A Facile Steam Reforming Strategy to Delaminate Layered Carbon Nitride Semiconductors for Photoredox Catalysis

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Abstract: The delamination of layered crystals that produces single or few-layered nanosheets while enabling exotic physical and chemical properties, particularly for semiconductor functions in optoelectronic applications, remains a challenge. Here, we report a facile and green approach to prepare few-layered polymeric carbon nitride (PCN) semiconductors by a one-step carbon/nitrogen steam reforming reaction. Bulky PCN, obtained from typical precursors including urea, melamine, dicyandiamide, and thiourea, are exfoliated into few-layered nanosheets, while engineering its surface carbon vacancies. The unique sheet structures with strengthened surface properties endow PCNs with more active sites, and an increased charge separation efficiency with a prolonged charge lifetime, drastically promoting their photoredox performance. After an assay of a H₂ evolution reaction, an apparent quantum yield of 11.3% at 405 nm was recorded for the PCN nanosheets, which is much higher than those of PCN nanosheets. This delamination method is expandable to other carbon-based 2D materials for advanced applications.

Light-driven hydrogen production has attracted great attention because it provides an ideal solution for global energy and environmental issues.[1] Therefore, the development of abundant, sustainable, and efficient photocatalysts is of particular importance for this purpose.[2] Recently, polymeric carbon nitride (PCN) has become a promising candidate for photocatalytic H₂ evolution due to its low costs, robust stability, and proper band structure.[3] Since 2009, PCN have been used as a photocatalyst to drive water splitting,[3] and much progress has been achieved. However, PCN obtained from the bulky polymerization of nitrogen-rich precursors such as melamine, dicyandiamide, and cyanamide, displays a relatively low surface area, limited active sites, and a fast charge recombination rate, which are basically caused by the van der Waals forces and dense π–π stacking between the PCN layers.[4] These interactions limit the application of PCNs in photocatalysis and other fields.

At present, various strategies have been developed to promote the photoactivity of pristine PCN. For example, a soft/hard template, supramolecular organization, and exfoliation approaches have been used to prepare special geometrically shaped or few-layered PCNs to increase the surface area and active sites.[5] To accelerate charge separation, coupling PCN with a secondary semiconductor or carbon material (i.e., graphene, carbon nanotube) has also been widely studied.[6] The exfoliation of PCN into single or few-layered nanosheets is an effective route to improve its photocatalytic performance.[5a,e] This is not surprising, because the peeling of layered materials to single or few-layered nanosheets, which are structurally analogous to graphene, has been shown to induce exotic physical properties. This has motivated large activity toward fabricating nanosheets from materials ranging from metal oxides, chalcogenide, and nitrides to emerging conjugated polymers, such as PCN. Subsequently, a variety of delamination methods have been developed, such as sonication exfoliation,[7] protonation exfoliation,[8] ball milling,[9] and thermal etching.[10] However, organic reagents or strong acids are inevitably used as solvents for such exfoliation processes, which are time consuming and inefficient. Therefore, the development of a green and efficient approach to fabricate few-layered PCN nanosheets is desired.

