ABSTRACT: Graphitic carbon nitride (g-C₃N₄) is a robust organic semiconductor photocathode with proven H₂ evolution ability. However, its application in a photoelectrochemical system as a photocathode for H₂ production is extremely challenging with the majority of reports representing it as a photoanode. Despite research into constructing g-C₃N₄ photocathodes in recent years, factors affecting an n-type semiconductor’s properties as a photocathode are still not well-understood. The current work demonstrates an effective strategy to transform an n-type g-C₃N₄ photoanode material into an efficient photocathode through introducing electron trap states associated with both N-defects and C₃N₄ (in fact, it is CN, H, as many protons are incorporated in the commonly prepared carbon nitrides; it is denoted as g-C₃N₄ in this work for consistence with all papers published in this field) in suspension systems. Such an H₂ evolution rate is significantly higher than those of the majority of inorganic photocathodes, indicating this nominal g-C₃N₄ would be an excellent candidate as a photocathode. Further applications on this polymer photocathode include the synthesis of a value-added molecule in a suspension system, such as CO₂ reduction, N₂ reduction, methane conversion, etc. The reason behind this inconsistency between its extremely excellent H₂ evolution ability and very poor photocathodic performance is not well studied but is of scientific significance for its application and efficiency improvement in photo-electrochemical water splitting, taking into account its potential to be an excellent photocathode for solar H₂ production. To address this challenge, fundamental factors that affect the photocathodic behavior of g-C₃N₄ have to be understood comprehensively.

INTRODUCTION

The need to replace fossil fuels with renewable sources of energy is widely recognized. Photocatalysis presents an efficient method for generating green and sustainable fuels for the future. In particular, hydrogen fuel generation using polymer photocatalysts has drawn intensive attention in the past decade because photocatalysts are abundant, environmentally benign, and have easily tunable band structure. As a benchmark polymer photocatalyst, great success in overall water cleavage and especially hydrogen evolution (up to 20 000 μmol h⁻¹ g⁻¹) has been achieved using a nominal g-C₃N₄, indicating this nominal g-C₃N₄ would be an excellent candidate as a photocathode. Further applications on this polymer photocathode include the synthesis of a value-added molecule in a suspension system, such as CO₂ reduction, N₂ reduction, methane conversion, etc. However, only a few works reported on the single-phase g-C₃N₄ as a photocathode with a low photocurrent density. The reason behind this inconsistency between its extremely excellent H₂ evolution ability and very poor photocathodic performance is not well studied but is of scientific significance for its application and efficiency improvement in photo-electrochemical water splitting, taking into account its potential to be an excellent photocathode for solar H₂ production. To address this challenge, fundamental factors that affect the photocathodic behavior of g-C₃N₄ have to be understood comprehensively.

The intrinsic property of the g-C₃N₄ film as an n-type semiconductor limits hydrogen generation at the electrode/electrolyte interface, as n-type semiconductors exhibit upward band bending, which results in accumulation of holes on the surface. This promotes anodic behavior, resulting in many literature reports of photoanodes based on pristine g-C₃N₄. To realize its potential to be an efficient photocathode, diverse strategies for preparing g-C₃N₄-based photocathodes were developed including heteroatom doping, biopolymer activation, and heterojunction construction, while the photocurrent of the prepared photocathode is still very moderate, as compared to a photoanode. The function of trap states has been shown to be essential to pristine g-C₃N₄’s performance in a suspension system, where cyanamide defects have been proven to be catalytically relevant sites, long-lived trapped electrons enabled H₂ evolution even in the...
dark condition, and shallow-trapped electrons significantly improved the photocatalytic activity. Trap states in g-C$_3$N$_4$ are commonly a result of structural defects and can be caused by structural nonideality, including C/N vacancies and/or –OH/–NH$_x$ terminal groups. Different defects give rise to different types of trap states, which in turn result in different PEC behavior.

