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COMMUNICATION

Photochemical Construction of Carbonitride Structures for Red-Light Redox Catalysis

Pengju Yang, Ruirui Wang, Min Zhou and Xinchen Wang*

Dedicated to Professor Xintao Wu on the occasion of his 80th birthday

Abstract: Metal-free carbonitride(CN) semiconductors are appealing light-transducers for photocatalytic redox reactions due to the unique bandgap and stability. To harness solar energy efficiently, CN catalysts that are active over a wider range of the visible spectrum are desired. Herein, we report a photochemical approach to prepare a new-type triazine-based CN structure. The obtained CN shows extraordinary light-harvesting characteristics, with suitable semiconductor-redox potentials. The light absorption edge of the CN reaches up to 735 nm, which is significantly longer than that of the conventional CN semiconductor at ~460 nm. As expected, the CN can efficiently catalyse oxidation of alcohols and reduction of CO2 with visible-light, even under red-light irradiation. The results represent an important step toward the development of red-lightresponsive triazine-based structure for solar applications.

At present, the world's energy demand largely originated from non-renewable fossil fuels, the combustion of which leads to severe environmental issues.^[1] Therefore, the development of clean and renewable energy resources is desirable. Photocatalysis has gained considerable attentions in the scientific community to address globe energy and environmental issues using sustainable catalysts and solar irradiation to run relevant chemical reactions at ambient conditions.^[2]

Polymeric carbon nitride (PCN) has attracted substantial interest due to its facile synthesis and suitable bandgap.^[3] PCN obtained from the thermal polymerization displays a narrow visible-light response at 460 nm.^[4] In the solar spectrum, visible light and near infrared light account for 45% and 50% of the solar light, respectively.^[5] In view of solar energy utilization, PCN necessitates to harvest the broad spectrum of solar light.^[6] To date, various strategies have been used to extend the light absorbing region of PCN.^[7] For example, Liu et al. found that the light absorption edge of amorphous PCN reached 682 nm.^[8] Zhang et al. extended the optical absorption of PCN from 462 to 700 nm by co-condensation.^[9] However, previous approaches usually require complicated and high-temperature processes.^[10] It is thus essential to explore facile pathways to synthesize PCN with a narrower bandgap.

Solar radiation was the largest source of energy on the early Earth.^[11] There is a consensus that ultraviolet irradiation could drive the synthesis of reactive molecules like cyanide and formaldehyde, which in turn would react to produce long-chain molecules even polymers that could serve as prebiotic molecules necessary for the evolution of life.^[12] Theoretically, when the photon energy was comparable to the energy of a chemical bond, light has the potential to break such bonds and then initiate bimolecular and/or polymer chemistry in thermodynamics.^[12a] Notably, excitation triggered by thermal process caused energy to be distributed according to Boltzmann

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equilibrium distributions.^[12a] Photochemistry depends on the absorption of a photon, which specifically stimulates a molecule or chemical bond, thus energy was distributed in a non-equilibrium field.^[12a] This feature of photochemistry implies greater energy agitation within the system, which may induce peculiar chemistries compared with thermal process. Therefore, it is expected to obtain a unique CN superstructure by a photosynthesis route, as it is an innovative tool to prepare functional materials.^[13] However, there is no report on the synthesis of CN semiconductor by photochemistry-induced polymerization of triazine subunits.

Herein, we prepared a new-type CN with a quasi-twodimensional structure by a photochemistry approach (Figure 1). The solid-state NMR and X-ray absorption near-edge spectra (XANES) confirmed that the CN was a unique triazine-based polymer. This sample showed extraordinary light-harvesting features and appropriate energy gap positions. The light absorption edge of the developed CN reached 735 nm, far exceeding all reported data of CN-based semiconductors. The CN can drive redox reactions, such as oxidation of alcohols and reduction of CO₂ even under red-light irradiation.



Figure 1. Illustration of the synthesis of CN by a photochemistry method

The bond energies of N-H, C-CI, C-N and C=N are 389, 328, 305 and 615 kJ/mol, respectively.^[14] In theory, N-H, C-CI, C-N and C=N can be cleaved by UV light at 307, 364, 392 and 194 nm, respectively. Although the bond energy of C-N is lower than those of N-H and C-CI bonds, the C-N bonds in triazine ring are stable due to the conjugation effect.^[15] Accordingly, the N-H and C-CI bonds in melamine and cyanuric chloride might be preferentially broken and synchronously constructed into CN-polymer under UV irradiation.

