant (k) for photocatalytic RhB degradation by various protonation-activated CN-400-C (C = 1, 3, 6, 12 μm) catalysts was calculated and found to be significantly improved (Figure S7a in the Supporting Information). The highest k, obtained for CN-400-1 μm (k = 0.01296 min⁻¹), was about seven times that of traditional bulk CN (k = 0.00184 min⁻¹; Figure S7a in the Supporting Information).

The photocatalytic activities of all as-prepared CN were also evaluated by photocurrent generation in a standard photoelectrochemical cell (PEC) configuration. As shown in Figure S7b in the Supporting Information, the cathodic photocurrent under visible light (λ > 420 nm) irradiation gradually increased when the biased potential became more negative. Meanwhile, the photocurrent was sensitive, steady, and reproducible during cyclic on/off with a fixed bias potential (Figure 3b). Moreover, the cathodic photocurrent of all CN-400-C (C = 1, 3, 6, 12 μm) catalysts was much higher than that of conventional bulk CN under identical conditions (Figure 3b and Figure S7b in the Supporting Information). For instance, the highest photocurrent, obtained for CN-400-3 μm (different from the sample for the best photocatalytic degradation of RhB, presumably due to different types of photochemical reactions), was 5 times that of CN biased at 0 V (Figure 3b).

To explore the mechanism for enhanced photochemical activities after protonation, the BET surface area, which is an important factor for photocatalysts, was investigated. However, it was noted that the surface area of CN-400-C (C = 1, 3, 6, 12 μm) was only moderately improved (ca. 50%; Figure S8 in the Supporting Information), in contrast to several tenfold increases observed in previous studies on protonation of precursors such as DCDA and melamine. This suggested that slight changes to the surface area could not fully account for the much improved photochemical activity (ca. 5–7 times). Because polymerization for the synthesis of CN consisted of multiple condensation steps, the solid-state reaction would limit free diffusion of intermediate species, and thus, result in many defects, which would hinder the effective separation of photogenerated electrons or holes. By engineering the polymerization kinetics of CN through protonation activation, the crystallinity/defects of the as-prepared CN would be modulated,
which would make the separation of photogenerated electrons or holes in photocurrent generation and photocatalytic dye degradation more efficient. In this sense, the crystallinity improvement would be the main factor for the much improved photochemical performances. To verify this speculation, nano-second-level time-resolved fluorescence decay spectra of all as-prepared CN were recorded (Figure 3c and Figure S9 in the Supporting Information). The radiative lifetimes of charge carriers in each CN and their percentages are also listed in Figure 3c and Figure S9 in the Supporting Information by fitting the decay spectra. Evidently, it was observed that the short (τ1 and τ2) and long (τ3) lifetimes of the charge carriers in CN both increased after the formation of an improved crystalline structure. The prolonged lifetime indicated that the material was more crystalline and had less grain boundaries, and might, in turn, lead to the increased possibility that excited electrons or holes would be captured by electron-acceptor or -donating species in the photocatalytic reactions.\(^{21}\)

Protonation activation during the polymerization process was further supported by faster weight loss of intermediate species with protonation than that without any protonation. Figure 3d shows the thermal gravity (TG) and differential thermal gravity (DTG) curves of the intermediate species that polymerized from DCDA at 400 °C with protonation (Intermediate-400-1 m) by using 1 mol HCl and without protonation (Intermediate-400) under the same heating conditions as those used for CN-based materials. Without protonation, a major weight loss at about 480 °C and a minor one at about 550 °C appeared; these corresponded to the formation of melon and CN, respectively, through the successive release of ammonia. Notably, it was observed that, after protonation, the minor weight loss partially moved to a lower temperature (∼450 °C), as a result of enhanced polymerization kinetics.

To gain more insight into the role of protonation activation in preparing CNs with improved crystallinity for enhanced photochemical activities, intermediate species that were obtained by condensing DCDA at 350 and 450 °C were also studied as controls in the same protonation activation experiments. Nevertheless, it was found that the crystallinity and photocurrent generation of as-obtained CN-350-3 m and CN-450-3 m were not improved (Figure S10 in the Supporting Information) with respect to that of CN-400-3 m; this evidently showed that the best polymerization kinetics were obtained by protonating the intermediate that was condensed at 400 °C. Because the intermediate species obtained by condensing DCDA below 400 °C during thermal condensation (see steps 1 and 2 in Scheme 2) were still small molecules and diffusible to a large extent by melting and/or sublimation, polymerization in this early stage would be easier compared with the later cross-linking of the less diffusible CN framework (see step 3 in Scheme 2). As shown, the protonation of the primary building unit (i.e., tri-s-triazine), which formed at 400 °C before cross-linking,\(^{21}\) could effectively promote the whole sluggish condensation kinetics to give CN with improved crystallinity. Therefore, the intermediate species should be critically selected to enhance the crystallinity by protonation activation. This could also explain why the protonation of precursors such as DCDA and melamine in previous studies did not lead to any enhancement of crystallinity of bulk CN.\(^{19}\)

A moderate difference in photochemical activities among CN-400-C (C = 1, 3, 6, 12 m) were also observed. This phenomenon may be ascribed to multiple mechanisms that were collaboratively influenced by different charge-carrier mobility kinetics (Figure 3c and Figure S9 in the Supporting Information), surface areas (Figure S8 in the Supporting Information), and light absorption abilities (Figures S11 and S12 in the Supporting Information), and needs further comprehensive investigation. It is also noteworthy that, superior to crystallinity improvement during the preparation of CN obtained by using the confinement effect of the AAO membrane\(^{11a}\) and molten salts as solvents\(^{19}\) with very limited yield, our proposed protonation activation is applicable to large-scale industrial applications because only a minor modification of using common mineral acids ($100/ton) was applied to the conventional preparation method.

