A Tour-Guide through Carbon Nitride-Land: Structure- and Dimensionality-Dependent Properties for Photo(Electro) Chemical Energy Conversion and Storage

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Despite the explosion in the number of publications on the graphitic carbon nitride family of materials, much still remains unknown about their structure and the underlying properties responsible for their various applications. This critical review covers the state-of-the-art in the understanding of their structure–property–photocatalysis relationship, from their molecular constituents to stacking as a (quasi) two-dimensional structure, highlighting the areas in which there is wide agreement and those still unresolved. This review first recounts how the structural understanding of these materials has evolved since the 19th century, followed by a commentary on the best practice for unambiguously characterizing their molecular structure and two-dimensional stacking arrangements. The recent literature is then examined to elucidate how individual molecular moieties affect their various material properties, particularly their chemical and opto–electronic properties, carrier dynamics, and catalytic reactivity, and how their use for energy applications can be impacted by the structural features across each dimension. Lastly, the translation of the aforementioned fundamental insights to rational molecular design is demonstrated, highlighting the synthesis of heptazine-based materials for order-of-magnitude improvement in photocatalytic reactivity, as well as the unusual phenomenon of stabilization of light-induced electrons, an effect currently exploited for a new paradigm in solar energy storage.

1. Introduction

The family of materials known collectively in the literature as graphitic carbon nitride or g-C₃N₄ is currently enjoying a second revival in research interest following the seminal report by Antonietti and coworkers on its photocatalytic properties in 2009. [1] Originally a niche subject of academic curiosity from the works of Berzelius, Liebig, [2] and Gmelin [3] nearly 200 years ago, interests in this material family was first revived as a proposed precursor to the computationally postulated ultrahard R-C₃N₄ in the 1990s. [4] In the last decade, the surge in publications on g-C₃N₄ materials arose primarily due to their favorable photo-/electro-chemical properties, especially for the photocatalytic synthesis of solar fuels such as hydrogen from water-splitting, a research direction motivated by concerns over the environmental and socio–political impacts of our reliance on fossil fuels. Many of these publications focus on the catalytic aspects of this class of materials, aiming to improve their reaction kinetics through chemical modification or material processing. In recent years, their scope of applications has since been extended into areas such as luminescent tracer and biomedical machinery in recognition of their opto–electronic properties and bio-compatibility. There is of course much more to this family of materials than their photo-/electro-chemical reactivity and catalytic applications. Elucidating their molecular and extended structure has been a long-standing problem, and the unambiguous delineation of their structural features from their chemical and physical...
properties remain a formidable challenge. Moreover, their reactivity in terms of synthetic derivatization and/or complexation, as well as their opto/electronic properties still lack a comprehensive understanding. This class of materials thus presents a fertile field for further academic studies, and our group amongst many others has investigated them from a fundamental perspective, not only as a matter of intellectual challenge, but also in following the philosophy that a basic understanding of their inherent characteristics is necessary for their future development toward real world applicability. This includes a better understanding of their structures ranging from their molecular building blocks and bonding arrangement in the 1D to 2D, to their extended structure in the 3D. These structural changes have an impact upon the processes governing the efficiency of photo-/electro-chemical energy production and storage, such as carrier photo-generation and transport, and interfacial charge transfer. Recent research has highlighted how such basic understanding of their molecular and extended structures enabled not only the rational design of highly active derivatives, but also the manifestation of new and exciting effects. However, prior to showcasing the current state-of-the-art in the field, it is instructive to provide a historic context of how our structural understanding of this rich family of compounds has evolved, commenting on the development of analytical techniques and methodologies while highlighting the knowledge gaps arising from experimental limitations. In referencing the classical 1D polymer melon and the truly 2D modications as well as other related compounds subsumed under the classification of “graphitic carbon nitride” or “g-C₃N₄,” this review will focus on the elucidation of their structure–property–functionality relationship from the perspective of structural dimensionality. In doing so, we will review the publications that are most influential as related to this theme, exploring the aspects that have reached consensus or are still contentious, and articulating the directions of future research that we consider to be most productive.