The CN sample was examined by X-ray diffraction (XRD), showing two peaks at 10.2° and 27.3° (Figure S1).^[16] The peak at 27.3° and 10.2° corresponded to the (002) and (100) planes, respectively.^[17] Transmission electron microscopy (TEM) showed that the CN was a lamellar-like structure (Figure S2a). High-resolution TEM (HRTEM) was displayed in Figure S2b. The CN exhibited worm-like features, indicating low crystallinity. Figure 2a displayed high-angle annular dark-field (HAADF) images and element mappings of the CN. Apparently, the N and C elements were distributed uniformly throughout the whole selected area, proving homogeneity of the CN. Moreover, we also observed the presence of CI and O elements (Figure S3). The mapping of CI and O suggested the contents of CI and O were low, supporting the EDX results (Figure S4).

were low, supporting the EDX results (Figure S4). To explore the structures of the CN, ¹³C and ¹⁵N solid-state NMR were performed. In Figure S5, two peaks at ¹³C chemical shifts of 164 and 155 ppm were observed, consistent with ¹³C NMR of triazine moiety.^[17-18] The¹⁵N NMR of CN was shown in Figures 2b and S6, which was different from those of the precursors (Figure S7). The signals at 167 and 96 ppm were attributed to the outer ring nitrogen of triazine ring and terminal NH₂, respectively.^[19] The signal at 140-117 ppm corresponded to

the bridging NH.^[19] The upfield shift of ¹⁵N NMR is due to the shielding of electron-donating OH groups, consistent with the density functional theory calculation results (Figure S8).^[20] To further determine the structure of CN, ¹⁵N cross-polarization polarization inversion (CPPI) NMR was performed. The NH and NH₂ groups showed lower signals, whereas the signal of the outer ring nitrogen remained unaffected. Moreover, the signal for the central nitrogen cannot be identified. These results indicated that the CN was a triazine-based polymer. To further confirm this, XANES was measured. The XANES spectra of C and N Kedges of the CN were displayed in Figures 2c and 2d, respectively. The peaks at 283.8 and 286.9 eV corresponded to the C=C and C=N bonds, respectively.^[21] The peaks at 397.5, 400.1 and 402.7 eV assigned to C=N-C, central nitrogen and bridging nitrogen, respectively.^[21] The CN and PCN demonstrated analogous C and N K-edges (Figure S9). However, the intensity of central nitrogen of CN was evidently lower than that of the PCN. This indicated that the CN was triazine structure, supporting the ¹⁵N NMR results. Elemental analysis and inductively coupled plasma optical emission spectrometer were measured to analyze the composition of the CN. The C/N ratio of the CN was 0.783, which was close to the theoretical value (0.75) for CN-polymer (Table S1). The content of Cl and O were 2.71at.% and 9.59at.%, respectively. Therefore, the formula of the CN was C₃N_{3.8}H_{5.2}O_{1.3}Cl_{0.37}, with the proposed structure in Figure S10.



Figure 2. a) HAADF image and element mappings, b) ¹⁵N NMR (black line) and ¹⁵N CPPI NMR(referenced to liquid ammonia), c) C *K*-edge XANES, d) N *K*-edge XANES, e) XPS C 1s and XPS N 1s of CN.

The surface compositions were investigated by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) spectroscopy. The survey XPS spectrum was shown in Figure S11. The C 1s (Figure 2e, Table S2) peaks at 284.6, 286.5 and 288.1 eV were assigned to C=C, C-NH_x and N-C=N bonds, respectively.^[22] The N 1s peak at 398.6, 399.8 and 401.3 eV, corresponded to C-N=C, N-(C)₃ and C-NH(Figure 2f, Table S3), respectively.^[22,23] The binding energy at 199.9 and 202.1 eV corresponded to Cl $2p_{3/2}$ and Cl $2p_{1/2}$ peaks (Figure S12a), respectively, attributable to C-Cl bond.^[24] The peaks at

532.1 and 533 eV assigned to OH groups and adsorbed water (Figure 12b, Table S4), respectively.^[24] The FTIR peaks at 800 and 1490 cm⁻¹ stem from the breathing mode of triazine units (Figure S13a).^[25] The bands between 1100 and 1700 cm⁻¹, belonged to the characteristic stretching modes of CN heterocycles.^[26] The band at 3400 cm⁻¹ was attributed to the -NH_x/OH groups.^[27] The band at 570 cm⁻¹ corresponded to the vibration of C-CI species.^[24, 27] Raman spectrum was analyzed in Figure S13b. The intensity for the CN was relatively weak caused by the fluorescent background. Some new peaks may relate to the exceptional configurations in CN.



Figure 3. a) UV/vis (Inset shows the bandgap, 298 K), b) normalized PL (298 K), c) Photocurrent (bias voltage: -0.2 V, 50 W LED as light source), d) EPR (298 K), e) XPS-VB and f) Energy band positions of CN.

UV/vis absorption spectrum of the CN was shown in Figure 3a. The absorption edge of the CN reached 735 nm, which far exceeded the values for PCN and the precursors (Figure S14).^[28] A bandgap of 1.68 eV was calculated for the CN (Figure 3a Inset). The radiative process of photogenerated charges in CN was analyzed by photoluminescence (PL) spectroscopy. The CN displayed an excitation-dependent PL emission (Figure 3b). This indicated that the CN possessed continuum mid-gap states. The PL and time-resolved PL of CN and PCN were shown in Figures S15 and S16, respectively. The CN displayed enhanced charge separation/transfer, which possibly originated from the donor-CN-acceptor configuration caused by the electron-donating -OH groups and electron-withdrawing -CI groups. The geometric structure of PCN displayed a tendency to distort by homogeneous amorphization, which modulated the electronic structure and thus increased its light absorption.^[8] It was observed that the distorted structure can narrow the bandgap of PCN by activating $n \rightarrow \pi^*$ transitions in the visible region.^[29] The HRTEM and NMR results revealed that the CN was an amorphous polymer. Thus, the narrowed bandgap of the CN may derive from the structure distortion, which resulted in $n \rightarrow \pi^*$ transitions, enhancing visible light harvesting.^[8,29] Additionally, the C/N ratio of CN was 0.783, indicating the presence of nitrogen vacancies in the CN matrix. This also reduced the bandgap by the formation of vacancy-related localized states.