To understand the impact of trap states on the photoelectrode characteristics of g-C$_3$N$_4$ in depth and more importantly to discover an efficient strategy for g-C$_3$N$_4$ to be an excellent photocathode, herein we tried to introduce N defects along with C–OH terminal groups to generate trap states in the g-C$_3$N$_4$ framework through ultrasonication. As compared to a reference g-C$_3$N$_4$ film that behaves as a photoanode, defect-introduced g-C$_3$N$_4$ exhibits clear cathodic PEC behavior. Open circuit photovoltage decay (OCVD), Mott–Schottky (MS) plot, and transient absorption spectroscopy (TAS) measurements provide strong and consistent evidence for the existence of a large portion of shallow-trapped electrons that exist over microsecond time scales after photoexcitation of defect-introduced g-C$_3$N$_4$. The results provide further evidence for the necessity of trap states associated with C–OH terminal groups and N defects for cathodic performance, reference g-C$_3$N$_4$ film was protonated using H$_2$O$_2$ treatment and shows a clear transformation from a photoanode to a photocathode. These findings provide a novel strategy for an efficient polymer photocathode for solar-driven H$_2$ fuel synthesis.

■ RESULTS AND DISCUSSION

Defects Characterization. To investigate the functions of trap states in g-C$_3$N$_4$, four different g-C$_3$N$_4$ samples were prepared, consisting of one reference film (ref-g-C$_3$N$_4$) with a low defect density and three defect-introduced films. The defect-introduced films were prepared by sonicating g-C$_3$N$_4$ powder for 1, 2, or 5 h in water, and then they were drop-cast onto FTO glass substrate and labeled as def-g-C$_3$N$_4$-1, def-g-C$_3$N$_4$-2, and def-g-C$_3$N$_4$-5, respectively. The XRD patterns of all four samples are shown in Figure 1a. All samples show a peak at 27.5°, which represents the interlayer spacing of g-C$_3$N$_4$. Obviously, sonicating has a significant impact on the crystallinity of g-C$_3$N$_4$. As the peak intensity at 27.5° shows a big variation with sonication duration. The lowest peak intensity of g-C$_3$N$_4$-1 indicates that 1 h of sonicating has introduced severe structure disorder, while a longer sonicating duration (2 and 5 h) could partially restore the crystallinity. It is probably due to the reassembly and recrystalization of exfoliated g-C$_3$N$_4$ layers, while unstable structures (with defects) would be eliminated by long-time sonication. The other broad peak at 13.2° is ascribed to the repeating heptazine structure, which is absent in def-g-C$_3$N$_4$-2 and def-g-C$_3$N$_4$-5 samples due to their poor crystallinity. The sharp peak at 26.7° is attributed to the (110) plane from the FTO substrate.

To investigate the impact of sonicating on the g-C$_3$N$_4$ structure in more detail, the carbon to nitrogen ratio and C–O bond to N=C–N bond ratio on the surface of all samples calculated from XPS spectra (Figure S1) are displayed in Figure 1b and c and summarized in Table S1. The ref-g-C$_3$N$_4$ has an N/C ratio of 4.10(±0.03)/3, close to the stoichiometric ratio of pristine g-C$_3$N$_4$. One hour of sonicating results in a decrease of N/C ratio to 3.18(±0.12)/3. The decreased N/C ratio likely indicates that N vacancies were created by sonicating. Further sonicating (2 and 5 h) increases the N/C ratio to 3.65(±0.04)/3 and 3.61(±0.01)/3. With longer sonicating time, the elementary component of g-C$_3$N$_4$ particles becomes more uniform, evident from the reduced error bar calculated by the three repeated experiments in Figure 1b. Consistent with XRD analysis, more N defects result in lower crystallinity of the g-C$_3$N$_4$ structure. The surface area of the def-g-C$_3$N$_4$-1, def-g-C$_3$N$_4$-2, and def-g-C$_3$N$_4$-5 samples was determined by BET measurements (Table S2 and Figure S2) to be 12.9, 13.4, and 18.5 m$^2$/g, respectively, which is a little larger than that of the bulk g-C$_3$N$_4$ (10.9 m$^2$/g).