2. Historical Development and Structure of Graphitic Carbon Nitride: The One-Dimensional versus Two-Dimensional Conundrum

Throughout the introduction, we have referred to g-C₃N₄ as a family of materials and made passing mentions of the members of this “family.” The key issue, and one of the most contentious aspects, relates to the chemical structures of the materials typically referred to in the literature as “graphitic carbon nitride” or “g-C₃N₄.” A peruse through contemporary literature illustrates the source of contention: the structure of g-C₃N₄ is depicted as either a polymer of heptazine or a sheet of heptazine units (Scheme 1). In the former, heptazine units are linked together by secondary amines into strands of 1D polymer that align together into sheets through a dense network of hydrogen bonds, and it is the stacking of these sheets that give rise to its seemingly graphitic structure.[5] In the latter depiction, heptazine units are conjoined by tertiary amine, giving rise to a true 2D structure.[6] This structural dichotomy inevitably led to how experimental results are interpreted and conclusions are drawn in many papers, as well as complicating the reliability of computational predictions of material properties. Since the structure of a material is the primary determinant of its properties, from optoelectronic and physicochemical properties to carrier dynamics and catalytic reactivity, we must first address the structural features of g-C₃N₄, particularly in terms of its dimensionality, before discussing the applications that take advantage of their inherent characteristics.

First and foremost, the terms “graphitic carbon nitride” or “g-C₃N₄” are misnomers, since they imply a stoichiometric composition of 3C:4N with no other elements present. In nearly all cases, careful elemental quantification of this material would reveal hydrogen to be present at 1–2 wt% which, though seemingly insignificant, would correspond to a sizeable amount on an atomic basis. Other elements originating from the precursor used (i.e., oxygen) may also be present, as will be evident in the discussions below. The pervasiveness of these misnomers can be traced back to when this class of materials was first brought into prominence in the computational work by Liu and Cohen in 1989.[4] Their paper describes five computationally predicted phases of stoichiometric carbon nitride, one of which is β-C₃N₄ that is isostructural with β-Si₃N₄ and is predicted to have a Young’s modulus greater than that of diamond (or more popularly interpreted as “harder than diamond”). Another of their five computed phases is the graphitic phase (Figure 1, 1990s), so-called because its bonding arrangement in 2D and stacking in the 3D are similar to those of graphite. This phase was modeled as a triazine-type network and calculated to be the thermodynamically most stable modification at ambient pressure. Analogous to the conversion of graphite into diamond, the triazine-based g-C₃N₄ was considered to be a possible precursor to α- or β-C₃N₄. Thus, this theoretical study instigated widespread research in the 1990s into calculating the structure and stability[10] of these phases of carbon nitride, as well as developing synthetic protocols.[11] Of relevance to our discussion, some of the papers during this period on the graphitic phase depict its structure to be triazine-based,[12] notwithstanding the lack of concrete evidence. In fact, by the end of the 1990s, despite the many publications on this subject, doubts persist whether any of the carbon nitride phases have been prepared at all, since most materials could not be unambiguously characterized.[13]

It was not until the early 2000s that work from the groups of Kroke and Schnick propose heptazine, rather than triazine, to be the likelier constituent motif of the hypothetical g-C₃N₄ (Figure 1, 2002–2003). Specifically, Kroke and coworkers established the synthetic protocol for trichloroheptazine and solved its crystal structure, enabling computational modeling to show that the heptazine unit is thermodynamically preferential to triazine.[16] Separately, the group of Schnick reported the synthesis and the structural solution of melem, a heptazine molecule with amines on the 2-, 5-, 8-position and was considered to be an intermediate to g-C₃N₄.[18] Neither of these two molecules was new: trichloroheptazine had been studied since 1940s by Redemann and Lucas,[20] while melem has been investigated by Liebig and Gmelin,[3] then later by May[21] and Pauling and Sturdivant,[15] who correctly proposed the heptazine unit for related compounds already in the 1930s (Figure 1). Nevertheless, the significance of the work of Schnick and Kroke is in establishing the synthetic protocols, analytical framework, and crystal structure solutions with which other compounds relevant to the synthesis of “graphitic carbon nitride” can be studied. In fact, the molecule melem
was named by Liebig himself who, in his publications\cite{2} in the 19th century, also described various related compounds derived from the pyrolysis of metal thiocyanates, which all bore chemical similarities (as he correctly noted) with the materials prepared by Gmelin and Berzelius. Curiously, the final condensation material that contemporary literature calls “graphitic carbon nitride” was named by Liebig as “melon” without any particular reason.\cite{2a} Perhaps somewhat intriguingly, the elemental analysis in his original paper gave an elemental ratio of 3C:4N interpreted on the basis that the precursor used had no hydrogen, although experimental determination of hydrogen content was not explicitly stated, unlike in Gmelin’s case where a minute amount of hydrogen was found.\cite{3}