Transient-state photocurrent was investigated to study the separation kinetics of charges. Obviously, the CN material

generated significant photocurrent under visible-light irradiation (Figure 3c), suggesting excellent separation and transfer of photogenerated charges. It was witnessed that the photocurrent decreased when increasing the incident-light wavelength. However, there was still a noticeable photocurrent found at paramagnetic resonance Electron *λ*=730 nm. (EPR) demonstrated one single Lorentzian line, originating from unpaired electrons on π -conjugated CN networks (Figure 3d). An enhanced EPR signal was seen under light irradiation, indicating the efficient generation of photoelectrons in the CN. XPS valence band spectrum was examined to determine the valence band (VB) of the CN. As exhibited in Figure 3e, the VB value of the CN was approximately 1.41 eV. Based on the bandgap determined from Tauc plot, the conduction band (CB) value of the CN was -0.27 eV. The VB and CB positions of the CN were schematically shown in Figure 3f.



Figure 4. a) Dependence of the alcohol-oxidation activity on the wavelength(10 h, 333 K), b) Conversion of different benzyl alcohol to aldehyde(420 nm LED, 10 h, 333 K), c) Dependence of the CO_2 reduction activity on the wavelength (1h, 303 K) and d) Time courses of CO production from CN(303 K).

We firstly employ the CN to activate O₂ for photocatalytic oxidation of benzyl alcohol. It can catalyze the oxidation of benzyl alcohol to benzaldehyde with>80% selectivity and 25% conversion rate under 420 nm LED irradiation. Without CN, trace conversion of benzyl alcohol was observed with light irradiation under O₂ atmosphere. In the absence of light, the conversion rate of benzyl alcohol was 1.5%. When the reaction was performed in N_2 atmosphere, the conversion rate was 7.2%, suggesting that the O2-mediated was the main channel for alcohol oxidation. These findings also suggested that the selective conversion of benzyl alcohol was driven by light. The dependence of the alcohol-oxidation activity on the wavelength was illustrated in Figure 4a. Expectedly, the CN still triggered the oxidation of benzyl alcohol under red-light irradiation. The conversion rates agreed with the light absorption. The selectivity of benzaldehyde under different irradiation wavelength was displayed in Figure S17. The high conversion rate of the CN can be ascribed to the donor-CN-acceptor configuration (Figure S15). The influence of substituent was also measured (Figure 4b). The conversion of benzyl alcohol was enhanced by electron-donating substituents and retarded by electron-withdrawing substituents.

The CN showed admirable CO_2 uptake compared with the PCN due to the abundant -NH_x/OH groups as Lewis bases (Figure S18), we thus employed CN for CO_2 photoreduction (Figure 4c). Upon 420 nm LED irradiation for 1 h, the system generated CO (1.8 µmol) and H₂ (0.87 µmol). The CO evolution rates of CN were depended on the incident wavelength,

illustrating that the reaction was induced by light. The CN still displayed the ability to drive CO_2 conversion under red light irradiation at 730 nm. Figure 4d showed the CO evolution from CN in a 6-hour reaction under different wavelengths. Noticeably, the activity had no noticeable loss, suggesting high stability. The H₂ production (as a byproduct) from the CN catalyst was displayed in Figure S19. The enhanced CO_2 adsorption and promoted charge separation are beneficial for photocatalytic CO_2 reduction. When ¹³CO₂ acted as reactant, only ¹³CO (m/z = 29) was detected (Figure S20), confirming that the CO was derived from CO_2 .

In conclusion, a photochemical polymerization approach was developed for the textural engineering of triazine monomers to CN-polymer. Results showed that the obtained CN is a triazine-based polymer. This CN possessed extraordinary light-harvesting properties. The light absorption edge reached 735 nm, which was significantly longer than that of the conventional PCN. As expected, the CN can efficiently catalyze oxidation of alcohols and reduction of CO_2 under red-light irradiation. Our results represent a significant step toward solar redox reactions. We believe that this photochemistry route may open up a new avenue to construct other CN-based polymers with desired electronic structure and surface functions for advanced applications.

Acknowledgments

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Keywords: Carbon nitride • Red light • Photochemistry • Organic catalysis

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An innovative photo-polymerization approach was developed to prepare triazine-based carbonitride with a narrow bandgap of 1.68 eV and an optical absorption edge at 735 nm, while still with suitable semiconductorenergetics for redox catalysis. This structure can efficiently catalyse the oxidation of alcohols and reduction of CO_2 under red-light irradiation.

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