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A 3D Hierarchical Pancake-Like Porous Carbon Nitride for Highly Enhanced Visible-Light Photocatalytic H₂ Evolution

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Abstract: Polymeric carbon nitride is a fascinating visible-light-response metal-free semiconductor photocatalyst in recent decades. Nevertheless, the photocatalytic H₂ efficiency is unsatisfactory due to the insufficient visible-light harvesting capacity and low quantum yields caused by the bulky structure seriously limited its applications. To overcome these defects, in this research, a 3D hierarchical pancake-like porous carbon nitride (PPCN) was successfully fabricated by a facile bottom-up method. The as-prepared photocatalyst exhibit enlarged surface area, enriched reactive sites, improved charge carrier transformation and separation efficiency, and expanded bandgap with a more negative conduction band towardan enhanced reduction ability. All these features synergistically enhanced the photocatalytic H₂ evolution efficiency of 3% Pt@PPCN (430 μ mol g⁻¹ h⁻¹) under the visible light illumination ($\lambda \ge 420$ nm), which was nine-fold higher than that of 3% Pt@bulk C₃N₄ (BCN) (45 μ mol g⁻¹ h⁻¹). The improved structure and enhanced photoelectric properties were systematically investigated by different characterization techniques. This research may provide an insightful synthesis strategy for polymeric carbon nitride with excellent light-harvesting capacity and enhanced separation of charges toward remarkable photocatalytic H₂ for water splitting.

Keywords: pancake-like porous carbon nitride; bottom-up method; water splitting; visible light photocatalyst

1. Introduction

With fossil fuel reserves dwindling every day, energy shortage and environmental pollution issues have become increasingly prominent. Developing clean and renewable energy sources is urgent to meet the sustained growth in energy demand [1–6]. Since the discovery of the Honda–Fujishima effect in 1972 [7], photocatalytic hydrogen evolution reaction (HER) through water splitting has gained considerable attention due to its enormous potential to convert renewable solar energy to clean sustainable energy [8–12]. Researchers have devoted a significant amount of effort to investigate more effective photocatalytic systems for hydrogen evolution via photocatalytic water splitting [13–16]. Among multitudinous proposed semiconductor photocatalysts, polymeric carbon nitride (CN) has been considered promising for visible-light driven hydrogen evolution due to its tunable bandgap, low cost, earth-abundant nature, nontoxicity, facile preparation, being environmentally benign, and its remarkable physical and chemical stability [17–22]. Unfortunately, the photocatalytic performance of bulky CN was severely limited, resulting from the small specific surface area, large recombination rates of photo-excited electron-hole pairs, weak light-harvesting capacity, and inadequate catalytic active sites [23–28]. To address these shortcomings, many strategies have been developed, such as heteroatom



doping [29,30], electronic structure modulation [31,32], nano-structuring [33,34], dye sensitization [35–37], and heterojunction construction [38–41]. Among them, nano-structuring is considered one of the most efficient and accessible strategies, as the enlarged specific surface area simultaneously abundant and quality active sites are not only favorable to the transfer of photo-excited charge carriers but also shortened the diffusion length for both ions and electrons [42,43]. On the other hand, the nano-structuring designed materials commonly exhibit the quantum confinement effect [24] with an enlarged electronic bandgap would be favorable to an enhanced redox ability toward photocatalytic reaction, promoting the quality and quantity of photo-induced charge carriers to some extent.

The nanostructural CN can be achieved by many methods. template-assistance strategies, top-down methods, and hydrothermal approaches have been regarded as representative and impelling strategies to fabricate multidimensional CN [44,45]. Nevertheless, these methods have many unsatisfactory deficiencies, such as a shortage of template species, large time consumption, and being environmentally unfriendly, resulting from the introduction of hazardous reagents, challenging the removal of the byproducts [46,47]. In contrast, the highly efficient photocatalysis materials benefited from the improved structure and accelerated the separation efficiency of photo-induced charge carriers, which is relatively convenient to obtain by a facile bottom-up method [48,49].

Porous carbon nitride as a photocatalyst was introduced by Kang et al. Nevertheless, the material showed undesirable photocatalytic performance with a poor quantum efficiency of ~0.5%. Rahman et al. improved it to some extent, which reached a benchmark quantum efficiency of ~6% [50,51]. The synthesized photocatalyst exhibited similar structure compared to that synthesized by Rahmanetal. While the PPCN presented a higher quantum efficiency of ~19%. In this work, we report a low-cost and straightforward bottom-up method for the production of hierarchical pancake-like porous carbon nitride, the typical synthesis procedure is presented in Scheme 1. Typically, the cyanuric acid–melamine complex, which is suitable for controlling molecular self-assembly [52], was firstly synthesized. Then, ethanol and glycerol intercalated into the framework of the precursor. Next, a thermal-induced exfoliation and polycondensation process was performed to obtain the resultant products. The as-synthesized PPCN exhibited unique hierarchical pancake-like porous morphology structure and remarkable photoelectric properties. As expected, by virtue of an enlarged specific surface area up to 79.663 m^2g^{-1} , enhancing the light-harvesting capacity, and enriching the reactive sites, the hierarchical porous architecture revealed a highly efficient photocatalytic H₂ evolution efficiency for water splitting under visible light irradiation $(\lambda \ge 420 \text{ nm})$, which is about nine-fold higher than that of the bulk carbon nitride (BCN). Various characterization approaches were performed to investigate the typical structure formation mechanism and the photoelectric properties of PPCN for the remarkably enhanced hydrogen evolution efficiency.



