Achieving Efficient Incorporation of \( \pi \)-Electrons into Graphitic Carbon Nitride for Markedly Improved Hydrogen Generation

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**Abstract:** A rapid and highly efficient strategy for introducing C into g-C\(_3\)N\(_4\) involves copolymerizing \( \pi \)-electron-rich barbituric acid with melamine via a facile microwave-assisted heating, thereby eliminating the issues in conventional electric furnace heating, such as the severe volatilization, owing to the mismatch of the sublimation temperatures of barbituric acid and melamine. The g-C\(_3\)N\(_4\) catalyst after optimizing the C-doping content actively generates increased amounts of H\(_2\) under visible light exposure with the highest H\(_2\) generation rate of 25.0 \( \mu \)mol h\(^{-1}\), which is nearly 20 times above that using g-C\(_3\)N\(_4\) produced by conventional electric furnace heating of two identical monomers (1.3 \( \mu \)mol h\(^{-1}\)). As such, the microwave-assisted heating strategy may stand out as an extremely simple route to incorporating \( \pi \)-electrons into g-C\(_3\)N\(_4\) with markedly improved photocatalytic performance.

**Solar water-splitting** has been widely recognized as a potential scalable means of storing solar energy in the form of renewable H\(_2\) fuel.\textsuperscript{[1–2]} However, rational design and synthesis of sustainable, efficient, and low-cost visible-light-responsive photocatalysts for efficient H\(_2\) generation remains challenging. In recent years, as metal-free, highly active and stable photocatalyst, g-C\(_3\)N\(_4\) has garnered much attention for H\(_2\) production upon exposure to visible light.\textsuperscript{[3–4]} Pristine g-C\(_3\)N\(_4\) has a 2.7 eV band gap, absorbing only light below 460 nm.\textsuperscript{[7]} To this end, to sufficiently utilize visible light, various strategies such as heterojunction, porosity, and heteroatom doping have been invoked to expand the light absorption range of g-C\(_3\)N\(_4\).\textsuperscript{[8–12]} Among them, C-substitution for N in g-C\(_3\)N\(_4\) is highly desirable owing to its \( \pi \)-rich nature.\textsuperscript{[13–15]}

Compared to graphite, g-C\(_3\)N\(_4\) possesses a \( \pi \)-deficiency conjugated aromatic framework owing to the symmetrical substitution of N for C in the carbon rings. As the valence electron of C is larger than that of N, the reverse substitution of C for N can greatly introduce \( \pi \)-electrons into the g-C\(_3\)N\(_4\) network. It is not surprising that effective methods to incorporate C into g-C\(_3\)N\(_4\) are comparatively few and limited because of low electronegativity of C in comparison with N.

In this context, to overcome the energetic barrier of C substitution for N, much effort has been centered on \( \pi \)-electron rich aromatic monomers, such as benzene derivatives, via copolymerization with melamine.\textsuperscript{[16–17]} Notably, C-incorporating renders g-C\(_3\)N\(_4\) with an extended optical absorption edge over 600 nm.\textsuperscript{[16–18]} However, copolymerization reactions noted above often suffer from the mismatch of physicochemical properties (for example, sublimation temperature) of two constituents (monomers; for example, benzene derivatives and melamine) in an electric furnace. Such mismatch results in the severe volatilization of one or several components prior to the completion of reaction. One solution to address this issue is to perform the copolymerization reaction quickly so the volatilization of components can be greatly suppressed. This, however, cannot be accomplished by conventional heating in electric furnace as the reaction temperature cannot be rapidly reached.

