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Key factors affecting photoelectrochemical performance of g-C₃N₄ polymer films†

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We investigated the relationship between crystallinity, deep trap states and PEC performance of g-C₃N₄ photoelectrodes. Long-lived charge carriers were present in the more poorly crystalline samples, due to deeper trap states, which inversely correlated with photoelectrochemical performance. The charge diffusion length in a compact g-C₃N₄ film was determined to be ca. 1000 nm.

The benchmark polymer photocatalyst g-C₃N₄ has attracted great attention due to its ease of processing, readily tunable band structure, very promising activity in suspension systems and being composed of abundant elements.¹ The fabrication of active g-C₃N₄ films has, as a result of these properties and the large-scale industrial use of such films, become a preferred area of research. The g-C₃N₄ films prepared so far, however, show only moderate photoelectrochemical performances, despite attempts to improve their performances.^{2–4} In contrast, the powder form has shown success in suspension systems as reported earlier.⁵ This moderate photoelectrochemical performance of g-C₃N₄ films has been speculated to be due to factors such as its poor charge separation, low electronic conductivity and small charge diffusion length.³ Obviously, clear and comprehensive insight into this issue is highly sought after.

Charge diffusion length has been observed to play a pivotal role in determining the quality of photocurrents and photoelectrochemical performance. For instance, the well-studied oxide film α-Fe₂O₃ was shown to suffer from unsatisfactory photocurrents despite its very good light absorption.⁶ A comprehensive investigation by Grätzel *et al.* revealed the key issue here to be the

short charge diffusion length (~2–4 nm); such a feature explained the very good performance of nanostructured, dendrite α-Fe₂O₃ films composed of rods with lengths of just a few nanometers, with this good performance specifically due to their shorter distances for electrons to migrate than found for bulk α-Fe₂O₃ films.^{7,8} Charge diffusion length is also believed to be an important factor in g-C₃N₄ in terms of charge separation, migration and surface reactions; the other factor heavily influencing photoelectrode performance is charge separation and recombination influenced predominantly by trap states in the bulk or on the surface of a semiconductor.^{9,10}

Our previous study related to charge trapping in g-C₃N₄ powders in a suspension system showed that a high concentration of electrons were deeply trapped by electron acceptors in g-C₃N₄ and remained unreactive.¹¹ These photogenerated electrons with long lifetimes can participate neither in photocatalytic reactions nor photoluminescence. It was also reported that the structural disorder in g-C₃N₄ could introduce both shallow and deep trap states, with the shallow ones positively contributing to its photocatalytic performance.¹⁰ The understanding of the impact of trap states on the activity of g-C₃N₄, while informative, was achieved in a powder-suspension system. In a PEC system where the directional charge migration is vital, the presence of many deep trap states would prohibit the directional charge transport and affect the charge diffusion length. The influences of both charge diffusion length and trap states on the performance of g-C₃N₄ photoelectrodes are very important but not yet well understood. Peng *et al.* has reported a remarkable charge diffusion length of up to 36 μm in g-C₃N₄/rGO films; but without rGO, diffusion length would be a factor limiting the PEC performance of g-C₃N₄.¹² It is thus necessary to investigate the trap state conditions in g-C₃N₄ and their influence on charge diffusion length.

It is speculated that deep trap states in g-C₃N₄ may be caused by terminal groups or defects.¹¹ A desired closely packed and well-crystallized g-C₃N₄ thin film in principle is expected to reduce the quantity of deep trap states and hence facilitate the charge transfer with a suitable charge diffusion

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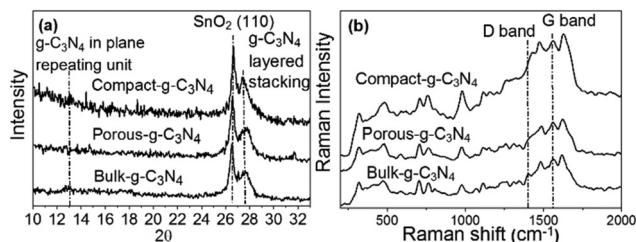


Fig. 1 (a) XRD patterns and (b) Raman spectra of the bulk, compact, and porous $g\text{-C}_3\text{N}_4$ films.

length.^{13,14} To explore the influence of trap states on the PEC performance of $g\text{-C}_3\text{N}_4$ films, here we fabricated three kinds of $g\text{-C}_3\text{N}_4$ films with different trap state conditions, including bulk- $g\text{-C}_3\text{N}_4$ film, porous- $g\text{-C}_3\text{N}_4$ film and the compact- $g\text{-C}_3\text{N}_4$ film previously reported by our group.³ The trap state conditions were determined using the open circuit photovoltage decay (OCVD) technique, and charge diffusion length was measured by taking a small perturbation photovoltage transient (TPV) measurement.