Figure 1S shows C$_{1s}$ XPS spectra, which elaborate the chemical surroundings of the C element in all four samples. The peak at 288.1 eV corresponds to the binding energy of the C–N bond, which is dominant in the heptazine structure. The peak centered at 284.8 eV is attributed to adventitious O bonding, which is dominant in the heptazine structure. The peak at 288.1 eV corresponds to the binding energy of the C–N bond to N=C–N bond is quite low (0.047 ± 0.007). The C$_{1s}$ XPS spectra of all samples, where the peak intensity at 284.8 eV is assigned to adventitious O bonds. In ref-g-C$_3$N$_4$, the ratio of the C–O bond to N=C–N bond is quite low (0.047 ± 0.007). Further sonicating (2 and 5 h) decreases the ratio to 0.33 ± 0.07 and 0.13 ± 0.01, respectively. The $^1$H solid-state NMR spectra of g-C$_3$N$_4$ contain three main peaks at 8.9 and 4.2 ppm, which can be attributed to the chemical shifts of the –NH$_x$ ending group and residual water, respectively. An additional clear peak located at 4.5 ppm is present in the def-g-C$_3$N$_4$-5 sample and can be ascribed to the formation of C–OH bonds. The appearance of C–OH in the def-g-C$_3$N$_4$-5 sample NMR spectrum is in agreement with XPS analysis.

XPS N 1s spectra are displayed in Figure S4, and a percentage breakdown of different bonds has been summarized in Table S3. Ratios of sp$^2$ N to the sum of sp$^3$ N and C–NH$_x$ have been calculated to illustrate the completeness of g-C$_3$N$_4$.
structure. In an ideal g-C3N4, the ratio should be 3. There are distinct differences among ratios of different samples. The ref-g-C3N4 has the highest bond ratio of 2.9, which is close to the ideal ratio. The higher ratio (up to 3) suggests a lower level of defects and structure disorder. The ratio of the other three samples increases in the order of def-g-C3N4-1 (1.8), def-g-C3N4-2 (2.0), and def-g-C3N4-5 (2.6), which is consistent with the C:N ratio and XRD analysis.

UV–vis spectra illustrating the light absorption of all samples are displayed in Figure S5a. The band gaps of ref-g-C3N4, def-g-C3N4-1, def-g-C3N4-2, and def-g-C3N4-5 are 2.6, 2.4, 2.4, and 2.6 eV, respectively, determined from the Tauc plots in Figure S5b. The creation of N defects and introduction of C–O bonds inevitably changed the band structure of the g-C3N4 samples. From Figure S5c, the linear extrapolations of the XPS valence-band plots intercept the x-axis at 2.0, 1.8, 2.2, and 2.3 eV for ref-g-C3N4, def-g-C3N4-1, def-g-C3N4-2, and def-g-C3N4-5, respectively. Combining this information with the band gap from UV–vis spectra, the relative band structures of all four g-C3N4 samples are depicted in Figure 1d.

Photoelectrochemical Performance Associated with Defects-Induced Electron Trap States. The photoelectrochemical performance of the ref-g-C3N4, def-g-C3N4-1, def-g-C3N4-2, and def-g-C3N4-5 samples was examined in Figure 2.

![Figure 2. Photocurrent versus potential curves of (a) ref-g-C3N4, (b) def-g-C3N4-1, (c) def-g-C3N4-2, and (d) def-g-C3N4-5 with 150 W xenon lamp illumination in 0.1 M Na2SO4 electrolyte (pH = 6.5).](image)

Using a three-electrode PEC system, the photoresponse of bare FTO substrate is shown in Figure S6, which is negligible. In Figure 2a, the ref-g-C3N4 sample exhibits a clear photoanodic current with a relatively low onset potential at +0.15 V vs RHE. Such a low potential indicates that the oxidation reaction could easily happen on the electrode/electrolyte interface, which is expected as holes accumulate on the surface of an n-type semiconductor, resulting in typical Schottky plots. As shown in Figure 3a, open circuit photovoltage decay (OCVD) plots of the ref-g-C3N4 and on a typical def-g-C3N4 sample (def-g-C3N4-5), and charge carrier density was studied with Mott–Schottky plots. As shown in Figure 3a, open circuit photovoltage decay (OCVD) plots of both samples show negative photovoltage with illumination, indicating that both films are n-type semiconductors. The generated photovoltage in ref-g-C3N4 is 10 times larger than that in def-g-C3N4. This could be due to the surface trap states below the conduction band in def-g-C3N4, which mediates the band bending, thus reducing the built-in electric field. The
photoelectrons then can accumulate at the trap states, resulting in a small photovoltage determined by the potential difference between the trapped electron states and surface hole states. In one word, the defect induction into the def-g-C$_3$N$_4$ photoelectrode mediates its n-type characteristic.