The steam reforming reaction [C₆H₆ + nH₂O → nCO + (n + m/2)H₂] is a well-known reaction that is used to produce H₂, CO, or other chemicals from hydrocarbons. Recently, some studies found that this conventional chemical reaction can be a facile tool for preparing activated carbon materials and making pores in carbon materials.[11] In particular, this reaction can spontaneously occur in low-crystalline region as well as at the interface between carbon materials and metal nanoparticles, suggesting the predictability and controllability of this reaction.[11a,b] Such reactions are based on the carbon-steam reforming reaction [C(s) + H₂O(g) →CO(g) + H₂(g)].[11a,b,12] PCN consists of carbon and nitrogen atoms, based on tri-s-triazine units as elementary building blocks that intrinsically possess chemical/physical properties similar to those of carbon materials. In principle, water can also react with the carbon atoms in PCN at high temperatures and synchronously introduce surface carbon vacancies due to the discrepancies between its in-plane and out-of-plane properties. Moreover, the diversity of its chemical bonds, such as C–N=C, N-(C), and C=N bonds, possibly endow the etch sites with selectivity and controllability.[13] This feature may have important ramifications not only for studying the basic chemical properties of surface defects but also for applying...
such materials toward applications in the fields of catalysis, sensing, and photonics. The size of a water molecule is about 0.25 nm, which is smaller than the interlayer distance of PCN (0.326 nm). Therefore, water molecules can intercalate into the layers of PCN. In addition, PCN has defective amino groups and is easily hydrated when exposed to liquid water.[14] Even for the steam with a size of 0.4 nm, the ease swelling nature of the polymer framework would allow the intercalation of steam into the layers to participate in the C/N-steam reforming reactions \[ \text{CN}(s) + \text{H}_2\text{O}(g) \rightarrow \text{CO}(g) + \text{H}_2(g) + \text{NO}(g) \] at high temperatures. Consequently, the bulk PCN can probably be exfoliated into single or few-layered PCN nanosheets through the produced CO, H2, and NO gas bubbles while still allowing control of the surface defective chemistry by the chemoselective etching of surface C/N atoms. Considering all these benefits, it is thus rational to obtain single or few-layered PCN nanosheets with strengthened surface and semiconductor properties by the steam reforming strategy.

Here, we successfully developed a green and general approach to prepare few-layered PCN nanosheets by steam reforming reactions. As expected, bulk PCN-U, using urea as the precursor, can be effectively exfoliated into few-layered nanosheets by steam reforming. This delamination remarkably prolongs the lifetime of the photogenerated charges from 57.01 ns for bulk PCN-U to 301.25 ns for PCN-U nanosheets and promotes the separation efficiency of photogenerated charges. Impressively, the PCN-U nanosheets (without any extra doping/modification) exhibit robust photocatalytic activity for hydrogen production under visible light irradiation, with an apparent yield (AQY) of 11.3% at 405 nm, which is higher than those of other PCN nanosheet photocatalysts.[7a,8,9,16] We also synthesized PCN-M, PCN-D, and PCN-T nanosheets using melamine, dicyandiamide, and thiourea as precursors, respectively, by the same steam reforming reaction, revealing the generality of this new delamination strategy.

The preparation of PCN nanosheets is illustrated in Scheme 1. Briefly, the bulk PCN was thermally treated at 500 °C for 4 h under a water atmosphere using an Ar-carrying gas. During this process, water molecules intercalate into the layer gaps within PCN and react with the carbon and nitrogen atoms of PCN by C/N steam reforming reactions at elevated temperatures, releasing CO, NO, and H2 gases. The internal gas pressure between PCN layers increases sharply, thus leading to the peeling of bulk PCN into few-layered PCN nanosheets.

Transmission electron microscopy (TEM) images of the bulk PCN-U and PCN-U nanosheets are shown in Figure 1a and b. After the steam reforming process, the PCN-U obviously displayed thin nanosheet structures, which significantly differed from the mainly dense and stacked sheets of the bulk PCN-U. Atomic force microscopy (AFM) was employed to measure the thickness of the bulk PCN-U and PCN-U nanosheets. The AFM analysis revealed that the thickness of the PCN-U nanosheets was approximately 1.2 nm (Figure 1d), whereas the thickness of the bulk PCN-U was 3.5 nm (Figure 1c), indicating that the steam reforming reaction effectively exfoliated the bulk PCN-U into few-layered nanosheets. The yield of the PCN-U nanosheets is about 20%, while was 6% in the literature using the thermal oxidation in air.[10] N2 adsorption–desorption isotherms of the bulk PCN-U and PCN-U nanosheets are shown in Figure S1 in the Supporting Information. The PCN-U nanosheets exhibited an increased nitrogen adsorption capacity. Correspondingly, the Brunauer–Emmett–Teller (BET) surface area of the PCN-U nanosheets reached 210 m² g⁻¹, which was 4.38 times higher than that of bulk PCN-U (48 m² g⁻¹), strongly supporting the AFM results. The crystal structures of the bulk PCN-U and PCN-U nanosheets were studied by X-ray diffraction (XRD). The peaks located at 13.1° and 27.2° were ascribed to the (100) and (002) planes, respectively, of the PCN-U nanosheets (Figure 2a).[10] Compared to the bulk PCN-U, the (002) peak of PCN-U nanosheets obviously became weaker and broader, which was ascribed to the reduced layer thickness, consistent with the AFM results.[20]