The acquired XRD patterns are shown in Fig. 1a. All samples yielded a main peak located at about 27.5° , attributed to the interlayer arrangement of the graphite-like structure. A weaker peak was observed at 13.0° and was attributed to the heptazine units in the $g\text{-C}_3\text{N}_4$ structure.¹⁵ The FWHM values of the peak at 27.5° for the bulk, porous, and compact $g\text{-C}_3\text{N}_4$ films were measured to be 1.0° , 1.1° and 0.7° , respectively. Since a small FWHM indicates high crystallinity, these results indicated a more ordered layer structure for the compact $g\text{-C}_3\text{N}_4$ film than for the bulk and porous $g\text{-C}_3\text{N}_4$ films. Raman spectra of all three samples, shown in Fig. 1b, were also acquired to confirm the level of order in each structure. For $g\text{-C}_3\text{N}_4$, the ratio of the intensity of the D band (located at 1405 cm^{-1}) to that of the G band (at 1570 cm^{-1}), abbreviated as I_D/I_G , could illustrate the distortion of the crystal structure and the defect conditions.¹⁶ Analysis of the Raman spectra displayed in Fig. S2 (ESI[†]) and summarized in Table 1 showed I_D/I_G increasing from 0.13 for the compact- $g\text{-C}_3\text{N}_4$ sample to 0.41 for bulk- $g\text{-C}_3\text{N}_4$ and to 0.55 for porous- $g\text{-C}_3\text{N}_4$. These results suggested the least structural distortion for compact- $g\text{-C}_3\text{N}_4$ and the most defect densities for the bulk and especially porous $g\text{-C}_3\text{N}_4$ samples, consistent with the XRD analysis.

SEM, UV-Vis and FT-IR spectra of all three samples, displayed in Fig. S3–S5 (ESI[†]), were acquired in order to characterize their morphologies, light absorption properties and structures. XPS spectra were also analyzed, and are displayed in Fig. S6 (ESI[†]). The N1s region of the XPS spectrum can be fitted by three components. The main peak located at 398.7 eV was attributed to C–N–C bonds. The other two peaks at higher energy accounted

for C–[N]₃ (399.9 eV) and C–NH_x bonds (401.1 eV) respectively.¹⁷ The percentage breakdown of different bonds is listed in Table S1 (ESI[†]). The percentages of the compact, bulk, and porous $g\text{-C}_3\text{N}_4$ films consisting of C–NH_x, recognized as forming the terminal groups of the $g\text{-C}_3\text{N}_4$ structure, were determined to be 8%, 13.6% and 18.8%, respectively. That is, the more ordered $g\text{-C}_3\text{N}_4$ structure showed a lower percentage of terminal groups (C–NH_x), and hence the structure of compact- $g\text{-C}_3\text{N}_4$ was most complete and that of porous- $g\text{-C}_3\text{N}_4$ least complete, in agreement with the XRD and Raman analyses.

To understand the fate of the trap states in the three samples, charge dynamics were investigated by taking OCVD measurements, which has proven to be a useful way to characterize the trap state conditions in photoelectrodes regardless of surface area.^{18,19} The average time elapsed between the generation and recombination of the electrons (average charge lifetime) was determined by fitting a biexponential function to the decay curve (Fig. 2 and Fig. S7, ESI[†]).¹⁸