**Conclusion**

A facile protonation was successfully applied to regulate the crystallinity of bulk CN by promoting the solid-state polymerization kinetics. Interestingly, the as-prepared CN with high crystallinity and preferred orientation exhibited much improved photocurrent generation and photocatalytic RhB degradation performances under visible-light irradiation due to the effective suppression of unwanted charge recombination. Different from the previous incorporation of heterojunction or cocatalysts, chemical doping, and templating methods, crystallinity engineering offered us a new way to improve the photocatalytic activities of emerging metal-free bulk CN materials. Moreover, because of only a slight modification of the conventional thermal condensation process, the proposed strategy was promising for development as a general way to produce large-scale industrial quantities of CN with enhanced performances for applications in sustainable energy production. Meanwhile, the ease of obtaining CN with high crystallinity and preferred orientation would greatly benefit the exfoliation of CN nanosheets of large lateral size, making it promising for broader potential applications, such as in solid-state photoelectric conversion devices.
Experimental Section

Chemicals and reagents

DCDA (99 %) was purchased from Aldrich. Hydrochloric acid (36–38 wt %) and ethanol (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. Orgacon poly(3,4-ethylenedioxythiophene) (PEDOT) inkjet ink (PEDOT/poly(styrene sulfonate) (PSS), UI-1005) was purchased from Agfa-Gevaert N.V. (Belgium). Ultrapure water (18.2 MΩ·cm) was obtained from a Thermal water purification system. Unless otherwise specified, other chemicals were of analytical grade and used without further purification.

Preparation of conventional bulk CN

In general, conventional bulk CN samples were prepared by condensing DCDA within a crucible with a cover at 550 °C for 4 h with a ramp time of 4 h in air or N₂. The resulting yellow products were then washed with water and ethanol and dried at 80 °C for 12 h. The final products were obtained by further heating at 550 °C for 2 h in N₂ with a ramp time of 2 h, and denoted as CN–T₂, in which T is the condensation temperature for the intermediates and C is the concentration of HCl.

Photoelectrochemical experiments

The photoelectrodes were prepared by spreading aqueous slurries of various CN-based materials over 0.49 cm² of indium tin oxide (ITO) glass substrate (≤7 Ω/□) by using adhesive tapes as spaces. The suspension was prepared by grinding CN-based materials (10 mg) with water (30 μL) and PEDOT/PSS ink (30 μL). Then the photoelectrodes were annealed in air at 80 °C and kept at this temperature for 30 min. The photoelectrochemical experiments were performed in a traditional three-electrode system in a quartz tank with a platinum wire as the auxiliary electrode and Ag/AgCl (saturated KCl) as the reference electrode. The 150 W Xe lamp (Beijing NBeT Co., Ltd.) was used as a light source with a Schott optical filter GG420 to give visible light (λ > 420 nm). The photoelectrodes were illuminated from the back (106 mW cm⁻²). The current difference between the light and dark was defined as the net photocurrent.

Photocatalytic degradation

The photocatalytic activity of the samples was evaluated by measuring the degradation of RhB in aqueous solution under visible-light irradiation (λ > 420 nm) induced by a 150 W Xe lamp. Typically, photocatalysts (300 mg) were dispersed in a solution of RhB (300 mL) with an initial concentration of 10 mg L⁻¹. This suspension was stirred for 2 h in the dark to give a good dispersion and establish an adsorption–desorption equilibrium between the photocatalysts and dye. After a certain time interval, an aliquot (800 μL) of the solution was taken out and centrifuged to remove the photocatalysts, and the concentration of RhB was measured by UV/Vis absorption spectroscopy at λ = 553 nm. The degradation rate was represented by ln(Ct/C0), in which C₀ and Cₜ are the concentration of the adsorption–desorption equilibrium and at a certain time, respectively.

Characterization

The UV/Vis absorption spectra were recorded with a 2450 UV/Vis spectrophotometer (Shimadzu, Japan) by using BaSO₄ as a reference. FTIR spectroscopy was recorded with a Nicolet 4700 FTIR spectrometer (Thermo, USA) equipped with an attenuated total reflection (ATR) setup. TG analysis was performed on an SDT-Q600 instrument (TA instrument corporation, USA) in N₂ (10 mL min⁻¹). The XRD patterns were recorded on SmartLab and Ultima IV diffractometers (Rigaku, Japan). A new peak located at about 25 ° for CN appeared when using the CXYD method. The exact assignment of this peak was not yet clear, but was presumably related to preferential orientation effects. SEM images were recorded by using JSM-7401F (JEOL, Japan) and Phenom ProX scanning electron microscopes (Netherlands). The BET surface area was calculated from 77 K N₂ adsorption–desorption isotherms obtained by using a NovaWin 1000e instrument (QuanchtachroA, USA). The photoluminescence (PL) spectra were recorded on a Fluoromax-4 fluorescence spectrometer (Horiba Jobin Yvon, Japan). Time-resolved PL spectroscopy was recorded on a Fluorolog 3-TCSPC steady transient fluorescence spectrometer (Horiba Jobin Yvon, Japan) with excitation at λ = 370 nm. XPS analysis was obtained using a Thermo ESCALAB 250Xi instrument with a monochromatized Alkα X-ray source (hv = 1486.6 eV). Elemental analysis was performed on a Vario EL elemental analyzer.

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