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Carbon Self-Doped Carbon Nitride Nanosheets with Enhanced Visible-Light Photocatalytic Hydrogen Production

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Abstract: In this study, we prepared carbon self-doped carbon nitride nanosheets through a glucose synergic co-condensation method. In the carbon self-doped structure, the N atoms in the triazine rings were substituted by C atoms, resulting in enhanced visible-light photocatalytic hydrogen production, which is three-times higher than that of bulk carbon nitride. The enhanced photocatalytic hydrogen production was attributed to the higher charge-carrier transfer rate and widened light absorption range of the carbon nitride nanosheets after carbon self-doping. Thus, this work highlights the importance of carbon self-doping for improving the photocatalytic performance. Meanwhile, it provides a feasible method for the preparation of carbon self-doped carbon nitride without destroying the 2D conjugated backbone structures.

Keywords: carbon nitride nanosheets; carbon self-doping; photocatalytic hydrogen production; charge transfer rate

1. Introduction

Environmental pollution and energy crises have been seriously threatening the survival of mankind and the sustainable development of society. The photocatalysis technique is considered as an environmentally friendly technology to solve these problems because of its characteristics of being green, its low energy consumption and sustainable recycling [1].

In 2009, Wang et al. [2] reported graphene-like carbon nitride $(g-C_3N_4)$ as a novel metal-free polymer semiconductor photocatalyst in water splitting for the first time. $g-C_3N_4$ has attracted a lot of attention because of its suitable bandgap, abundant composition elements and visible-light response. However, $g-C_3N_4$ is limited in practical applications due to its small specific surface area and serious photocarrier recombination. Therefore, it is urgent to increase the specific surface area and the photocarrier transport rate of $g-C_3N_4$.

Traditional g-C₃N₄ generally shows a layered structure that is formed by stacking a large number of two-dimensional triazine ring nanosheets [3]. Modification of the micromorphology can effectively increase the specific surface area and improve the photocatalytic performance. Ultrathin g-C₃N₄ flake (UF-CN) was prepared through a facile wet mechanical grind method [4]. With a yield rate of 90%, the prepared UF-CN showed higher photocatalytic hydrogen production and photocatalytic degradation rate. Han et al. [5] treated "seaweed" architecture g-C₃N₄ by direct calcination of the freeze-dried precursor. The as-prepared samples showed increased active sites, improved electron transfer ability and increased visible-light response, which resulted in the enhancement of the photocatalytic performance.

Design and construction of $g-C_3N_4$ -based heterojunctions can effectively accelerate the transport and transfer of photocarriers, greatly reducing the recombination rate of photocarriers and improving the photocatalytic performance. Various materials, such as CdS [6,7], MoS₂ [8], ZnO [9] and TiO₂ [10], have been used for constructing g-C₃N₄-based heterojunctions. However, the heterostructure would reduce the redox ability of the photocarriers, which weakened the energy driving the photocatalytic process. Another commonly used modification method is doping, which can modulate the electronic structure of $g-C_3N_4$ to improve the photocatalytic performance. Lan et al. [11] proposed a Br-modified $g-C_3N_4$ through thermal polycondensation of the mixture of urea and NH₄Br. The introduction of bromine modulated the electronic structure, optical absorption, conductivity and charge-carrier transfer rate of $g-C_3N_4$ without changing the polymer architecture of the $g-C_3N_4$, leading to enhanced photocatalytic performance. Zhang et al. [12] prepared I-modified $g-C_3N_4$ by a simple in-situ surface modification method. The modification enhanced the visible-light absorption, accelerated the transfer rate of photocarriers, and finally increased the photocatalytic hydrogen production rate. Many other dopant atoms, such as S [13], P [14], B [15] and F [16], have been adopted to dope in the triazine structure of g-C₃N₄. However, the introduction of heterogeneous atoms is likely to cause asymmetric doping or impurities, which can serve as recombination centers for the photogenerated electrons and holes, therefore reducing the photocatalytic performance. Carbon materials such as graphene, graphdiyne, carbon nanotube and carbon quantum dots have been considered as potential materials to couple with photocatalysts to construct effective composite photocatalysts due to their unique physical properties and optical properties [17]. Moreover, the introduction of carbon into $g-C_3N_4$ could effectively avoid the generation of impurities. Therefore, morphology control and element doping may effectively improve the photocatalytic performance of g-C₃N₄.