Scheme 1. Schematic illustration of hierarchical pancake-like porous C₃N₄ formation.

2. Results and Discussion

2.1. Morphology and Structure Characterization

The morphologies of BCN and PPCN were investigated via SEM and TEM. It can be seen that BCN appears as a large solid block material (Figure 1a) with seriously agglomerated structure. The light absorption, charge transport, and mass immigration were severely restrained owing to this bulky structure. In contrast, a 3D hierarchical pancake-like porous carbon nitride (Figure 1b–d) exhibited the opposite morphology with an enlarged dimension and abundant pores, which is greatly favorable for the dispersion and diffraction of the light toward the enhanced light absorption capacity. Meanwhile, TEM images (Figure 1e–g) displayed the mesoporous and lattice distance (Figure 1h) of 0.348 nm.



Figure 1. (a) SEM image of BCN, (b–d) SEM images of PPCN, (e–g) TEM images, and (h) lattice distance pattern of PPCN.

The structure can be exfoliated into hierarchical porous architecture and generated abundant pores using a suitable hybrid of alcohol and glycerol as the imbedding reagents which supporting abundant gas at the polycondensation process, leading to a hierarchical pancake-like porous architectural carbon nitride formation. N₂ adsorption/desorption isotherms (Figure 2a) was performed to prove this unique structure. The calculated BET specific surface area of PPCN is 79.663 m²g⁻¹, which is seven-fold

higher than that BCN (10.643 m^2g^{-1}). Meanwhile, the peak intensity centered at 37.2 nm in BJH pore distribution curves of PPCN sample (Figure 2b) also exhibited a larger value than BCN implying an abundant nanoporosity.



Figure 2. (**a**) N₂ adsorption-desorption isotherm curves and (**b**) BJH pore size distribution curves of BCN and PPCN.

The XRD patterns of PPCN is shown in Figure 3a. Compared to the BCN, PPCN presented a broader and weaker diffraction peak located at 27.2° (002), which is originated from the stacking reflection of interlayer toward a reduced dimension structure [53]. Meanwhile, the peak at 12.9°, ascribed to the repeats in the plane of tri-s-triazine unit could hardly been observed owing to the abundant pores in the interface. Fouriertransform infrared (FT-IR) spectroscopy (Figure 3b) demonstrates that the PPCN possessing a similar chemical structure with BCN. The 810 cm⁻¹ peaks are characteristic signal of triazine unit, and the peaks ranges from 1200 to 1600 cm⁻¹ is corresponding to the C-N heterocycles. In addition, the broad band peaks located at 3000–3600 cm⁻¹ were contributed to-NH stretching vibrations [54]. It is notably that the terminal-NH absorption peak at 3000–3600 cm⁻¹ of PPCN vibrate more strongly compared to that of BCN, which can be attributed to the difference in the crystal structural between BCN and PPCN.

X-ray photoelectron spectroscopy (XPS) was further performed to investigate the composition and chemical states of BCN and PPCN. As can be seen in Figure 3c, the presence peaks of C, N, and O are found both in the PPCN and BCN. It should be noted that the higher intensity of O 1s signal of PPCN is easy for the absorption of water and CO₂ due to the hierarchical porous architecture structure. The corresponding high-resolution spectra of C 1s, N 1s, O1s are shown in Figure 3d–f, respectively. The C 1s XPS spectrum revealed three peaks, which can be ascribed to the adventitious carbon species (284.4 eV) [55], C–NH_X species on the edges of aromatic rings (286.03 eV) [56], and the sp²-hybridized C atom in N==C(–N)₂ (288.0 eV) [57], which is consistent with that of BCN. The intensity of the sp²-bonded carbon of PPCN was increased compared to the BCN may be attributed to the loss of lattice nitrogen. The N 1s XPS signals can be deconvolved into three peaks at398.46, 399.75, and 400.93 eV, which originated from the sp²-hybridized N attached to C–N=C groups, bridging N in N–(C)₃ groups, and the amine functional groups (C–N–H), respectively [58,59]. Additionally, the O 1s spectra can be divided into two peaks located at 532.68 and 530.71 eV, which belongs to the adsorbed water and CO₂ [60].



Figure 3. (**a**) XRD and (**b**) FT-IR spectra of BCN and PPCN, Survey and high-resolution XPS spectra of BCN and PPCN, (**c**) survey, (**d**) C 1s, (**e**) N 1s, and (**f**) O 1s of BCN and PPCN.

2.2. Photoelectric Property

UV–VIS diffuse reflectance (DRS) was used to assess the optical absorption properties of BCN and PPCN. Figure 4a indicates that BCN has an absorption edge at 460 nm. Compared with BCN, the PPCN edge shows apparent blue shift, indicating the increase in band gap of semiconductors caused by the quantum confinement effect. The bandgaps for PPCN and BCN were 2.97 and 2.80 eV according to the Kubelka–Munk function [61] (Figure 4b). Consequently, the enlarged bandgap of PPCN would endow the photo-induced electrons and holes with relatively stronger redox abilities toward photocatalytic reactions. The energy band structure of materials can be determined by the conduction band or valence band together with the band gap. In this article, we use the valence band to estimate the conduction band position [62]. The valence band (VB) in Figure 4b, the valence band potentials of PPCN and BCN were 1.98 and 2.30 eV vs. NHE, respectively. Finally, the energy band structure was depicted in Figure 4d. Obviously, the more negative conduction band levels of PPCN would contribute to a more powerful e⁻ reduction ability owing to the more negative CB.