Photovoltage decay in the compact- $g\text{-C}_3\text{N}_4$ sample was much faster than in the other two samples. Specifically, the average lifetimes of the electrons were found to be 0.9 s, 5.0 s and 12.8 s for the compact, bulk, and porous $g\text{-C}_3\text{N}_4$ samples, respectively. The rapid photovoltage decay or short average lifetime indicated that electrons rapidly recombined with holes in the absence of an electron donor in the electrolyte, while the long lifetimes of electrons observed in the other samples were mainly due to a severe electron trap effect.¹⁸ Most long-lifetime electrons in such samples are trapped at deep levels and located at low energy levels (more positive levels) that are insufficient to participate in redox reactions.¹¹ These deep trap states can also hinder the migration of electrons in a photoelectrode. As photogenerated electrons tend to migrate from the conduction band to the deep trap states after excitation, reducing the deep trap state density can promote the charge transfer efficiency, thereby enhancing the photocurrent

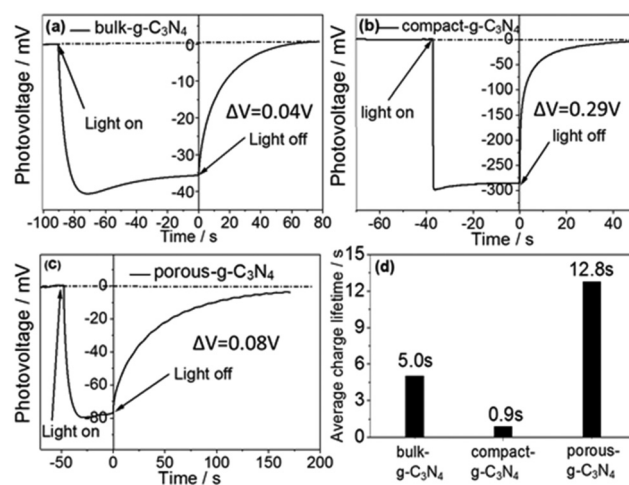


Fig. 2 Open circuit voltage decay (OCVD) plots of (a) bulk $g\text{-C}_3\text{N}_4$, (b) compact $g\text{-C}_3\text{N}_4$, and (c) porous $g\text{-C}_3\text{N}_4$ with 150 W xenon lamp illumination from the electrolyte–electrode (EE) side. (d) Calculated average charge lifetimes in the $g\text{-C}_3\text{N}_4$ films. (Generated photovoltage ΔV is the difference in voltage between dark and illumination conditions.)

Table 1 The FWHM value of the XRD peak at 27.5° (Fig. 1a) and the ratio of the intensity of the Raman spectrum D band to that of the G band (Fig. 1b) for each of the three $g\text{-C}_3\text{N}_4$ films

	Porous- $g\text{-C}_3\text{N}_4$	Bulk- $g\text{-C}_3\text{N}_4$	Compact- $g\text{-C}_3\text{N}_4$
XRD(FWHM)	1.1°	1.0°	0.7°
I_D/I_G	0.55	0.41	0.13



density of a photoelectrode. Apparently, the significantly reduced average lifetime in the compact-g-C₃N₄ film (0.9 s) indicated that the majority of photogenerated electrons were less likely deeply trapped here than in the bulk g-C₃N₄ sample (5.0 s) and porous g-C₃N₄ sample (12.8 s). Also, the long average electron lifetime in the porous-g-C₃N₄ sample (12.8 s) suggested the presence of very deep electron-trapping states. Therefore, for the samples investigated, the degree of the crystallinity showed an inverse relationship with the quantity of trap states.

More information about the trap state conditions was extracted from the photovoltage (ΔV), shown in Fig. 2. The photovoltage generated in the compact-g-C₃N₄ sample, ($\Delta V = 0.29$ V) was much larger than those in the bulk and porous g-C₃N₄ films ($\Delta V < 0.1$ V). Since low photovoltage (ΔV) is believed to be related to deep defects,^{20,21} the higher photovoltage generated in the compact g-C₃N₄ sample indicated that its density of deep defects was much less than those in the bulk and porous g-C₃N₄ films.

The results described so far indicated a clear relationship between trap-state conditions and crystallinity of the g-C₃N₄ films. The compact-g-C₃N₄ film with the most ordered structure mainly consisted of shallow trap states, resulting in the shortest average electron lifetime (0.9 s) and highest photovoltage (0.29 V) of all three samples. In contrast, both the bulk g-C₃N₄ film and porous g-C₃N₄ film included deep trap states due to their low crystallinity levels, leading to long charge lifetimes (5.0 s for the bulk g-C₃N₄ film and 12.8 s for the porous g-C₃N₄ film), which limited the charge transfer and resulted in low photovoltages (0.04 V for the bulk g-C₃N₄ film and 0.08 V for the porous g-C₃N₄ film).