Inspired by these works, we prepared a carbon self-doped $g-C_3N_4$ nanosheet (C-C₃N₄ NS) by heating the mixture of bulk $g-C_3N_4$ and glucose, expecting to improve the photocatalytic performance of $g-C_3N_4$. The bulk $g-C_3N_4$ was obtained by the traditional thermal polymerization, while the secondary heat treatment can effectively exfoliate the layered $g-C_3N_4$ into the C_3N_4 nanosheet (C₃N₄ NS) and introduce the C element into the triazine structure. Therefore, the obtained C-C₃N₄ NS showed enhanced visible-light photocatalytic hydrogen production.

2. Results and Discussion

Figure 1A,B presents typical SEM images of C_3N_4 NS and 0.4 C- C_3N_4 NS. The C_3N_4 NS (Figure 1A) exhibits a simple typical layered structure, which is similar to that of bulk C_3N_4 . The layered structure of the C_3N_4 NS was exfoliated by a thermal oxidation etching process [18].

However, the layered structures of 0.4 C-C₃N₄ NS (Figure 1B) are corroded, which might be ascribed to the introduction of C atoms. To investigate the state of C, high-resolution transmission electron microscope (HRTEM) was tested. As shown in Figure 1C,D, C_3N_4 NS and 0.4 C-C₃N₄ NS samples exhibit ultrathin nanoflakes with layered structure, and no obvious carbon particles adhered to the C_3N_4 NS surface are observed in the 0.4 C-C₃N₄ NS, indicating that the C might be embedded in the structure of the tri-s-triazine ring.



Figure 1. Cont.



Figure 1. SEM images of (**A**) C_3N_4 NS and (**B**) 0.4 C- C_3N_4 NS. High-resolution transmission electron microscope (HRTEM) images of (**C**) C_3N_4 NS and (**D**) 0.4 C- C_3N_4 NS.

Figure 2A shows the FTIR spectra of C_3N_4 NS and $C-C_3N_4$ NS. The peaks at 1200–1600 and 805 cm⁻¹ are corresponding to the characteristics of C–N heterocycle stretches and tri-s-triazine ring modes, respectively. This phenomenon indicates that the original C_3N_4 backbones are not damaged after the introduction of carbon doping. The peaks between 3000–3300 cm⁻¹ are assigned to the N–H stretching vibrations, and the peaks for the C-C₃N₄ NS are weaker than those for the C₃N₄ NS, which can be ascribed to the decrease of N atoms caused by the doping of C atoms at the N sites [19,20].



Figure 2. FTIR spectra of C₃N₄ NS and C-C₃N₄ NS samples.

The solid-state ¹³C-magic-angle spinning (MAS)-NMR spectra of C_3N_4 NS and $0.4 \text{ C-}C_3N_4$ NS (Figure 3A) showed two strong peaks at 158.4 and 166.4 ppm, which correspond to C_{3N} (1) and C_{2N} -NHx (2) in the triazine ring units, respectively. No other peak is observed for $0.4 \text{ C-}C_3N_4$ NS, indicating that the introduction of carbon does not cause the open-loop reaction of the triazine ring, and that the C- C_3N_4 NS remained in the original C_3N_4 triazine ring structure, which is similar to the above Fourier-transform infrared (FTIR) results [21]. The maintenance of these 2D conjugated backbone structures provides the prerequisite for the π -delocalized electronic systems [12].

The atomic distributions of C and N are further revealed by the electron-energy loss spectroscopy (EELS) elemental mapping. Figure 3B shows the EELS mapping of $0.4 \text{ C-C}_3\text{N}_4$ NS, the distribution of C and N elements being shown in Figure 3C,D. C and N elements are evenly distributed throughout all the $0.4 \text{ C-C}_3\text{N}_4$ NS material, and no more carbon is observed to be coated on the edge of $0.4 \text{ C-C}_3\text{N}_4$ NS, indicating that the C is not clustered on the C_3N_4 surface in the form of a coated surface. Moreover, there are no carbon particles adhered to the surface of the $0.4 \text{ C-C}_3\text{N}_4$ NS, as shown in the HRTEM results. Therefore, traces of introduced C atoms might be embedded into the structure of the tri-s-triazine ring. The NMR results exhibit that the introduced C atoms do not cause the open-loop reaction of the triazine ring, and the FTIR results show that the N–H stretching vibrations get weaker

after the C doping. It can be concluded that the N atoms in the tri-s-triazine ring were substituted by the introduced C atoms.