Figure 4. (**a**) UV–VIS DRS spectra and (**b**) Kubelka-Munk transformed function of BCN and PPCN, (**c**) valence band XPS spectra, (**d**) energy band structure of BCN and PPCN.

The photoluminescence tests were further performed with a 325 nm excitation wavelength to assess the separation efficiency of photo-induced electron-hole pairs. As shown in Figure 5a, PPCN presented a lower emission intensity compared with BCN, which indicated of reduced recombination of photo-induced electron-hole pairs in PPCN. It is apparent from this image that the absorption peak of PPCN shifted to a lower value resulted from the quantum size confinement, which is consistent with the DRS.

The time-resolved PL decay spectra were also performed to evaluate the photo-physical characteristics of photogenerated charge carriers of BCN and PPCN. As shown in Figure 5b, the PPCN exhibited a slower exponential decay and fluorescence than that of BCN. τ_1 is originated from the free excitons recombination in semiconductor and τ_2 is ascribed to the non-illuminated recombination of charge carriers in the surface defect states [63]. The short-lived and long-lived lifetime of charge carriers in PPCN (1.743 and 7.595 ns) are both higher than that BCN (1.211 and 5.733 ns). Mostly, the calculated average lifetime in PPCN was 5.089 ns which substantially exceeds 3.696 ns in BCN. The prolonged carriers lifetime and larger percentage of long lifetime charge carriers in PPCN are undoubtedly favorable for promoting the probability of charge carries to involve in photocatalytic reactions. The photocurrent response can also prove this similar conclusion [64]. As depicted in Figure 5c, the PPCN exhibited increased photocurrent intensity than BCN during six light on–off recycles, demonstrating a more efficient separation and transfer of photo-induced electrons. Furthermore, PPCN exhibited a smaller charge transfer resistance (Figure 5d) than that of BCN. Therefore, the hierarchical pancake-like porous architectural structure of PPCN is benefit to the highly efficient separation and migration of photo-induced electron-hole pairs.



Figure 5. (**a**) Fluorescence emission spectra and (**b**) time-resolved fluorescence excited by incident light of 365 nm of BCN and PPCN, (**c**) photocurrent, and (**d**) EIS spectra of BCN and PPCN.

2.3. Photocatalytic Performance

Though photocatalyst based on carbon nitride without precious Pt is a trend in recent years [65–67], platinum plays a remarkable role in photocatalytic hydrogen production due to the low overpotential and the optimal Gibbs free energy for proton [68,69]. Figure 6a presented the HER of PPCN with 3%Pt loading under visible light ($\lambda \ge 420$ nm) using 15 vol% TEOA as electron donor. As shown in Figure 6a, 3%Pt@PPCN had an HER of 430 µmol g⁻¹ h⁻¹, which was nine-fold higher than that of 3%Pt@BCN (45 µmol g⁻¹ h⁻¹). The apparent quantum yield (AQE) for the Pt@PPCN reached as high as 19%at 420 nm (see the calculation in Supplementary Materials). Recycling production H₂ evolution test of 3%Pt@PPCN was further performed to assess the reusability of photocatalyst. As can be seen in Figure 6b, the PPCN maintained an excellent HER stability under visible light irradiation, demonstrating the excellent structure stability of PPCN.

Overall, a rational photocatalytic HER mechanism is illustrated in Scheme 2 based on the above results and discussions. Under visible light illumination, the electrons in the valence band (VB) of PPCN are activated to the conduction band (CB) and then are trapped by the Pt for proton reduction. The holes in the VB (+1.98 eV) of PPCN oxidized the sacrificial regent TEOA and converted H₂O into oxidation products (such as H₂O₂). The CB level of PPCN (-0.99 eV) is more negative than that of BCN (0.50 eV), which greatly boosted the reduction capacity of the PPCN. As a consequence, benefited from the 3D hierarchical pancake-like porous architecture, the utilization capacity of light absorption of PPCB would be forcefully enhanced by the scattering and diffraction in the pores and vertical plane, which significantly effective to boost the light-harvesting. More than that, the enlarged specific surface

area offered more reactive sites and reduced the recombination rate of photogenerated h^+ – e^- pairs, boosting a highly efficient photocatalytic H₂ evolution reaction.



Figure 6. (a) H₂ production of the BCN and PPCN with 3%Pt loading, (b) cycling H₂ production of 3 wt % Pt@PPCN, Reaction conditions: (**a**,**b**) purified water photocatalytic H₂ production with TEOA as sacrificial under visible light ($\lambda \ge 420$ nm), every 6 h as a period by recovering the catalyst and started with fresh purified water.



Scheme 2. Proposed photocatalysis charge transfer mechanism of Hierarchical pancake-like porous C_3N_4 in TEOA solution.

3. Experimental

3.1. Reagents

Melamine was purchased from Tianjin Damao Chemical Regent Co., Ltd. (Tianjin, China). Phosphorous acid, glycerol, and ethanol were all supplied by Xilong Scientific Co., Ltd (Jiangsu, China). All reagents used in this study were at least of analytic grade without further purification. DI water was used in the whole experiment.