Herein, we report a simple yet viable route to effectively incorporate \( \pi \)-electrons into g-C\(_3\)N\(_4\) to yield highly active photocatalysts via microwave-assisted heating of two monomers (that is, \( \pi \)-rich barbituric acid and melamine) for H\(_2\) generation. In sharp contrast to conventional electric-furnace heating, microwave-assisted heating offers the rapid heating rate. Depending on the microwave-absorber, the temperature can promptly rise from ambient temperature to above 1000 K in a few minutes.\textsuperscript{[19]} Such rapid heating and high temperature can suppress the volatilization issues noted above and thus enable efficient heteroatom incorporation into g-C\(_3\)N\(_4\). Furthermore, microwave radiation can itself interact with constitutive monomers through strong collisions.\textsuperscript{[20–22]} As a result, the C-incorporated g-C\(_3\)N\(_4\) with high crystallinity is expected to possess increased H\(_2\) generation activity. Owing to its high C/N ratio, the \( \pi \)-rich aromatic monomer barbituric acid (2,4,6-trihydroxy-1,3-diazine; denoted THD) is chosen to copolymerize with melamine in our study (Supporting Information, Figure S1). It is noteworthy that the resulting g-C\(_3\)N\(_4\) after the \( \pi \)-electron incorporation is found to harvest substantial...
visible light. Furthermore, microwave-assisted heating promotes highly crystalline g-C$_3$N$_4$. The synergy of the increased amount of π-electrons and high crystallinity of C-incorporated g-C$_3$N$_4$ photocatalyst capacitates a nearly twentyfold enhancement in H$_2$ generation (25.0 μmol h$^{-1}$) over g-C$_3$N$_4$ produced by copolymerization of THD and melamine with conventional heating (1.3 μmol h$^{-1}$).

A series of g-C$_3$N$_4$ precursors were prepared by adding various amount of THD to an aqueous melamine suspension (Supporting Information, Figure S1, left panel), followed by stirring at ambient temperature for 4 h. The molar ratios for THD/melamine are 0, 0.033, 0.05, 0.067, and 0.1, respectively. Subsequently, the precursors were irradiated with microwave for 18 min owing to the high H$_2$ generation rate at this time (see the Experimental Section in the Supporting Information and Figure S2).[19,21,22] The products are denoted m-CN$_x$, where m, CN, and x refer to microwave heating, g-C$_3$N$_4$, and the theoretical molar ratio of THD/melamine (x = 0, 0.033, 0.05, 0.067, and 0.1), respectively. The precursor with a THD/melamine ratio of 0.067 was also thermally heated in an electric furnace at 520°C for 4 h in air to yield the reference sample (referred to as f-CN-0.067, where f represents the conventional furnace heating).

Figure 1a shows essentially the same XRD patterns of m-CN-0.067 and f-CN-0.067 as that of crystalline g-C$_3$N$_4$, validating the retained g-C$_3$N$_4$ frameworks with THD incorporation. Compared to the f-CN-0.067 sample, the m-CN-0.067 sample displays relatively sharp peaks and slightly enhanced peak intensity, signifying the improved crystal quality after an 18 min microwave heating. It is notable that the XRD peak intensity of the resulting m-CN$_x$ is progressively improved with increased amount of THD incorporation (Supporting Information, Figure S3). The exact mechanism merits a detailed study and will be investigated in a future work.

The FTIR spectra of m-CN-0.067 and f-CN-0.067 are similar. It is interesting to note that m-CN-0.067 displays intensified FTIR absorption peaks in the fingerprint bands between 1200 and 1640 cm$^{-1}$ (insets in Figure 1b). Furthermore, the reduced intensity of the –NH$_2$ stretching vibration band at 3200 cm$^{-1}$ is indicative of a reduced amount of N content in the final g-C$_3$N$_4$ due to the THD introduction,[23] which is further revealed by the gradual weakening of the 3200 cm$^{-1}$ peak as the THD concentration increases (Supporting Information, Figure S4).

Solid-state $^{13}$C MAS NMR depicts the structure of m-CN-0.067 (Figure 1c). The spectrum shows two resonance peaks at $\delta_1 = 155.8$ and $\delta_2 = 163.8$ ppm, corresponding to C(i) atoms in the CN$_x$ groups and C(e) atoms in CN$_x$(–NH$_2$)C, respectively.[22] It should be noted that these values differ slightly from those for g-C$_3$N$_4$ derived from urea under microwave-assisted heating ($\delta_1 = 152.7$ and $\delta_2 = 160.5$ ppm).[2] Furthermore, no peaks from THD were detected.