Scheme 1. Illustration of the delamination of bulk PCN by steam reforming.
X-ray photoelectron spectroscopy (XPS) and elemental analysis were employed to investigate the chemical compositions and elemental valence states. The elemental analysis (Table S1) showed that the C/N atomic ratio for the PCN-U nanosheets was 0.657, which was smaller than that of the bulk PCN-U (0.671), indicating that the water preferentially reacted with C and then creating C vacancies. A gas analysis mass spectrometer (GMS) was used to analyze the gaseous composition of the CN-steam reforming process. The GMS results showed that the gaseous molecules were mainly composed of H₂, CO, CO₂, NO, and NO₂ (Figure S2), which suggests that the water molecules triggered the carbon/nitrogen-steam reforming reactions and water gas shift reactions \( \text{CO(g)} + \text{H₂O(g)} \rightarrow \text{CO₂(g)} + \text{H₂(g)} \). This is consistent with the elemental analysis results. The surface atomic ratio from XPS revealed that the C/N molar ratio of the PCN-U nanosheets (0.704) was much smaller than that of the bulk PCN-U (0.892) (Figure S3, Table S2), indicating the presence of surface carbon vacancies in the PCN-U nanosheets. This result also suggests that the delamination mechanism of steam reforming is different from that of the thermal oxidation in air.\(^\text{[10]}\) The C1s spectrum was resolved into two peaks located at 288.2 and 284.6 eV, which were assigned to C–N and C–C bonds, respectively (Figure S4).\(^\text{[16]}\) The peaks located at 398.5 ± 0.2, 399.6 ± 0.1, 401 ± 0.2, and 403.8 ± 0.3 eV from the N1s spectrum depict that nitrogen was present in the form of C–N=C, N-(C)ₓ, C–NH and positively charged localization in heptazine rings, respectively (Figure S5).\(^\text{[22]}\) Compared to the bulk PCN-U, the peak area ratios of C–NH and N-(C)ₓ in the PCN-U nanosheets were significantly decreased (Tables S3 and S4), implying that the loss of C and N atoms mainly occurred at the C–NH and N-(C)ₓ lattice sites. Figure S6 shows the XPS spectra of PCN-U by steam reforming with different reaction times. Clearly, the C/N molar ratio of PCN-U decreased gradually with an increasing reaction time, suggesting the controllability of carbon vacancies. Fourier transform infrared (FTIR) spectra of the bulk PCN-U and PCN-U nanosheets (Figure S7) showed similar IR patterns, indicating that the molecular structure of PCN nanosheets was mostly unaltered, in spite of the presence of carbon vacancies.

Photocatalytic activity of the bulk PCN-U and PCN-U nanosheets was examined by measuring the photocatalytic hydrogen production with visible light. The photocatalytic activity of the bulk PCN-U and PCN-U nanosheets was blue-shifted, which probably resulted from the reduced layer thickness reducing the interlayer electron coupling.\(^\text{[7a,19]}\) However, a strong absorption tail in the visible light region was clearly observed, which could be related to the introduced carbon vacancies.\(^\text{[19]}\) The band gaps from the Tauc plots were 2.82 eV for the PCN-U nanosheets and 2.61 eV for the bulk PCN-U (Figure S9). The band gap of the PCN-U nanosheets widened to 0.21 eV, which was further confirmed by the blue shifting of its fluorescence emission peak in Figure 2b. The strong photoluminescence quenching in the PCN-U nanosheets suggested that the recombination of photogenerated charges was substantially suppressed. Time-resolved PL spectra of the bulk PCN-U and PCN-U nanosheets were investigated to provide more information about the charge carriers. The PL decay spectra monitored at their maximum emission wavelength (bulk PCN-U: 472 nm; PCN-U nanosheets: 441 nm) are shown in Figure 2c.\(^\text{[20]}\) The decay spectra of the bulk PCN-U and PCN-U nanosheets exhibited three radiative lifetimes with different percentages, which is summarized in the inset of Figure 2c. The average PL lifetimes were 301.25 ns for the PCN-U nanosheets and 57.01 ns for the PCN-U. The average PL lifetime can be regarded as a crude yet rational measure for evaluating the separation efficiency of photogenerated charges. In the present case, the remarkable 5.28-fold increase in the average PL lifetime indicated that the PCN-U nanosheets offered more opportunities for free charges to participate in the surface redox reaction.\(^\text{[21]}\) In accordance with the PL spectra, PCN-U nanosheets showed a much smaller arc radius in the electrochemical impedance spectrum (Figure 2d), suggesting faster surface charge transport.\(^\text{[22]}\) An obvious enhanced photocurrent in the PCN-U nanosheets also implied that the separation efficiency of the photogenerated charge carriers was promoted (Figure 2d), which is supported by the time-resolved PL results.\(^\text{[23]}\)