Figure 3. (A) Solid-state ¹³C-magic-angle spinning (MAS)-NMR spectra of C_3N_4 NS and 0.4 C- C_3N_4 NS. (B) Electron-energy loss spectroscopy (EELS) mapping of 0.4 C- C_3N_4 NS for merged mapping, (C) C mapping and (D) N mapping.

Figure 4A shows the XRD results of the C_3N_4 NS and $C-C_3N_4$ NS. All the samples exhibit two characteristic peaks at 13° and 27.4° corresponding to the (100) in-planar peak and the (002) interlayer-stacking peak of $g-C_3N_4$, respectively [2]. Enlarged XRD patterns (Figure 4B) show the gradual shift of the (002) peak to a higher angle with the introduction of carbon, indicating disturbance of the packing and undulations of the single layers. The introduction of the carbon dopant could form delocalized π -bonds that complete the π -delocalized electronic systems [22]. High-resolution C 1s XPS spectra (Figure 4C) shows that the C_3N_4 NSs were deconvoluted into two peaks at 284.9 eV and 288.4 eV, which can be ascribed to graphitic carbon atoms and sp^2 -bonded carbon atoms in the heterocycle (N–C=C) of aromatic g- C_3N_4 , respectively [23]. For the 0.4 C- C_3N_4 NS, the peak corresponding to sp²-bonded carbon slightly shifted to 288.3 eV, which indicated that the binding energies of carbon atoms were affected by the doped carbon. High-resolution N 1s XPS spectra (Figure 4D) shows that all peaks of the $0.4 \text{ C-C}_3\text{N}_4$ NS shifted to lower binding energy compared to those of C₃N₄ NS. Therefore, the assumption that the N atoms in tri-s-triazine ring were substituted by C atoms, as shown in Figure 5, is further confirmed. The doped C atoms substituting N atoms maintained the original 2D conjugated backbone structures and reduced the number of N–H bonds, which resulted in the abovementioned results [24].

Figure 6A shows the photocatalytic hydrogen production performance of C_3N_4 NS and C- C_3N_4 NS. For C_3N_4 NS, the H₂ evolution rate reaches 2200.6 ± 210.4 µmol/g at 4 h, while all the C- C_3N_4 NS samples exhibit higher evolution rate. Among them, 0.4 C- C_3N_4 NS reaches the highest H₂ evolution rate of 6545.8 ± 260.3 µmol/g at 4 h, which is almost three-times higher than that of C_3N_4 NS; in order to rule out the contingency of the experiment, we did three sets of parallel experiments for each set of data. Corresponding error bars are given in Figure 6A, and the error ranges of the H₂ evolution rates are within reasonable tolerances. The corresponding volume histogram of hydrogen production is shown in Figure 6B, and the 0.4 C- C_3N_4 NS exhibits the highest hydrogen production performance as well (1636.45 ± 65.075 µmol/g/h). Additionally, the photocatalysis stability of the 0.4 C- C_3N_4 NS was tested further, as shown in Figure 6C. After four cycles, the hydrogen evolution performance of the 0.4 C- C_3N_4 NS sample only decreased a little, and stabilized in the third and fourth cycles, indicating the stable photocatalysis performance of 0.4 C- C_3N_4 NS.



Figure 4. (**A**) XRD patterns and (**B**) enlarged XRD patterns of series samples. High-resolution XPS spectra of (**C**) C 1*s* and (**D**) N 1*s* of C₃N₄ NS and 0.4 C-C₃N₄ NS.



Figure 5. Atomic structure of C₃N₄ NS and C-C₃N₄ NS.

Figure 6D shows the photocatalytic rhodamine B (RhB) degradation results of the series of samples under visible-light illumination. Three sets of parallel experiments were presented to rule out the contingency of the experiment. All data errors are within reasonable tolerances, which might result from the difference in degree of centrifugation. As shown in Figure 6D, after visible-light illumination, for the C_3N_4 NS photocatalyst, only 50% RhB could be degraded in 60 min. However, all C- C_3N_4 NS samples exhibited higher photocatalytic degradation rates. Among them, the 0.4 C- C_3N_4 NS showed the highest degradation performance, which reached approximately 95% RhB degradation in only 40 min.