With careful observation of the OCVD, one can see that def-g-C$_3$N$_4$ has much slower photovoltage decay after the illumination cutoff as compared to ref-g-C$_3$N$_4$. The average electron lifetimes of ref-g-C$_3$N$_4$ and def-g-C$_3$N$_4$ were, respectively, determined to be 0.9 and 5.5 s, calculated by fitting the photovoltage decay curves as shown in Figure 58. This could be indicative of a significantly higher concentration of surface trap states in def-g-C$_3$N$_4$ as compared to that in ref-g-C$_3$N$_4$.

To investigate the charge carrier density in ref-g-C$_3$N$_4$ and the typical and most reproducible defect-introduced g-C$_3$N$_4$ sample (g-C$_3$N$_4$-5), Mott–Schottky (MS) plots of these two samples under different illumination intensities were analyzed, respectively, in Figure 3b and c. The charge carrier density is determined from the slope of MS plots to be 1.2 × 10$^{21}$ cm$^{-3}$ for ref-g-C$_3$N$_4$ and def-g-C$_3$N$_4$-5, respectively, and the $W_s$ is determined to be 22 and 0.4 nm for ref-g-C$_3$N$_4$ and def-g-C$_3$N$_4$-5, respectively (analysis process is shown in the Supporting Information and Table S4). Because the particle sizes of both samples shown in the SEM graphs in Figure 57 are much larger than their $W_s$, a band bending is presented here.

Clear differences in slope were observed under different illumination conditions for ref-g-C$_3$N$_4$ as shown in Figure 3b. As compared to the dark condition, ref-g-C$_3$N$_4$ illuminated with 10% light intensity shows slopes dramatically reduced to one third of their original value (dark condition). The slope of the MS plot is inversely correlated with the charge carrier density. It could therefore be explained that, with illumination, photogenerated electrons are promoted to the conduction band of ref-g-C$_3$N$_4$ boosting the charge carrier density in the film by a factor of 3. Increasing the incoming light density to 100% does not further improve the carrier density level significantly, probably because of fast charge recombination with stronger light intensity. For the def-g-C$_3$N$_4$-5 film, as shown in Figure 3c, the slope of MS plots is 3 orders of magnitude lower than that of the ref-g-C$_3$N$_4$ samples in the dark condition, suggesting that introducing N defects in the g-C$_3$N$_4$ structure could significantly improve its carrier density and electron conductivity. In contrast, increasing the illumination intensity for def-g-C$_3$N$_4$-5 only slightly increases its charge carrier density, as shown in Figure 3c. This is consistent with the significantly lower photovoltage developed by def-g-C$_3$N$_4$-5 under illumination as compared to ref-g-C$_3$N$_4$ as the relatively weak illumination does not dramatically increase the surface trapped electrons.