X-ray photoelectron spectroscopy (XPS) analysis confirms the carbon and nitrogen composition of m-CN-0.067 (Figure 1d). The oxygen peak is from the introduced THD (Supporting Information, Figure S5). The strongest peaks of C 1s at 286.26 eV and N 1s at 396.76 eV substantiates the sp$^3$ C=N bond of the triazine ring. The other peaks at 282.62 eV for C 1s and 396.76 and 402.32 eV for N 1s can be assigned to the graphitic carbon, amino groups (C-N-H), and the charging effect, respectively.[22]

Elemental analysis reveals the C/N molar ratio of 0.733 for m-CN-0.067, which is higher than that of f-CN-0.067 (0.701) (Supporting Information, Table S1). The higher C content in m-CN-0.067 is the direct evidence of effectiveness on introducing C into g-C$_3$N$_4$ by microwave-assisted heating compared to conventional heating in electric furnace. The C/N molar ratio is 0.676 for pristine m-CN-0 and progressively increases to 0.728 for m-CN-0.033 and 0.738 for m-CN-0.1 (Supporting Information, Table S1). Clearly, the elemental analysis results affirm the efficient incorporation of C into g-C$_3$N$_4$ by microwave-assisted heating strategy.

The color differences shown in the inset of Figure 2a reflect well in the UV/Vis spectra of these samples. Pristine g-C$_3$N$_4$ has an optical absorption edge of 460 nm, corresponding to a 2.7 eV band gap. While m-CN-0.067 displays an absorption edge of nearly 700 nm. Furthermore, compared to f-CN-0.067, m-CN-0.067 possesses an intensive visible light absorption. Interestingly, all the THD-introduced samples, m-CN$_x$ ($x = 0.033, 0.05, 0.067, \text{and } 0.1$) have virtually the similar extended absorption edge (Supporting Information, Figure S6). This phenomenon may be attributed to the efficient incorporation of C in g-C$_3$N$_4$ by microwave heating, which in turn lead to the higher C content in m-CN-0.033 sample. The further increase in THD cannot introduce more C in g-C$_3$N$_4$, as revealed by the elemental analysis (Supporting Information, Table S1). Anyway, the markedly enhanced light harvesting in the visible region can be attributed to an increase of the delocalized π-electrons due to the introduction of THD.

Photocatalytic H$_2$ generation from all g-C$_3$N$_4$ samples (10 mg) was performed in the triethanolamine (TEOA) solution (15 vol%) with the assistance of 0.5 wt% of Pt co-catalyst to boost H$_2$ generation. Control experiments confirmed no H$_2$ evolution in the absence of either g-C$_3$N$_4$ or visible light irradiation. Pristine m-CN-0 shows a H$_2$ gener-
This result was a direct consequence of the generation of m-CN-0.067 at 470 nm, signifying C-incorporation in g-C3N4 network. In wavelength. Similar trend was also seen in other heteromolecule-incorporated g-C3N4.[17]

The charge mobility of semiconductor is highly dependent on its chemical composition. Thus, we measured the steady-state photoluminescence (PL) of g-C3N4 samples excited at 350 nm (Figure 3 a). f-CN-0.067 has an intense emission peak at 482 nm, longer than that of pristine g-C3N4 of about 470 nm, signifying the C-incorporation in g-C3N4 network. In

Figure 2. UV/Vis absorption spectra of m-CN-0 (black), m-CN-0.067 (red), and f-CN-0.067 (blue) samples. The color of three samples is shown in the inset. b) Photocatalytic H2 generation of m-CN-0, m-CN-0.067, and f-CN-0.067 under visible light irradiation. c) H2 generation of the m-CN-0.067 sample over the course of 15 h visible light irradiation. d) Wavelength-dependent H2 generation of m-CN-0.067 (right axis), where the optical absorption spectrum of m-CN-0.067 is shown on the left axis.