Figure 6. (A) Photocatalysis hydrogen evolution and (B) volume histogram of series of samples. (C) Photocatalysis hydrogen evolution stability test of $0.4 \text{ C-}C_3\text{N}_4 \text{ NS}$. (D) Photocatalysis rhodamine B (RhB) degradation performances of series of samples.

Figure 7A shows the photoinduced current with time i–t curve of the as-prepared photoelectrodes. As shown in Figure 7A, the photoinduced currents of all C-C₃N₄ NS photoelectrodes are much higher than those of C₃N₄ NS. Among all C-C₃N₄ NS samples, 0.4 C-C₃N₄ NS exhibits the highest photocurrent of 1.2 μ A/cm². The electrochemical impedance spectroscopy (EIS) measurement result is shown in Figure 7B; the resistance arc radius of the 0.4 C-C₃N₄ NS was smaller than that of the C₃N₄ NS, suggesting that the introduction of C could facilitate the charge transport of C₃N₄ NS [25].



Figure 7. Cont.



Figure 7. (**A**) Photoinduced current–time curves and (**B**) Electrochemical impedance spectroscopy (EIS) results of C_3N_4 NS and 0.4 C- C_3N_4 NS electrodes. (**C**) Photoluminescence spectra of series of samples. (**D**) Time-resolved fluorescence spectra of C_3N_4 NS and 0.4 C- C_3N_4 NS.

In order to detect the recombination rate of photocarriers in the samples, Photoluminescence (PL) spectra were tested. As shown in Figure 7C, all C-C₃N₄ NS samples show decreased PL emission intensity in comparison with C_3N_4 NS ones, indicating that the recombination rate of charge carriers is suppressed by the carbon doping. Photocurrent and PL results show that the introduction of carbon improves the separation of photocarriers and inhibits the recombination rate, which promotes the photocatalytic performance [26]. Time-resolved PL spectra also support the above assumption. It is clear that the fluorescence lifetime of $0.4 \text{ C-}C_3N_4$ NS samples is shorter than that of C_3N_4 NS (Figure 7D), and the decreased lifetime manifests more efficient separation of electrons and holes. Therefore, the doped carbon can accelerate the separation and transfer of the photogenerated carriers [27].

Diffuse reflectance spectra of the series of samples are shown in Figure 8A. It is clear that the C-C₃N₄ samples show a progressive redshift with increasing C content, confirming that the bandgap can be narrowed by introducing C. The estimated bandgaps (Figure 8B) of the series of samples are 2.04 eV, 2.18 eV, 2.36 eV and 2.44 eV, corresponding to the 0.6 C-C₃N₄ NS, 0.4 C-C₃N₄ NS, 0.2 C-C₃N₄ NS and C₃N₄ NS, respectively. To further investigate the influence of C on the band position of the C₃N₄ NS, Valence band X-ray photoelectron spectroscopy (VB-XPS) was tested for the C₃N₄ NS and 0.4 C-C₃N₄ NS. As shown in Figure 8C, the VB maximum was similar for both the C₃N₄ NS and 0.4 C-C₃N₄ NS located at 2.07 eV, which was estimated to be 1.51 V versus normal hydrogen electrode at pH = 7 through formula: $E_{\text{NHE}}/V = \phi + 2.07 \text{ eV} - 4.44$ ($\phi = 3.88 \text{ eV}$: the electron work function of the analyzer) [28,29].



Figure 8. (**A**) UV–Vis diffuse reflection and (**B**) the estimated band gaps of series of samples. (**C**) VB-XPS spectra for C₃N₄ NS and 0.4 C-C₃N₄ NS samples.

According to the above analysis, the VB maximum potential of C_3N_4 NS and 0.4 C- C_3N_4 NS samples were both located at 1.51 V (vs. Normal Hydrogen Electrode NHE), indicating that the valence

band positions of the samples were unaffected by the introduction of C into g-C₃N₄, and the estimated band gaps of the C₃N₄ NS and 0.4 C-C₃N₄ NS were 2.44 eV and 2.18 eV (Figure 8B), respectively. According to $E_g = E_v - E_c$, the calculated conduction band minimum potentials of C₃N₄ NS and 0.4 C-C₃N₄ NS were -0.93 V and -0.67 V (vs. NHE), respectively. The positive shift of the conduction band for the 0.4 C-C₃N₄ NS was caused by the formation of doped energy level which comes from the C. The estimated band structure schematic is exhibited in Figure 9.