In addition, the extrapolations of MS plots in dark condition incetped the x-axis at ~0.59 V vs RHE (the flat-band potential, $E_{fb}$ was calculated to be ~0.62 V vs RHE) for ref-g-C$_3$N$_4$, while for def-g-C$_3$N$_4$, the flat-band potential is ~0.30 V vs RHE, which also fits the conduction band edge in Figure 1d. Increasing the light intensity has positively shifted the $E_{fb}$, which is a characteristic of n-type semiconductor, due to the change in hole density at the interface. Obviously, ref-g-C$_3$N$_4$ has experienced a larger $E_{fb}$ shift of 0.15 V from ~0.62 V (in dark) to ~0.47 V (100% illumination) than that of def-g-C$_3$N$_4$-5 (0.07 V) whose $E_{fb}$ shifted from ~0.30 V (in dark) to ~0.23 V (100% illumination). The surface states in a typical n-type semiconductor should result in a large positive shift of $E_{fb}$. The opposite phenomenon (smaller shift) observed here implies that the n-type characteristic of def-g-C$_3$N$_4$-5 is moderated. This indicates that electrons are more easily transferred to the photoelectrode surface for reduction reaction. Impedance plots of the two samples are displayed in Figure 3d and analyzed in Table S5. The def-g-C$_3$N$_4$-5 has a 2 orders of magnitude smaller charge-transfer resistance ($5.6 \times 10^5$ Ω cm$^2$) than that of ref-g-C$_3$N$_4$ (1.3 × 10$^5$ Ω cm$^2$). The significantly enhanced conductivity is in agreement with the observation in MS analysis.

Shallow Electron Trap States with Extended Lifetime. To further investigate the behavior of photoexcited charges and trap state distribution in the g-C$_3$N$_4$ photoelectrodes, transient absorption spectroscopy (TAS) was performed on ref-g-C$_3$N$_4$ and def-g-C$_3$N$_4$-1, def-g-C$_3$N$_4$-2, and def-g-C$_3$N$_4$-5 samples in Figure 4 with a time resolution of ca. 1 ns. The ref-g-C$_3$N$_4$ sample exhibits a positive TAS signal that monotonously increases toward longer probe wavelengths up to the instrumentation limit of 660 nm, in agreement with literature reporting the TAS signal of bulk g-C$_3$N$_4$ due to strong absorption of the excited photoelectrons. However, TAS spectra of def-g-C$_3$N$_4$ samples exhibit only negative TA signals in the visible probe region (in Figure 4b–d), which are quite different from those of ref-g-C$_3$N$_4$. Broadly speaking, the obtained TAS signal consists of three components: excited-state absorption (positive), stimulated emission (negative), and ground-state bleach (negative). For def-g-C$_3$N$_4$, the negative signal that dominates its TAS spectrum in the visible region can be attributed to stimulated emission, as its UV–vis spectrum shows that the ground-state material does not significantly absorb in the probe wavelength region (between 490 and 660 nm) used in TAS (Figure S5). Godin et al. suggested that photoexcited electrons can either be in emissive states close to the CB or be in deep nonemissive states, and water reduction can be driven by electrons trapped in shallow emissive states but not by electrons in nonemissive deep trap states. The current observations are consistent with this model, as ref-g-C$_3$N$_4$ exhibits long-lived positive TAS signals over microsecond time scales, commonly reported for

![Figure 4](https://dx.doi.org/10.1021/jacs.9b10476)
photocatalytically less reductive g-C$_3$N$_4$. However, def-g-C$_3$N$_4$ exhibits negative TAS signals attributable to electrons in shallow emissive states with reduction potentials close to that of the conduction band, with lifetimes extending into the microsecond time scale. This is different from the submicrosecond lifetime observed by Godin et al. for electrons in emissive states. It is therefore possible that the N-defects and C–OH groups introduced in def-g-C$_3$N$_4$ help further trapping of electrons in shallow emissive states. There is thermodynamically sufficient driving force for proton reduction by these long-lived shallow-trapped electrons, which allows electron transfer from def-g-C$_3$N$_4$ to adsorbed species, resulting in cathodic behavior. Additionally, it may be observed from Figure 4 that the TA signal for def-g-C$_3$N$_4$ drastically decreases to almost zero within 1 μs after photoexcitation, which is consistent with the previous conjecture that fast recombination (over submicrosecond time scales) is accelerated in this material as compared to in ref-g-C$_3$N$_4$.