Figure 3. a) Steady-state photoluminescence (PL) spectra, b) time-resolved PL spectra, c) Nyquist plots for m-CN-0.067 and f-CN-0.067, respectively. Nyquist plots are measured in 0.1 M Na2SO4 solution. d) Photocurrent–potential curves for ITQ/m-CN-0.067 and ITQ/f-CN-0.067 at −1.0 V vs. Ag/AgCl in 0.5 M Na2SO4 exposed to visible light (λ ≥ 420 nm, 300 W Xe lamp).
C₃N₄ through density functional theory (DFT) calculations. As for g-C₃N₄, there are three different equivalent sites for C substitution (Figure 4a). Taking into account the synthesizing process and previous reports,[14,15] the bridge site of N1 was chosen as the substitution site for C dopant in this work. In contrast to the absence of π electrons on the top of the valence band for pristine g-C₃N₄, the contribution of π electrons on the top of valence band is substantially increased after C-incorporation (Figure 4b). More π-electron distribution owing to the C-incorporation efficiently narrows the band gap of g-C₃N₄ via lowering of the conduction band (Figure 4b), thereby enhancing the light harvesting of g-C₃N₄ in the visible region. Notably, the calculated HOMO and LUMO for pristine g-C₃N₄ show a uniform distribution of electrons and holes around the tri-s-triazine motifs (Figure 4c). In stark contrast, the C incorporation results in the spatial separation of holes in HOMO and electrons in LUMO, that is, the electrons localize around the pristine tri-s-triazine motifs in LUMO while holes localize around the C-incorporated tri-s-triazine motif in HOMO (Figure 4d). In other words, the C-incorporation facilitates the charge separation in g-C₃N₄, which is of key importance in improving the photocatalytic activity.

The H₂ absorption energy was also calculated to evaluate the H₂ production ability of materials[7] (Figure 4e, see the Supporting Information for details). The absolute value of H₂ absorption energy was found to largely decrease from 0.31 eV for pristine g-C₃N₄ to 0.14 eV after C-incorporation (Figure 4e), revealing that H₂ production becomes much readily in C-incorporated g-C₃N₄ compared to pristine g-C₃N₄. Taken together, the DFT calculation results described above substantiate that the C-incorporation not only increases the π-electron availability and decreases the band gap, but also decreases the H₂ absorption energy, thereby leading to markedly improved photocatalytic H₂ generation. The microwave-assisted heating strategy renders the highly efficient C-incorporation, and thus high photocatalytic H₂ generation efficiency.

In summary, we developed a viable microwave-assisted heating strategy for effective C-incorporation into g-C₃N₄. Such C-incorporation not only raises the π-electron availability and narrows the band gap of g-C₃N₄, but also decreases the H₂ absorption energy. As a result, C-incorporated g-C₃N₄ harvests more visible light. Furthermore, microwave irradiation induces the improved crystallinity of g-C₃N₄, leading to rapid charge transfer. The synergistic effect of much increased π-electrons and high crystallinity of C-incorporated g-C₃N₄ accounts for an approximately twofold enhancement in H₂ generation upon exposure to visible light, representing a rate of 25.0 μmol h⁻¹ over 1.3 μmol h⁻¹ from g-C₃N₄ produced by conventional heating. Such simple and rapid microwave-assisted heating strategy is robust for effective copolymerization of monomers with a large mismatch in sublimation temperature to yield desired functional polymer with potential application in energy conversion, environmental remediation, and sustainable chemistry.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (51872003, 51572003).

Conflict of interest

The authors declare no conflict of interest.

Keywords: carbon nitride · microwaves · photocatalysis · π-electrons


Manuscript received: November 15, 2018
Accepted manuscript online: December 7, 2018
Version of record online: January 3, 2019