3.2. Synthesis of Bulk C_3N_4

In the typical procedure, 10.0 g melamine powders were placed into a crucible sealed with a cover followed by calcinating at 550 °C for 4 h in a silica oxide tube furnace with a ramping rate of 2.5 °C/min under N₂ flow (99.999%, 50 mL/min). The as-obtained solid blocks were named bulk C_3N_4 .

3.3. Synthesis of Precursor

A total of 1.0 g melamine and 1.2 g phosphorous acid were added to 100 mL deionized water in a magnetic stirrer kept vigorous stirring for 1h at 80 °C. Next, the solution was transferred into Teflon-lined stainless-steel autoclave at 180 °C for 10 h. The mixture was centrifuged, washed with deionized water for several times to obliterate the phosphorus species. Finally, the precursors were obtained after drying at 60 °C.

3.4. Preparation of Hierarchical Pancake-Like Porous Carbon Nitride

Typically, 0.6 g precursor was refluxed with a mixed aqueous solution of 5 mLglycerol and 15 mL ethanol for 3 h in the temperature 90 °C. Then, the powders were washed by ethanol three times and dried at 60 °C. After that, the powders were transferred into a crucible tightly coated with a single layer aluminum foil paper. Finally, the crucible was placed into a muffler and heated to 500 °C for 6 h with a ramping rate of 2 °C/min to obtain the PPCN.

3.5. Characterization

X-ray diffraction (XRD, Shimadzu XRD-6100, Kyoto, Japan) was performed to identify the crystal phase and structural variation of the samples with a Cu–Ka radiation at 40 kV and 30 mA. Scanning electron macroscopy (SEM, Zeiss Sigma, Jena, Germany) and transmission electron microscope (TEM, JEM-2010, JEOL, Tokyo, Janpan) images was recorded to study the morphologies of the samples. Fourier transform infrared (FT-IR) spectra (PerkinElmer Spectrum, Waltham, USA) were recorded to examine the surface functional groups of samples. X-ray photoelectron spectroscopy (XPS) was conducted on thermo ESCALAB 250XI (Axis Ultra DLD Kratos AXIS SUPRA; phi-5000 versaprobe). Nitrogen-adsorption-desorption isotherms (Quantachrome autosorb-IQ2, Quantachrome Instruments, Florida, USA) were performed to measure the specific surface area and pore volume of the samples in a Brunauer-Emmett-Teller (BET) method. UV–VIS diffusion reflectance spectra (DRS) of the samples were recorded on a PerkinElmer Lambda with BaSO₄ as a reference. Photoluminescence (PL) spectra were acquired on a Hamamatsu compact fluorescence lifetime spectrometer (C11367, Quantaurus-Tau, Hamamatsu, Japan) with 365 nm excitation wavelength and 470 nm emission wavelength.

3.6. Electrochemical Analysis

The photocurrent and electrochemical impedance spectroscopy (EIS) were investigated with a CHI660C electrochemical workstation equipped with standard three-electrodes in 0.5 M Na₂SO₄ aqueous solution. Among the electrodes, Photocatalyst was deposited on the Fluorine doped Tin Oxide (FTO) electrode and served as the photoanode. Pt wire as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. The preparation approach of photoanode was presented as follows: 50 mg catalyst was dispersed in 100 μ L ethanol to obtain a slurry. Next, the slurry was carefully coated onto a 7 mm × 14 mm FTO conductive glass and dried in room temperature. A 500 W Xe lamp quipped with a 420 nm cut-off filter was used as the light irradiation source. The EIS spectrum was recorded using the PPCN as the working electrode at a potential of 0.24 V versus SCE with the frequency ranging from 1 MHz to 0.01 Hz.

3.7. Photocatalytic Hydrogen Evolution

Photocatalytic hydrogen production performance was performed via a sealed reactor and a recirculated cooling water system. Typically, 25 mg of photocatalyst powder was dissolved in 80 mL aqueous solution (68 mL 3 wt % H₂PtCl₆ solution and 12 mL triethanolamine). After that, the reactor was degassed and illuminated 2 h under a full arc light 120 mW·cm⁻² (λ > 300 nm) with a 420 nm wavelength cut off. Finally, the generated hydrogen was monitored by GC.

4. Conclusions

In summary, a 3D hierarchical pancake-like porous carbon nitride with remarkable photocatalytic H₂ production efficiency was synthesized by a facile bottom-up strategy. 3 wt % @Pt/PPCN showed 430 µmol g⁻¹ h⁻¹for photocatalytic H₂ production under visible light ($\lambda \ge 420$ nm), which was nine times higher than that of 3 wt % @Pt/BCN (45 µmol g⁻¹ h⁻¹). The enlarged specific surface area, prolonged charge carriers lifetime, boosted light-harvesting and utilization capacity, and improved charge separation and transfer efficiency are all contributed to the optimized photocatalytic capacity. In addition, this research provides a simple and environmental-friendly approach to design highly-efficient polymeric carbon nitride catalysts for potential applications in solar energy-driven photocatalytic water splitting.