Interestingly, g-C$_3$N$_4$-1 (Figure 2b) exhibits the highest cathodic photocurrent density among def-g-C$_3$N$_4$ samples. This is likely because of the much lower nitrogen to carbon ratio and a consequently higher amount of C–O bond in g-C$_3$N$_4$-1, as evidenced in Figure 1b and c. Similar to def-g-C$_3$N$_4$-2 and def-g-C$_3$N$_4$-5 samples, the TAS spectrum of def-g-C$_3$N$_4$-1 is also negative across the visible probe wavelength region between 490 and 660 nm, as shown in Figure 4b. Following from previous discussions, the negative TAS signal is attributed to stimulated emission associated with electrons in shallow emissive states. However, in Figure 5, the decay of the TAS signal for def-g-C$_3$N$_4$-1 is slower than that for def-g-C$_3$N$_4$-2 and def-g-C$_3$N$_4$-5, which indicates that the lifetime of electrons in shallow emissive states is longer in def-g-C$_3$N$_4$-1 than in the other two samples. This is consistent with the higher photocathode current exhibited by def-g-C$_3$N$_4$-1 and could be due to the greater amount of structural disorder that might facilitate charge separation in def-g-C$_3$N$_4$-1. In addition, the TAS spectrum for def-g-C$_3$N$_4$-5 becomes more positive toward 490 nm, which is opposite to the trend observed for def-g-C$_3$N$_4$-2 and def-g-C$_3$N$_4$-5. As the wavelength-dependence of stimulated emission should approximately follow the form of photoluminescence (with a Stokes shift) because they have the same physical origins, its contribution to the TAS spectrum should be similar for def-g-C$_3$N$_4$-1, def-g-C$_3$N$_4$-2, and def-g-C$_3$N$_4$-5 (Figure S10). As such, it is likely that def-g-C$_3$N$_4$-1 has a significant population of trapped electrons that exhibit stronger excited-state absorption toward shorter wavelengths (490 nm). The final TAS spectrum in Figure 4b is a combination of the positive excited-state absorption and stimulated emission. The population of electrons exhibiting excited-state absorption that increases toward shorter wavelengths is absent in def-g-C$_3$N$_4$-2 and def-g-C$_3$N$_4$-5, which could be due to the destruction of the trap states responsible for this excited-state absorption feature after prolonged sonication.

The TA decay kinetics monitored with a 660 nm probe for ref-g-C$_3$N$_4$, def-g-C$_3$N$_4$-1, and def-g-C$_3$N$_4$-5 are directly compared in Figure 5. The def-g-C$_3$N$_4$-2 and def-g-C$_3$N$_4$-5 samples exhibit significantly faster decay as previously discussed. The TAS signal for def-g-C$_3$N$_4$-1 remains negative up to millisecond time scales, whereas the TAS signal for def-g-C$_3$N$_4$-2 and def-g-C$_3$N$_4$-5 decays to zero (within the signal-to-noise) in under 100 μs.

However, the TAS signal for ref-g-C$_3$N$_4$ is mostly positive, attributed to deep-trapped carriers as previously discussed. The decay kinetics 50 ns after photoexcitation of ref-g-C$_3$N$_4$ is well-fitted by a power-law function. Before 50 ns, the kinetic curve strongly deviates from the fitted power-law function due to significant contributions from stimulated emission. However, this negative component becomes negligible within 50 ns after photoexcitation, indicating that the lifetime of electrons in shallow emissive states is <50 ns in ref-g-C$_3$N$_4$, whereas the negative TA signal observed for def-g-C$_3$N$_4$ is still significant up to tens of a microsecond. As such, as compared to ref-g-C$_3$N$_4$ the lifetime of shallow-trapped electrons is extended by 3 orders of magnitude in time in the optimized def-g-C$_3$N$_4$-1 sample.

To conclude that the trapped photoelectrons in the def-g-C$_3$N$_4$ sample studied by TAS have a potential to be able to produce H$_2$, the TAS spectra were compared under N$_2$ and AgNO$_3$ solution, as shown in Figure S11. The negative TAS signal has been dramatically reduced in AgNO$_3$ solution, which is evidence for electrons in emissive states readily being scavenged by Ag$. The TAS signal in water is also substantially reduced as compared to N$_2$, which suggests that electrons are capable of being transferred to water/protons.