Figure 9. Band structure of the C_3N_4 NS and 0.4 C- C_3N_4 NS.

Figure 10 shows the mechanism for the improvement of the photocatalysis performance under visible light. The substitution of C atoms for N atoms in the tri-s-triazine ring maintained the 2D conjugated system of $g-C_3N_4$, while the introduction of doped carbon atoms accelerates the charge mobility, thus enhancing the photocatalytic performance.



Figure 10. Mechanism of the photocatalysis performance improvement under visible light.

3. Experimental Section

3.1. Fabrication of g- C_3N_4

The bulk $g-C_3N_4$ was prepared through traditional thermal condensation [4]. 10 g dicyandiamide (Aladdin Co., Shanghai, China) was annealed at 550 °C with a ramping rate of 10 °C·min⁻¹ in air in a muffle furnace for 3 h to obtain a yellow powder.

3.2. Fabrication of C-Modified g-C₃N₄

In a typical synthesis, 1 g g- C_3N_4 was dissolved in 50 mL deionized water and sonicated for a few minutes. Then, a different mass of glucose (0.2 g, 0.4 g, 0.6 g, Aladdin Co., Shanghai, China) was added with stirring and then kept stirring for 1 h. The product was centrifuged at 8000 r/min for 2 min

and rinsed with water and ethanol for three times, and then dried at 60 °C for 12 h. The mixture was annealed at 550 °C with a ramping rate of 10 °C/min in air in a muffle furnace for 3 h, the samples being denoted as 0.2 C-C₃N₄ NS, 0.4 C-C₃N₄ NS, 0.6 C-C₃N₄ NS, respectively. For comparison, C₃N₄ NS was prepared at the same condition in the absence of glucose. The procedure is shown as Figure 11.



Figure 11. Schematic illustration for the formation of C-C₃N₄ NS.

3.3. Characterization

The crystalline structures of the samples were identified through X-ray diffraction (XRD, D/MAX-2500/PC, Rigaku Co., Tokyo, Japan). The micro-morphologies of the samples were observed using a field-emission scanning electron microscope (SEM, JSM-6700F, JEOL, Tokyo, Japan) and a high-resolution transmission electron microscope (HRTEM, Tecnai G2 F20, FEI, Hillsboro, OR, USA). The atomic distributions of samples were further revealed by the electron energy loss spectroscopy (EELS, GIF Quantum 965, Gatan, Pleasanton, CA, USA) elemental mapping. The C atomic chemical states of samples were conducted by solid-state ¹³C magic-angle spinning (MAS) NMR (DiscoveryMR750 3.0T, General Electric Company, Boston, MA, USA) measurements at room temperature. The elementary compositions and bonding information of the samples were analyzed by using X-ray photoelectron spectroscopy (XPS, Axis Ultra, Kratos Analytical Ltd., Manchester, England, UK). The optical absorptions of the solid-state samples were tested by a UV-visible diffuse reflectance spectrophotometer (UV-vis DRS, U-41000, HITACHI, Tokyo, Japan). The photoluminescence and fluorescence decay times of the as-prepared materials were characterized using a fluorescence spectrometer (PL, Fluoro Max-4, HORIBA Jobin Yvon, Paris, France) with excitation wavelength at 350 nm. The molecular structures of the samples were identified through Fourier-transform infrared (FT-IR) spectra which used a Nicolet IS10 infrared spectrophotometer (Thermo Fisher Scientific, Waltham, MA, USA) in the transmission mode using a KBr pellet method.