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References

- 1. Asif, M.; Muneer, T. Energy supply, its demand and security issues for developed and emerging economies. *Renew. Sustain. Energy Rev.* **2007**, *11*, 1388–1413. [CrossRef]
- 2. Wang, X.; Blechert, S.; Antonietti, M. Polymeric Graphitic Carbon Nitride for Heterogeneous Photocatalysis. *ACS Catal.* **2012**, *2*, 1596–1606. [CrossRef]
- 3. Zhang, C.; Zeng, G.; Huang, D.; Lai, C.; Chen, M.; Cheng, M.; Tang, W.; Tang, L.; Dong, H.; Huang, B.; et al. Biochar for environmental management: Mitigating greenhouse gas emissions, contaminant treatment, and potential negative impacts. *Chem. Eng. J.* **2019**, *373*, 902–922. [CrossRef]
- Mahmood, J.; Li, F.; Jung, S.M.; Okyay, M.S.; Ahmad, I.; Kim, S.J.; Park, N.; Jeong, H.Y.; Baek, J.B. An efficient and pH-universal ruthenium-based catalyst for the hydrogen evolution reaction. *Nat. Nanotechnol.* 2017, 12, 441–446. [CrossRef]
- Liu, J.; Liu, Y.; Liu, N.; Han, Y.; Zhang, X.; Huang, H.; Lifshitz, Y.; Lee, S.-T.; Zhong, J.; Kang, Z. Metal-free efficient photocatalyst for stable visible water splitting via a two-electron pathway. *Science* 2015, 347, 970–974. [CrossRef] [PubMed]
- Zhang, C.; Lai, C.; Zeng, G.; Huang, D.; Yang, C.; Wang, Y.; Zhou, Y.; Cheng, M. Efficacy of carbonaceous nanocomposites for sorbing ionizable antibiotic sulfamethazine from aqueous solution. *Water Res.* 2016, 95, 103–112. [CrossRef]
- Fujishima, A.; Honda, K. Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature* 1972, 238, 37–38. [CrossRef]
- 8. Xiong, B.; Chen, L.; Shi, J. Anion-Containing Noble-Metal-Free Bifunctional Electrocatalysts for Overall Water Splitting. *ACS Catal.* **2018**, *8*, 3688–3707. [CrossRef]

- Wu, J.; Li, N.; Fang, H.-B.; Li, X.; Zheng, Y.-Z.; Tao, X. Nitrogen vacancies modified graphitic carbon nitride: Scalable and one-step fabrication with efficient visible-light-driven hydrogen evolution. *Chem. Eng. J.* 2019, 358, 20–29. [CrossRef]
- 10. Rahman, M.Z.; Davey, K.; Qiao, S.Z. Carbon, nitrogen and phosphorus containing metal-free photocatalysts for hydrogen production: Progress and challenges. *J. Mater. Chem. A* **2018**, *6*, 1305–1322. [CrossRef]
- 11. Rahman, M.Z.; Davey, K.; Mullins, C.B. Tuning the intrinsic properties of carbon nitride for high Quantum yield photocatalytic hydrogen production. *Adv. Sci.* **2018**, *5*, 1800820. [CrossRef] [PubMed]
- 12. Rahman, M.Z.; Mullins, C.B. Understanding charge transport in carbon nitride for enhanced photocatalytic solar fuel production. *Acc. Chem. Res.* **2019**, *52*, 248–257. [CrossRef] [PubMed]
- 13. Yang, J.; Wang, D.; Han, H.; Li, C. Roles of cocatalysts in photocatalysis and photoelectrocatalysis. *Acc. Chem. Res.* 2013, 46, 1900–1909. [CrossRef] [PubMed]
- 14. Walter, M.G.; Warren, E.L.; McKone, J.R.; Boettcher, S.W.; Mi, Q.; Santori, E.A.; Lewis, N.S. Solar water splitting cells. *Chem. Rev.* **2010**, *110*, 6446–6473. [CrossRef] [PubMed]
- Tu, W.; Zhou, Y.; Zou, Z. Versatile graphene-promoting photocatalytic performance of semiconductors: Basic principles, synthesis, solar energy conversion, and environmental applications. *Adv. Funct. Mater.* 2013, 23, 4996–5008. [CrossRef]