The PEC performances of the three samples were examined in a PEC system and the results are shown in Fig. 3. The compact g-C₃N₄ film exhibited the highest anodic photocurrent density (e.g., 180 $\mu\text{A cm}^{-2}$ at 0.6 V vs. Ag/AgCl) of the three photoelectrodes, apparently due to its significantly reduced deep trap-state density caused by high crystallinity and uniform morphology. In contrast, the bulk and porous g-C₃N₄ films, each with a low crystallinity and rough morphology resulting in deeper trap states, exhibited less than a 30 times lower photocurrent density (5 $\mu\text{A cm}^{-2}$ at 0.6 V vs. Ag/AgCl). This result revealed that significantly reducing the density of deep trap states in g-C₃N₄ films could help improve charge transfer across the film and facilitate charge collection on the electrode and electrolyte interface, resulting in a significantly enhanced photoelectrochemical performance. The stability of compact g-C₃N₄ is shown in Fig. S8 (ESI[†]). At +0.1 V vs. Ag/AgCl, the photocurrent density was roughly stable at 65 $\mu\text{A cm}^{-2}$.

Charge diffusion length is a key factor that determines photoelectrode performance. A long charge diffusion path guarantees efficient charge transfer across the electrode. Metal oxide photoelectrodes made of different materials often show different diffusion lengths. For example, TiO₂ has an ~ 10 micrometer diffusion length,²² while Fe₂O₃ has a much smaller diffusion length of 2–4 nm.^{7,8} The charge diffusion lengths of polymer photoelectrodes have been much less extensively investigated. TPV is herein used to determine this important factor for the g-C₃N₄ film. The photovoltage rise and decay corresponding to

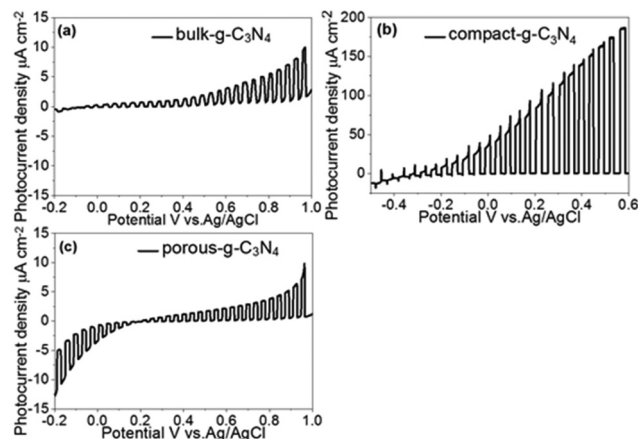


Fig. 3 Plots of photocurrent density vs. potential for the (a) bulk-g-C₃N₄ film, (b) compact-g-C₃N₄ film and (c) porous-g-C₃N₄ film using a 150 W xenon lamp illuminating the substrate–electrode (SE) side, electrolyte: 0.1 M Na₂SO₄, pH = 6.5.

pulsed light were recorded and the electron diffusion length was derived as described as follows.

The electron diffusion length for the compact-g-C₃N₄ film was measured under a range of light intensities modulated by varying the LED light power (25–100 W). We were able to vary the amplitude of the transient photovoltage between 5 mV and 20 mV by tuning the output power of the LED light. Time constants for photovoltage rise (τ_{rise}) and decay (τ_n) were determined by using the initial phase of the photovoltage rise and decay, as shown in Fig. 4a. The duration of the pulse light was 1 ms. As shown in Fig. 4b, the corresponding τ_{rise} and τ_n were calculated using eqn (a) and the resultant electron diffusion length (L) was then determined by using eqn (b) and (c) in ESI[†].^{22,23}