XPS valence band spectra were analyzed to investigate the band edges of the bulk PCN-U and PCN-U nanosheets. As shown in Figure S10, the valence band (VB) values of the bulk PCN-U and PCN-U nanosheets were, respectively, approximately 2.17 and 2.36 eV. Based on the band gaps obtained from the Tauc plots, the conduction band (CB) values of the bulk PCN-U and PCN-U nanosheets were calculated to be −0.44 and −0.46 eV, respectively, compared with the vacuum energy level. The energy band positions of the bulk PCN-U and PCN-U nanosheets are schematically shown in Figure 3a. It is obvious that the shift in the CB and VB of the PCN-U nanosheets led to a larger thermodynamic driving force for photocatalytic redox reactions.\(^\text{[23]}\)
It is widely accepted that the surface area, evolution in the PCN-U nanosheets. To further promote the photocatalytic performance, the PCN-U nanosheets, both 2-aminothiophene-3-carbonitrile (AC) condensation with urea and steam reforming were employed. TEM, N₂ adsorption–desorption isotherms, and PL spectra revealed that the PCN-U-AC showed thin sheet structures and enhanced charge carrier separation rates after steam reforming (Figures S12 and S13). Moreover, compared to the PCN-U-AC, the PCN-U-AC nanosheets still retained strong light absorption within the visible region (Figure S14). As a result, the hydrogen evolution rate of the PCN-U-AC nanosheets reached 261.1 µmol h⁻¹ with visible light (Figure 3d), which was a 54% increase compared with the PCN-U nanosheets.

To show the generality of the steam reforming strategy, we also studied the effect of steam reforming on PCN-M, PCN-D, and PCN-T samples. The TEM results indicated that the PCN-M, PCN-D and PCN-T samples showed thin sheet structures after steam reforming (Figures S15a, S16a, and S17a), which is well supported by the BET surface area results (Figures S15b, S16b, and S17b). The UV-visible absorption, FTIR and PL spectra of the PCN-M, PCN-D and PCN-T nanosheets are shown in Figures S18, S19, and S20, respectively. All PCN-M, PCN-D, and PCN-T nanosheets exhibited increased charge separation and more active sites due to the unique thin sheet structure. [25] Expectedly, the PCN-M, PCN-D and PCN-T nanosheets displayed obviously improved photocatalytic activity. The hydrogen evolution rates of the PCN-M, PCN-D, and PCN-T nanosheets were 14.5, 32.8, and 6.27 times higher than those of the bulk PCN-M, PCN-D, and PCN-T, respectively. The difference of exfoliation behavior of PCN from different precursors is mainly due to the different degree of polymerization.

To conclude, a general and green method was developed to prepare few-layered PCN nanosheets. This method has the advantages of using no chemical reagents, being highly efficient, and being easy to scale up. Moreover, PCN nanosheets obtained from the steam reforming route demonstrated unique thin 2D structures and more active sites, and they promoted photogenerated charge separation, thus displaying excellent photocatalytic activity. The extension of such a steam reforming approach to ternary BCN semiconductors and graphite oxides also produced thin-layered BCN and graphene nanosheets (Figures S21 and S22), demonstrating the effectiveness and generality of the current method to delaminate conjugated layered compounds containing carbon. It is envisaged that this facile and green method can also be expanded to produce other ultrathin 2D carbon-based nanomaterials for a variety of potential applications.

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**Conflict of interest**

The authors declare no conflict of interest.

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