- Kapilashrami, M.; Zhang, Y.; Liu, Y.S.; Hagfeldt, A.; Guo, J. Probing the optical property and electronic structure of TiO₂ nanomaterials for renewable energy applications. *Chem. Rev.* 2014, 114, 9662–9707. [CrossRef]
- Li, X.; Wang, T.; Duan, P.; Baldini, M.; Huang, H.T.; Chen, B.; Juhl, S.J.; Koeplinger, D.; Crespi, V.H.; Schmidt-Rohr, K.; et al. Carbon nitride nanothread crystals derived from pyridine. *J. Am. Chem. Soc.* 2018, 140, 4969–4972. [CrossRef]
- Li, J.; Zhang, Z.; Cui, W.; Wang, H.; Cen, W.; Johnson, G.; Jiang, G.; Zhang, S.; Dong, F. The spatially oriented charge flow and photocatalysis mechanism on internal van der waals heterostructures enhanced g-C₃N₄. *ACS Catal.* 2018, *8*, 8376–8385. [CrossRef]
- Huang, D.; Luo, H.; Zhang, C.; Zeng, G.; Lai, C.; Cheng, M.; Wang, R.; Deng, R.; Xue, W.; Gong, X.; et al. Nonnegligible role of biomass types and its compositions on the formation of persistent free radicals in biochar: Insight into the influences on Fenton-like process. *Chem. Eng. J.* 2019, *361*, 353–363. [CrossRef]
- Han, C.; Meng, P.; Waclawik, E.R.; Zhang, C.; Li, X.H.; Yang, H.; Antonietti, M.; Xu, J. Palladium/graphitic carbon nitride (g-C₃N₄) stabilized emulsion microreactor as a store for hydrogen from ammonia borane for use in alkene hydrogenation. *Angew. Chem. Int. Ed.* **2018**, *57*, 14857–14861. [CrossRef]
- 21. Cao, S.; Yu, J. g-C3N4-Based Photocatalysts for hydrogen generation. *J. Phys. Chem. Lett.* **2014**, *5*, 2101–2107. [CrossRef] [PubMed]
- 22. Cao, S.; Li, H.; Tong, T.; Chen, H.-C.; Yu, A.; Yu, J.; Chen, H.M. Single-atom engineering of directional charge transfer channels and active sites for photocatalytic hydrogen evolution. *Adv. Funct. Mater.* **2018**, *28*. [CrossRef]
- Zhang, J.; Chen, X.; Takanabe, K.; Maeda, K.; Domen, K.; Epping, J.D.; Fu, X.; Antonietti, M.; Wang, X. Synthesis of a carbon nitride structure for visible-light catalysis by copolymerization. *Angew. Chem. Int. Ed.* 2010, 49, 441–444. [CrossRef] [PubMed]
- Xiao, Y.; Tian, G.; Li, W.; Xie, Y.; Jiang, B.; Tian, C.; Zhao, D.; Fu, H. Molecule self-assembly synthesis of porous few-layer carbon nitride for highly efficient photoredox catalysis. *J. Am. Chem. Soc.* 2019, 141, 2508–2515. [CrossRef] [PubMed]
- Wen, X.; Sun, N.; Tan, Y.; Wang, W.; Yan, C.; Wang, H. One-step synthesis of petals-like graphitic carbon nitride nanosheets with triazole defects for highly improved photocatalytic hydrogen production. *Int. J. Hydrogen Energy* 2019, 44, 2675–2684. [CrossRef]
- Shu, Z.; Wang, Y.; Wang, W.; Zhou, J.; Li, T.; Liu, X.; Tan, Y.; Zhao, Z. A green one-pot approach for mesoporous g-C₃N₄ nanosheets with in situ sodium doping for enhanced photocatalytic hydrogen evolution. *Int. J. Hydrogen Energy* 2019, 44, 748–756. [CrossRef]
- Liu, Q.; Shen, J.; Yu, X.; Yang, X.; Liu, W.; Yang, J.; Tang, H.; Xu, H.; Li, H.; Li, Y.; et al. Unveiling the origin of boosted photocatalytic hydrogen evolution in simultaneously (S, P, O)-codoped and exfoliated ultrathin g-C₃N₄ nanosheets. *Appl. Catal. B Environ.* 2019, 248, 84–94. [CrossRef]
- 28. Kessler, F.K.; Zheng, Y.; Schwarz, D.; Merschjann, C.; Schnick, W.; Wang, X.; Bojdys, M.J. Functional carbon nitride materials-design strategies for electrochemical devices. *Nat. Rev. Mater.* **2017**, *2*, 17030. [CrossRef]