The effective electron lifetime (τ_n) was observed to decrease with increasing illumination power, specifically from 950 ms at 25 W to 350 ms at 100 W. With high light intensity, the reduced electron lifetime was due to an increased rate of recombination of electron–hole pairs.²⁴ As expected, though a series of pulse light intensities resulted in different values of τ_{rise} and τ_n , the electron diffusion length was determined to be ca. 1000 nm. A TPV measurement was performed on another sample, S1, to check the reproducibility of the diffusion length. The thickness of sample S1 was ca. 800 nm (Fig. S10, ESI[†]) and the charge

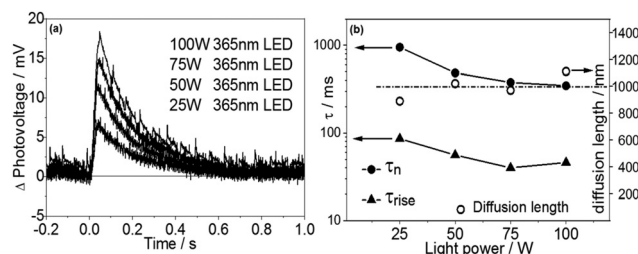


Fig. 4 (a) Transient photovoltage vs. time plots at various illumination power values, and (b) dependence of photovoltage rise time (τ_{rise}), effective electron lifetime (τ_n) and charge diffusion length on illumination power for the compact-g-C₃N₄ sample.



diffusion length was derived again to be close to 1000 nm (Fig. S11, ESI†), very close to that of the compact g-C₃N₄ sample. Taking into account the thickness of the compact g-C₃N₄ film (600 nm), such a considerable electron diffusion length could guarantee efficient charge transfer and collection across the photoelectrode, which significantly contributed to its excellent PEC performance. To further confirm our measurement of the electron diffusion length in compact g-C₃N₄, the photocurrent densities of films with different thicknesses were compared by illuminating them on their front and back sides (Fig. S12, ESI†). For a thin film (*ca.* 500 nm) with a thickness much less than the calculated electron diffusion length (1000 nm), the illumination of the front side gave a photocurrent density a little bit higher than that achieved by illuminating the back side, demonstrating the ability of all photoelectrons to traverse the film. However, when the film thickness was close to the electron diffusion length (such as *ca.* 900 nm), the illumination of the front side yielded a 40% lower photocurrent density at 1.0 V *vs.* Ag/AgCl than did the illumination of the back side, attributed to an inability of some of the electrons to move across the film. In addition, TPV measurements on the bulk and porous g-C₃N₄ samples showed neither a reliable nor reproducible response. A presence of many deep trap states is believed to result in a severe decrease in the charge diffusion length, causing difficulties in taking such measurements using this technology. It is worth noticing that g-C₃N₄ has a 2D structure, whose charge diffusion length may be highly directional (diffusion length may be different in the plane or across stacks of structures). And the XRD pattern of the compact g-C₃N₄ sample did not indicate a highly orientated crystal lattice (Fig. 1a). We believe that the g-C₃N₄ polycrystalline sample was randomly orientated and the electron diffusion length obtained was on average isotropic.

In summary, we have demonstrated a good relationship between crystallinity and the trap states in g-C₃N₄. Worse crystallinity was concluded to result in deeper trap states, which would lead to unusually long-lived charge carriers that do not guarantee good photoelectrochemical performance. Low trap-state density and long electron diffusion paths could be achieved in g-C₃N₄ photoelectrodes by manipulating its crystallinity. The significantly shortened charge lifetime and large transient photovoltage illustrated the low trap state density in a well-crystallized, closely packed, high-quality g-C₃N₄ electrode. The charge diffusion length in this g-C₃N₄ photoelectrode was determined to be *ca.* 1000 nm. The reduced deep trap state density and the long electron diffusion path finally contributed to a facilitated charge transfer, efficient charge collection across the electrode, and photocurrent density of 180 $\mu\text{A cm}^{-2}$, 30 times greater than that of the bulk g-C₃N₄ photoelectrode prepared using g-C₃N₄ powders. This study underscored the effect of trap states on the PEC performance of our g-C₃N₄

benchmark polymer photocatalyst and determined its electron diffusion length. We expect the results of this study to further encourage future mechanistic studies of highly efficient polymer photoelectrodes for photosynthesis.

Conflicts of interest

There are no conflicts to declare.

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