3.4. Photocatalytic Reaction

The photocatalytic activities of the samples were tested by photocatalytic hydrogen production and photocatalytic dye degradation under visible light. In photocatalytic hydrogen production test, 50 mg catalyst powder was dispersed in 100 mL aqueous solution which contained 10 vol % triethanolamine as sacrificial electron donor and 3 wt % H₂PtCl₆·6H₂O (Aladdin Co., Shanghai, China) as a co-catalyst [30]. Before the test, the photoreaction system was vacuumed until the pressure gage was stable. Externally illuminating 150 W Xe lamp (PLS-SXE300, Beijing Changtuo Co., Ltd., Beijing, China) was used as light source, and we added a 420 nm cut-off filter to achieve visible light, and adjusted the photo density to 250 mW/cm². The illuminated area of the photocatalytic reaction is 28.3 cm² (light spot diameter is 6 cm). The entire reaction system was kept at a constant 5 °C with condensed water. In photocatalytic dye degradation test, rhodamine B (RhB, Aladdin Co., Shanghai, China) was selected as the target degradant. The specific experimental steps are as follows: 0.05 g photocatalyst was dispersed in 100 mL RhB with a concentration of 10 mg·L⁻¹. Before illumination, the mixture kept stirring for 30 min in the dark to achieve adsorption–desorption equilibrium. The light source and photo density were kept the same with the photocatalytic hydrogen production test. The entire reaction system was maintained at 25 °C with circulating water. The light absorptivity of solutions were decided by the UV-visible absorption spectrophotometer (U-41000, HITACHI, Tokyo, Japan) every 10 min after centrifugation with the speed of 8000 r/min for 2 min.

3.5. Photoelectrode Preparation and Photoelectrochemical Reaction

The photoelectrodes were prepared through electrophoretic deposition method. In total, 20 mg photocatalyst was dispersed in 50 mL water containing 5 mg I₂, the mixture was stirred for 30 min to completely dissolve. Then, two Fluorine-doped Tin Oxide (FTO) conductive glasses with the deposition area of 1 cm \times 1 cm and a distance 1 cm were immersed into the solution, maintaining a bias voltage of 20 V and a deposition time of 5 min. The obtained photoelectrodes were annealed at 300 °C for 30 min to improve adhesion. The photoelectrochemical systems were measured in a three-electrode system. The as-prepared photoelectrodes, and platinum and Ag/AgCl electrodes, were used as the working, counter and reference electrodes, respectively. 0.1 M Na₂SO₄ was used as electrolyte. All photoelectrochemical tests were measured using a CHI-660D (Chenhua Instrument Co., Shanghai, China) electrochemical workstation. The photoinduced current density–time (i–t) curves were measured at 1 V (vs. Ag/AgCl) bias under visible light with the photo density at 100 mW/cm². The electrochemical impedance spectroscopy (EIS) was measured at 0 V (vs. Ag/AgCl) bias with the frequency range from 10^5-10^{-1} Hz.

4. Conclusions

In summary, we developed C self-doped g-C₃N₄ by a simple co-condensation method, and carbon atoms were successfully introduced into the tri-s-triazine structure of g-C₃N₄. The secondary heat treatment exfoliated the bulk g-C₃N₄ to nanosheets, which endows materials with higher specific surface area. Compared with pure g-C₃N₄, the modified C substitutes N atoms in the triazine ring, which broadens the range of light absorption, accelerates the transfer rate of charge carriers as well as increases the photocatalysis performance. Among all the C-C₃N₄ NS samples, the optimal 0.4 C-C₃N₄ NS unfolds the superior photocatalytic hydrogen rate of 1636.45 µmol/g/h, which is almost three-times higher than that of pure C₃N₄ NS. Simultaneously, the 0.4 C-C₃N₄ NS shows a better photocatalytic RhB degradation rate than that of the C₃N₄ NS under visible light illumination, the former of which could achieve approximately 95% degradation in 40 min. The photoelectrochemical test results verify that the introduction of C accelerates the transfer rate and inhibits the combination of photo-induced carriers, while also enhancing the photocatalytic performance. This work highlights how carbon modification incorporated into g-C₃N₄ has improved the photocatalytic performance without destroying the 2D conjugated backbone structures.

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References

- Maeda, K. Photocatalytic water splitting using semiconductor particles: History and recent developments. J. Photochem. Photobiol. C 2011, 12, 237–268. [CrossRef]
- Wang, X.; Maeda, K.; Thomas, A.; Takanabe, K.; Xin, G.; Carlsson, J.M.; Domen, K.; Antonietti, M. A metal-free polymeric photocatalyst for hydrogen production from water under visible light. *Nat. Mater.* 2009, *8*, 76–80. [CrossRef] [PubMed]
- Ong, W.; Tan, L.; Ng, Y.; Yong, S.; Chai, S. Graphitic carbon nitride (g-C₃N₄)-based photocatalysts for artificial photosynthesis and environmental remediation: Are we a step closer to achieving sustainability? *Chem. Rev.* 2016, *116*, 7159–7329. [CrossRef] [PubMed]