As previously mentioned, significant trap states in the def-g-C$_3$N$_4$ samples have been attributed to N defects and C–OH groups. To further investigate their roles in a g-C$_3$N$_4$ photocathode, the ref-g-C$_3$N$_4$ sample, which has shown good photoanodic performance, was protonated by H$_2$O$_2$ treatment. After being treated with 30% H$_2$O$_2$ at 70 °C for 2 weeks, ref-g-C$_3$N$_4$ clearly shows a photocathodic performance, exhibiting a negative photocurrent with an onset potential at +0.8 V vs RHE (Figure 6a). The average charge lifetime derived from OCVD plots of treated ref-g-C$_3$N$_4$ in Figure 6b has increased from 0.9 to 2.8 s (Figure S12), indicating an increase of surface trap state density after treatment. The C 1s XPS spectra in Figure 6c displays a clear left-shift peak of the C–O bond after H$_2$O$_2$ treatment, which is due to the appearance of the C–OH group. In Table 1, the ratio of the C–O bond to the N=C–N bond increases from 0.043 ± 0.007 to 0.066 ± 0.002 after H$_2$O$_2$ protonation, indicating an increase in the amount of C–OH bond as well, with N=C–N bond as a reference. Meanwhile, the carbon to nitrogen ratio has changed from

![Figure 5. TAS kinetics of ref-g-C$_3$N$_4$, def-g-C$_3$N$_4$-1, def-g-C$_3$N$_4$-2, and def-g-C$_3$N$_4$-5 samples under N$_2$ atmosphere after 355 nm excitation (200 Hz, 850 μJ/cm$^2$/pulse), monitored with a 660 nm probe (the kinetic data for ref-g-C$_3$N$_4$ 50 ns after photoexcitation are fitted by a power-law decay function).](https://dx.doi.org/10.1021/jacs.9b10476)
It has been demonstrated that by introducing N defects along with C−OH terminal groups in the g-C3N4 structure, this n-type photoanode material (def-g-C3N4) is modified to behave as a photocathode (def-g-C3N4). The g-C3N4 photoanode shows ca. 90 μA/cm² at 1.0 V vs RHE, and the optimized def-g-C3N4-1 shows a photocathodic performance with ca. −10 μA/cm² at 0 V vs RHE. This photocathodic performance is rationalized by the presence of shallow electron traps associated with the synergy of N-defects and C−OH terminal groups introduced through ultrasonication in water, as indicated by XPS and NMR. The ultrasonicated sample also develops 2 orders of magnitude higher conductivity and 1000 times longer-lived shallow-trapped charges as compared to the g-C3N4. Furthermore, the average OCVD lifetime observed for def-g-C3N4 is 5 times longer than that of the reference, which can be attributed to residual surface-trapped electrons that gradually recombine with photogenerated holes in the bulk material that slowly diffuse to the surface. In addition, TAS revealed that, as compared to the reference material (ref-g-C3N4), in def-g-C3N4 there is a large portion of photoexcited electrons in shallow emissive states with enough driving force for proton reduction, and the lifetime of these electrons is extended by 3 orders of magnitude in time into the microsecond time scale. As such, OCVD, MS plots, and TAS collectively provide evidence that long-lived electrons in shallow surface trap states associated with N-defects and C−OH terminal groups are key to the photocathodic characteristics of def-g-C3N4. This is further evidenced by a clear transformation of a ref-g-C3N4 photoanode to photocathodic performance after H2O2 treatment. This new understanding demonstrates that g-C3N4 can be both a photoanode and a photocathode candidate and could aid the rational development and improvement of sustainable organic photoelectrochemical systems for water splitting.

**EXPERIMENTAL SECTION**

**Material Synthesis.** g-C3N4 powder was synthesized by calcinating 2 g of dicyandiamide (Alfa Aesar, 99%) at 600 °C for 4 h with a ramping of 5 °C/min in air atmosphere. Ten milligrams of as-prepared g-C3N4 particles were sonicated by an ultrasonic cleaning bath (US00H, Ultrawave Ltd., ultrasonic power 100 W) in 30 mL of distilled water for 1, 2, and 5 h. One milliliter of as-obtained suspension was drop-casted on a 2 cm × 2 cm FTO glass and dried at 70 °C for 1 h. The fabricated films made from 1, 2, and 5 h sonicated g-C3N4 suspension were labeled as def-g-C3N4-1, def-g-C3N4-2, and def-g-C3N4-5, respectively. Reference g-C3N4 film was fabricated by a rapid thermal condensation method as we reported before.15,26