- Wang, Y.; Zhang, J.; Wang, X.; Antonietti, M.; Li, H. Boron- and fluorine-containing mesoporous carbon nitride polymers: Metal-free catalysts for cyclohexane oxidation. *Angew. Chem. Int. Ed.* 2010, 49, 3356–3359. [CrossRef]
- Cao, S.; Fan, B.; Feng, Y.; Chen, H.; Jiang, F.; Wang, X. Sulfur-doped g-C₃N₄ nanosheets with carbon vacancies: General synthesis and improved activity for simulated solar-light photocatalytic nitrogen fixation. *Chem. Eng. J.* 2018, 353, 147–156. [CrossRef]
- Yang, C.; Wang, Z.; Lin, T.; Yin, H.; Lu, X.; Wan, D.; Xu, T.; Zheng, C.; Lin, J.; Huang, F.; et al. Core-shell nanostructured black rutile titania as excellent catalyst for hydrogen production enhanced by sulfur doping. *J. Am. Chem. Soc.* 2013, 135, 17831–17838. [CrossRef] [PubMed]
- 32. Asahi, R.; Morikawa, T.; Ohwaki, T.; Aoki, K.; Taga, Y. Visible-light photocatalysis in nitrogen-doped titanium oxides. *Science* 2001, 293, 269–271. [CrossRef] [PubMed]
- Zhou, G.; Shan, Y.; Hu, Y.; Xu, X.; Long, L.; Zhang, J.; Dai, J.; Guo, J.; Shen, J.; Li, S.; et al. Half-metallic carbon nitride nanosheets with micro grid mode resonance structure for efficient photocatalytic hydrogen evolution. *Nat. Commun.* 2018, *9*, 3366. [CrossRef] [PubMed]
- Tong, Z.; Yang, D.; Li, Z.; Nan, Y.; Ding, F.; Shen, Y.; Jiang, Z. Thylakoid-inspired multishell g-C₃N₄ nanocapsules with enhanced visible-Light harvesting and electron transfer properties for high-Efficiency photocatalysis. *ACS Nano* 2017, *11*, 1103–1112. [CrossRef] [PubMed]
- Youngblood, W.J.; Lee, S.-H.A.; Kobayashi, Y.; Hernandez-Pagan, E.A.; Hoertz, P.G.; Moore, T.A.; Moore, A.L.; Gust, D.; Mallouk, T.E. Photoassisted overall water splitting in a visible light-absorbing dye-sensitized photoelectrochemical Cell. *J. Am. Chem. Soc.* 2009, 131, 926–927. [CrossRef]
- Xue, Y.; Lei, Y.; Liu, X.; Li, Y.; Deng, W.; Wang, F.; Min, S. Highly active dye-sensitized photocatalytic H₂ evolution catalyzed by a single-atom Pt cocatalyst anchored onto g-C₃N₄ nanosheets under long-wavelength visible light irradiation. *New J. Chem.* 2018, *42*, 14083–14086. [CrossRef]
- Wang, P.; Guan, Z.; Li, Q.; Yang, J. Efficient visible-light-driven photocatalytic hydrogen production from water by using Eosin Y-sensitized novel g-C₃N₄/Pt/GO composites. J. Mater. Sci. 2017, 53, 774–786. [CrossRef]
- Zhu, M.; Kim, S.; Mao, L.; Fujitsuka, M.; Zhang, J.; Wang, X.; Majima, T. Metal-Free Photocatalyst for H₂ evolution in visible to near-infrared region: Black phosphorus/graphitic carbon nitride. *J. Am. Chem. Soc.* 2017, 139, 13234–13242. [CrossRef]
- Sun, J.; Guo, Y.; Wang, Y.; Cao, D.; Tian, S.; Xiao, K.; Mao, R.; Zhao, X. H₂O₂ assisted photoelectrocatalytic degradation of diclofenac sodium at g-C₃N₄/BiVO₄ photoanode under visible light irradiation. *Chem. Eng. J.* 2018, 332, 312–320. [CrossRef]
- Liu, Y.; Yang, S.; Yin, S.-N.; Feng, L.; Zang, Y.; Xue, H. In situ construction of fibrous AgNPs/g-C₃N₄ aerogel toward light-driven COx-free methanol dehydrogenation at room temperature. *Chem. Eng. J.* 2018, 334, 2401–2407. [CrossRef]
- 41. Bafaqeer, A.; Tahir, M.; Amin, N.A.S. Well-designed ZnV₂O₆/g-C₃N₄ 2D/2D nanosheets heterojunction with faster charges separation via pCN as mediator towards enhanced photocatalytic reduction of CO₂ to fuels. *Appl. Catal. B Environ.* **2019**, 242, 312–326. [CrossRef]
- 42. Tan, C.; Cao, X.; Wu, X.J.; He, Q.; Yang, J.; Zhang, X.; Chen, J.; Zhao, W.; Han, S.; Nam, G.H.; et al. Recent Advances in Ultrathin Two-Dimensional Nanomaterials. *Chem. Rev.* **2017**, *117*, 6225–6331. [CrossRef]
- 43. Rahman, M.Z.; Kwong, C.W.; Davey, K.; Qiao, S.Z. 2D phosphorene as a water splitting photocatalyst: Fundamentals to applications. *Energy Environ. Sci.* **2016**, *9*, 709–728. [CrossRef]
- 44. Wang, J.; Liu, J.; Yang, H.; Chen, Z.; Lin, J.; Shen, Z.X. Active sites-enriched hierarchical MoS₂ nanotubes: Highly active and stable architecture for boosting hydrogen evolution and lithium storage. *J. Mater. Chem. A* **2016**, *4*, 7565–7572. [CrossRef]
- 45. 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]
- Han, Q.; Wang, B.; Gao, J.; Cheng, Z.; Zhao, Y.; Zhang, Z.; Qu, L. Atomically thin mesoporous nanomesh of graphitic C₃N₄ for high-efficiency photocatalytic hydrogen evolution. *ACS Nano* 2016, *10*, 2745–2751. [CrossRef]
- Jiang, Y.; Sun, Z.; Tang, C.; Zhou, Y.; Zeng, L.; Huang, L. Enhancement of photocatalytic hydrogen evolution activity of porous oxygen doped g-C₃N₄ with nitrogen defects induced by changing electron transition. *Appl. Catal. B Environ.* 2019, 240, 30–38. [CrossRef]