- 4. Bu, Y.; Chen, Z.; Xie, T.; Li, W.; Ao, J. Fabrication of C₃N₄ ultrathin flakes by mechanical grind method with enhanced photocatalysis and photoelectrochemical performance. *RSC Adv.* **2016**, *6*, 47813–47819. [CrossRef]
- 5. Han, Q.; Wang, B.; Zhao, Y.; Hu, C.; Qu, L. A Graphitic-C₃N₄ "Seaweed" Architecture for Enhanced Hydrogen Evolution. *Angew. Chem. Int. Ed.* **2015**, *54*, 11433–11437. [CrossRef] [PubMed]
- Fu, J.; Chang, B.; Tian, Y.; Xi, F.; Dong, X. Novel C₃N₄-CdS composite photocatalysts with organic-inorganic heterojunctions: In situ synthesis, exceptional activity, high stability and photocatalytic mechanism. *J. Mater. Chem. A* 2013, *1*, 3083–3090. [CrossRef]
- Zhang, J.; Wang, Y.; Jin, J.; Zhang, J.; Lin, Z.; Huang, F.; Yu, J. Efficient visible-light photocatalytic hydrogen evolution and enhanced photostability of core/shell CdS/g-C₃N₄ nanowires. *ACS Appl. Mater. Interfaces* 2013, 5, 10317–10324. [CrossRef] [PubMed]
- 8. Li, Q.; Zhang, N.; Yang, Y.; Wang, G.; Ng, D.H. High efficiency photocatalysis for pollutant degradation with MoS₂/C₃N₄ heterostructures. *Langmuir* **2014**, *30*, 8965–8972. [CrossRef] [PubMed]
- 9. Wang, Y.; Shi, R.; Lin, J.; Zhu, Y. Enhancement of photocurrent and photocatalytic activity of ZnO hybridized with graphite-like C₃N₄. *Energy Environ. Sci.* **2011**, *4*, 2922–2929. [CrossRef]
- 10. Yan, H.; Yang, H. TiO₂-g-C₃N₄ composite materials for photocatalytic H₂ evolution under visible light irradiation. *J. Alloys Compd.* **2011**, *509*, L26–L29. [CrossRef]
- 11. Lan, Z.; Zhang, G.; Wang, X. A facile synthesis of Br-modified g-C₃N₄ semiconductors for photoredox water splitting. *Appl. Catal. B Environ.* **2016**, *192*, 116–125. [CrossRef]
- 12. Zhang, G.; Zhang, M.; Ye, X.; Qiu, X.; Lin, S.; Wang, X. Iodine modified carbon nitride semiconductors as visible light photocatalysts for hydrogen evolution. *Adv. Mater.* **2014**, *26*, 805–809. [CrossRef] [PubMed]
- 13. Tian, H.; Zhang, X.; Bu, Y. Sulfur-and Carbon-Codoped Carbon Nitride for Photocatalytic Hydrogen Evolution Performance Improvement. *ACS Sustain. Chem. Eng.* **2018**, *6*, 7346–7354. [CrossRef]
- Guo, S.; Tang, Y.; Xie, Y.; Tian, C.; Feng, Q.; Zhou, W.; Jiang, B. P-doped tubular g-C₃N₄ with surface carbon defects: Universal synthesis and enhanced visible-light photocatalytic hydrogen production. *Appl. Catal. B Environ.* 2017, 218, 664–671. [CrossRef]
- 15. Yan, S.; Li, Z.; Zou, Z. Photodegradation of rhodamine B and methyl orange over boron-doped g-C₃N₄ under visible light irradiation. *Langmuir* **2010**, *26*, 3894–3901. [CrossRef] [PubMed]
- 16. Wang, Y.; Di, Y.; Antonietti, M.; Li, H.; Chen, X.; Wang, X. Excellent visible-light photocatalysis of fluorinated polymeric carbon nitride solids. *Chem. Mater.* **2010**, *22*, 5119–5121. [CrossRef]
- Zhang, H.; Zhao, L.; Geng, F.; Guo, L.; Wan, B.; Yang, Y. Carbon dots decorated graphitic carbon nitride as an efficient metal-free photocatalyst for phenol degradation. *Appl. Catal. B Environ.* 2016, 180, 656–662. [CrossRef]
- 18. Niu, P.; Zhang, L.; Liu, G.; Cheng, H. Graphene-like carbon nitride nanosheets for improved photocatalytic activities. *Adv. Funct. Mater.* **2012**, *22*, 4763–4770. [CrossRef]
- Liu, C.; Zhang, Y.; Dong, F.; Reshak, A.H.; Ye, L.; Pinna, N.; Zeng, C.; Zhang, T.; Huang, H. Chlorine intercalation in graphitic carbon nitride for efficient photocatalysis. *Appl. Catal. B Environ.* 2017, 203, 465–474. [CrossRef]
- 20. Liu, G.; Zhao, G.; Zhou, W.; Liu, Y.; Pang, H.; Zhang, H.; Hao, D.; Meng, X.; Li, P.; Kako, T.; Ye, J. In situ bond modulation of graphitic carbon nitride to construct p-n homojunctions for enhanced photocatalytic hydrogen production. *Adv. Funct. Mater.* **2016**, *26*, 6822–6829. [CrossRef]
- Tian, N.; Zhang, Y.; Li, X.; Xiao, K.; Du, X.; Dong, F.; Waterhouse, G.I.N.; Zhang, T.; Huang, H. Precursor-reforming protocol to 3D mesoporous g-C₃N₄ established by ultrathin self-doped nanosheets for superior hydrogen evolution. *Nano Energy* 2017, *38*, 72–81. [CrossRef]
- Ding, Y.; Tang, Y.; Yang, L.; Zeng, Y.; Yuan, J.; Liu, T.; Zhang, S.; Liu, C.; Luo, S. Porous nitrogen-rich carbon materials from carbon self-repairing g-C₃N₄ assembled with graphene for high-performance supercapacitor. *J. Mater. Chem. A* 2016, *4*, 14307–14315. [CrossRef]
- Cao, S.; Low, J.; Yu, J.; Jaroniec, M. Polymeric photocatalysts based on graphitic carbon nitride. *Adv. Mater.* 2015, 27, 2150–2176. [CrossRef] [PubMed]
- Li, H.; Li, F.; Wang, Z.; Jiao, Y.; Liu, Y.; Wang, P.; Zhang, X.; Qin, X.; Dai, Y.; Huang, B. Fabrication of carbon bridged g-C₃N₄ through supramolecular self-assembly for enhanced photocatalytic hydrogen evolution. *Appl. Catal. B Environ.* 2018, 229, 114–120. [CrossRef]