**Photoelectrochemical Measurements.** The photoelectrochemical properties were investigated in a conventional three-electrode cell using an electrochemical analyzer (IVIUM Technologies). The as-prepared film, a Pt net, and an Ag/AgCl electrode were used as the working, counter, and reference electrodes, respectively. The photocurrent of samples was measured in 0.1 M Na2SO4 aqueous solution under a 150 W xenon lamp (Newport). Samples were illuminated from the SE side (FTO substrate/semiconductor interface). In the open circuit voltage decay (OCVD) measurement, electrodes were placed in dark condition until the voltage became stable. A 150 W xenon lamp (Newport) was illuminated to the electrolyte–electrode (EE) side of the electrode. After the stable photovoltage was observed, the light source was turned off to obtain the photovoltage decay. The electrolyte–electrode (EE) side of each sample was exposed to intense irradiation to generate a photovoltage. The Mott–Schottky curves were measured at a certain DC potential range with an AC amplitude of 5 mV and a frequency of 1000 Hz under 0–100% illumination.

**TAS Measurement.** A home-built transient absorption spectrometer was used to collect TAS data. The pump source is a Bright Solutions Wedge HF 1064 nm Q-switch YAG laser, the third harmonic (355 nm) of which is used to excite the sample at a repetition rate of 200 Hz. The probe source is a Fianium SC400-PP white-light laser. Because of poor pulse-to-pulse stability of the optical output, the probe beam is split in two using a beam splitter to allow referencing. Light reflected from the beam splitter is used as a reference, and its total path-length (to the detector) is closely matched with the path-length of the transmitted beam. Both the sample and the reference beams are focused onto Si-photodetectors, and variable ND filters are used in front of both detectors to attenuate and match light intensities that are incident on the two detectors. The samples were mounted into a Harrick cell sandwiched between two 2 mm thick UV-grade CaF2 windows (Crystalan), with the sample separated from the front window using a 0.2 mm spacer. Prior to each measurement, N2 was flowed through the Harrick cell for >1 h, and all samples were kept under continuous N2 flow throughout the measurement.

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**Table 1. Carbon to Nitrogen Ratio and C−O Bond to N=C−N Bond Ratio in ref-g-C3N4 before and after H2O2 Treatment**

<table>
<thead>
<tr>
<th>Treatment</th>
<th>C−N Bond/N=C−N bond ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>before H2O2</td>
<td>0.043 ± 0.007</td>
</tr>
<tr>
<td>after H2O2</td>
<td>0.066 ± 0.002</td>
</tr>
</tbody>
</table>

C3N4,0.10±0.02 to C3N4,3.96±0.04, which suggests the introduction of N defects in the structure of g-C3N4 after H2O2 treatment. This provides further evidence that the introduction of both N defects and C−OH end groups, not just one of them, generates the trap states, which are responsible for the cathodic behavior of an n-type g-C3N4 semiconductor. In addition, as the amount of N defects and C−OH end groups induced by H2O2 treatment is not as high as that in def-g-C3N4 samples, its photocathodic performance is also weaker as compared to that of other samples.

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**Figure 6.** (a) Photocurrent versus potential plot, (b) open circuit photovoltage decay curve, and (c) C1s XPS spectra of ref-g-C3N4 before and after H2O2 treatment.
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.9b10476.

Synthetic procedures for the synthesis of ref-g-C$_3$N$_4$ and def-g-C$_3$N$_4$; $^1$H and $^{13}$C solid-state NMR spectra; open circuit photovoltage decay plots fitting and analysis; and impedance plots analysis (PDF)

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Q.R. and T.M. contributed equally to this work.

**Notes**

The authors declare no competing financial interest.

**REFERENCES**


(23) Godin, R.; Wang, Y.; Zwijnenburg, M. A.; Tang, J.; Durrant, J. R. Time-resolved spectroscopic investigation of charge trapping in...