- 48. Shalom, M.; Inal, S.; Fettkenhauer, C.; Neher, D.; Antonietti, M. Improving carbon nitride photocatalysis by supramolecular preorganization of monomers. *J. Am. Chem. Soc.* **2013**, *135*, 7118–7121. [CrossRef]
- 49. Gu, Q.; Gao, Z.; Xue, C. Self-sensitized carbon nitride microspheres for long-lasting visible-light-driven hydrogen generation. *Small* **2016**, *12*, 3543–3549. [CrossRef]
- 50. Kang, Y.; Yang, Y.; Yin, L.C.; Kang, X.; Liu, G.; Cheng, H.M. An amorphous carbon nitride photocatalyst with greatly extended visible-light-responsive range for photocatalytic hydrogen generation. *Adv. Mater.* **2015**, *27*, 4572–4577. [CrossRef]
- Rahman, M.Z.; Tapping, P.C.; Kee, T.W.; Smernik, R.; Spooner, N.; Moffatt, J.; Tang, Y.; Davey, K.; Qiao, S.-Z. A benchmark quantum yield for water photoreduction on amorphous carbon nitride. *Adv. Funct. Mater.* 2017, 27, 1702384. [CrossRef]
- 52. Guo, S.; Deng, Z.; Li, M.; Jiang, B.; Tian, C.; Pan, Q.; Fu, H. Phosphorus-doped carbon nitride tubes with a layered micro-nanostructure for enhanced visible-light photocatalytic hydrogen evolution. *Angew. Chem. Int. Ed.* **2016**, *55*, 1830–1834. [CrossRef]
- 53. 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]
- 54. Niu, P.; Zhang, L.; Liu, G.; Cheng, H.-M. Graphene-like carbon nitride nanosheets for improved photocatalytic activities. *Adv. Funct. Mater.* **2012**, *22*, 4763–4770. [CrossRef]
- Shinde, S.S.; Lee, C.H.; Yu, J.Y.; Kim, D.H.; Lee, S.U.; Lee, J.H. Hierarchically designed 3D holey C₂N aerogels as bifunctional oxygen electrodes for flexible and rechargeable Zn-Air batteries. ACS Nano 2018, 12, 596–608. [CrossRef]
- Wulan, B.-R.; Yi, S.-S.; Li, S.-J.; Duan, Y.-X.; Yan, J.-M.; Jiang, Q. Amorphous nickel pyrophosphate modified graphitic carbon nitride: An efficient photocatalyst for hydrogen generation from water splitting. *Appl. Catal. B Environ.* 2018, 231, 43–50. [CrossRef]
- 57. Shinde, S.S.; Sami, A.; Lee, J.-H. Sulfur mediated graphitic carbon nitride/S-Se-graphene as a metal-free hybrid photocatalyst for pollutant degradation and water splitting. *Carbon* **2016**, *96*, 929–936. [CrossRef]
- 58. Shen, R.; Xie, J.; Zhang, H.; Zhang, A.; Chen, X.; Li, X. Enhanced solar fuel H₂ generation over g-C₃N₄ nanosheet photocatalysts by the synergetic effect of noble metal-free Co₂P cocatalyst and the environmental phosphorylation strategy. *ACS Sustain. Chem. Eng.* **2017**, *6*, 816–826. [CrossRef]
- Shinde, S.S.; Sami, A.; Lee, J.-H. Nitrogen- and phosphorus-doped nanoporous graphene/graphitic carbon nitride hybrids as efficient electrocatalysts for hydrogen evolution. *ChemCatChem* 2015, 7, 3873–3880. [CrossRef]
- Tang, H.; Wang, R.; Zhao, C.; Chen, Z.; Yang, X.; Bukhvalov, D.; Lin, Z.; Liu, Q. Oxamide-modified g-C₃N₄ nanostructures: Tailoring surface topography for high-performance visible light photocatalysis. *Chem. Eng. J.* 2019, 374, 1064–1075. [CrossRef]
- Marci, G.; Garcia-Lopez, E.I.; Pomilla, F.R.; Palmisano, L.; Zaffora, A.; Santamaria, M.; Krivtsov, I.; Ilkaeva, M.; Barbierikova, Z.; Brezova, V. Photoelectrochemical and EPR features of polymeric C₃N₄ and O-modified C₃N₄ employed for selective photocatalytic oxidation of alcohols to aldehydes. *Catal. Today* 2019, 328, 21–28. [CrossRef]
- 62. Rahman, M.; Davey, K.; Qiao, S.Z. Counteracting blueshift optical absorption and maximizing photon harvest in carbon nitride nanosheet photocatalyst. *Small* **2017**, *13*, 1700376. [CrossRef]
- 63. Zeng, Y.; Liu, X.; Liu, C.; Wang, L.; Xia, Y.; Zhang, S.; Luo, S.; Pei, Y. Scalable one-step production of porous oxygen-doped g-C₃N₄ nanorods with effective electron separation for excellent visible-light photocatalytic activity. *Appl. Catal. B Environ.* **2018**, 224, 1–9. [CrossRef]
- Yang, L.; Huang, J.; Shi, L.; Cao, L.; Yu, Q.; Jie, Y.; Fei, J.; Ouyang, H.; Ye, J. A surface modification resultant thermally oxidized porous g-C₃N₄ with enhanced photocatalytic hydrogen production. *Appl. Catal. B Environ.* 2017, 204, 335–345. [CrossRef]
- 65. Rahman, M.; Davey, K. Enabling Pt-free photocatalytic hydrogen evolution on polymeric melon: Role of amorphization for overcoming the limiting factors. *Phys. Rev. Mater.* **2018**, *2*, 125402. [CrossRef]
- 66. Rahman, M.Z.; Tang, Y.; Kwong, P. Reduced recombination and low-resistive transport of electrons for photo-redox reactions in metal-free hybrid photocatalyst. *Appl. Phys. Lett.* **2018**, *112*, 253902. [CrossRef]

- 67. Rahman, M.Z.; Moffatt, J.; Spooner, N. Topological carbon nitride: Localized photon absorption and delocalized charge carrier separation at intertwined photocatalyst interfaces. *Mater. Horiz.* **2018**, *5*, 553–559. [CrossRef]
- Zhu, M.; Osakada, Y.; Kim, S.; Fujitsuka, M.; Majima, T. Black phosphorus: A promising two dimensional visible and near-infrared-activated photocatalyst for hydrogen evolution. *Appl. Catal. B Environ.* 2017, 217, 285–292. [CrossRef]
- 69. Jiang, B.; Sun, Y.; Liao, F.; Shen, W.; Lin, H.; Wang, H.; Shao, M. Rh-Ag-Si ternary composites: Highly active hydrogen evolution electrocatalysts over Pt–Ag–Si. *J. Mater. Chem. A* 2017, *5*, 1623–1628. [CrossRef]



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