- 25. Wang, R.; Xie, T.; Zhang, T.; Pu, T.; Bu, Y.; Ao, J.P. Fabrication of FTO-BiVO₄-W-WO₃ photoanode for photoelectrochemical performance improving: Based on the Z-scheme electron transfer mechanism. *J. Mater. Chem. A* **2018**, *6*, 12956–12961. [CrossRef]
- 26. Jing, L.; Qu, Y.; Wang, B.; Li, S.; Jiang, B.; Yang, L.; Fu, W.; Fu, H.; Sun, J. Review of photoluminescence performance of nano-sized semiconductor materials and its relationships with photocatalytic activity. *Sol. Energy Mater. Sol. Cells* **2006**, *90*, 1773–1787.
- 27. Li, Y.; Xu, H.; Ouyang, S.; Lu, D.; Wang, X.; Wang, D.; Ye, J. In situ surface alkalinized g-C₃N₄ toward enhancement of photocatalytic H₂ evolution under visible-light irradiation. *J. Mater. Chem. A* **2016**, *4*, 2943–2950. [CrossRef]
- Yu, H.; Shi, R.; Zhao, Y.; Bian, T.; Zhao, Y.; Zhou, C.; Waterhouse, G.I.N.; Wu, L.; Tung, C.; Zhang, T. Alkali-Assisted Synthesis of Nitrogen Deficient Graphitic Carbon Nitride with Tunable Band Structures for Efficient Visible-Light-Driven Hydrogen Evolution. *Adv. Mater.* 2017, *29*, 1605148. [CrossRef] [PubMed]
- 29. Trasatti, S. The absolute electrode potential: An explanatory note (Recommendations 1986). *Pure Appl. Chem.* **1986**, *58*, 955–966. [CrossRef]
- Iqbal, W.; Qiu, B.; Zhu, Q.; Xing, M.; Zhang, J. Self-modified breaking hydrogen bonds to highly crystalline graphitic carbon nitrides nanosheets for drastically enhanced hydrogen production. *Appl. Catal. B Environ.* 2018, 232, 306–313. [CrossRef]



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