With the benefit of modern analytical tools and established synthetic protocols, all these molecules as documented by Liebig, Gmelin, and Berzelius (Figure 1, 1800s) could be revisited. During the early half of the 2000s also, a large number of cyameluric (heptazine-based) and related compounds were structurally characterized, including the dimer melam,\cite{7} melonates,\cite{23} and cyamelurates,\cite{24} as well as derivatives of melem and trichloroheptazine (Scheme 2). Collating these results enabled a mapping of the thermal condensation pathways starting from dicyandiamide via melam and melamine to the hypothetical g-C$_3$N$_4$ (Scheme 1), as well as providing an understanding of the condensation mechanism\cite{7a,8} and chemical reactivity of the heptazine core. Related compounds such as hydrates of melem\cite{25} and melam,\cite{26} as well as melamine–melam,\cite{27} and melam–melem\cite{26} adducts add further insights to the condensation mechanism and chemical properties of this class of compounds, especially their basicity and propensity for functionalization. These aspects will be elaborated in later sections.

In 2007, the structure of Liebig’s melon was finally solved based on a multifaceted approach involving spectroscopic and diffraction techniques (Figure 1, 2007).\cite{5} To produce sufficiently crystalline products for structure solution, melon was prepared following a “closed synthesis,” where the synthesis is conducted in a closed vessel (e.g., flame-sealed glass/quartz ampoule), trapping all evolved volatiles, predominantly ammonia as seen from Scheme 1 that is formed as a by-product in a sequence of condensation equilibria. As such, an autogenous pressure of ammonia is allowed to build up within the closed reaction vessel so that the polymerization and depolymerization processes can equilibrate, (i.e., allowing for a mechanism of bond formation and breaking) and, hence, error correction to take place. In fact, subsequent structural studies of the intermediate adduct phases of melamine–melem and melam–melem (vide infra) have suggested that the synthesis reaction occurs at the solid–gas interface involving the sublimation and ring-opening of melamine and ring-closing to melem, followed by condensation to melon through a range of intermediates such as melem.
Figure 1. Historic development and milestones of graphitic carbon nitride since 19th century to modern day, guided by benchmark structure solutions. 1800s: initial work by Liebig, Berzelius, and Gmelin; photograph from ref. [14] shows the Pharaoh’s serpent by ignition of Hg(SCN)$_2$; 1930s: identification of the heptazine unit as shown in the publication of Pauling and Sturdivant[15,16]; 1990s: computationally simulated structure of graphitic C$_3$N$_4$[4,10b]; 2002–2003: structure solution of trichloroheptazine[17] and melem[18]; 2007: structure solution of melon[5]; 2008: claimed synthesis of heptazine-based g-C$_3$N$_4$ by a salt melt route[6]; 2009: structure solution of poly(triazine imide)[30]; 2011: structure revision of the 2008 claimed synthesis of heptazine-based g-C$_3$N$_4$ by salt melt route to poly(triazine imide)[28]; 2014: structure solution of triazine-based g-C$_3$N$_4$[19]; 2019: structure solution of K$^+$/H$^+$ poly(triazine imide).[29d] Reproduced with permission. [5,6,14,19,28a] Copyright 2007, 2008, 2017, 2014 and 2011, John Wiley & Sons. Reproduced with permission.[4,15] Copyright 1989 and 1937, the American Association for the Advancement of Science. Reproduced with permission.[17,19] Copyright 2002 and 2009, the Royal Society of Chemistry. Reproduced with permission.[18,29a] Copyright 2003 and 2019, the American Chemical Society.

Scheme 2. Reactivity of melem and melon, and the activation of the heptazine center for further reactivity in trichloroheptazine, which is synthesized via the cyamelurates.
oligomers. In other words, a closed synthesis ultimately leads to the thermodynamic state at equilibrium yielding a product that is largely free of kinetically trapped species such as crystal defects, which would otherwise be present if the melon were prepared in an “open synthesis” where no counter-pressure can build up to ensure near-equilibrium conditions. In the structure solution, rather than a true 2D material, melon was demonstrated to have the 1D polymeric structure as described above, and the proposed crystal structure suggests hydrogen bonding between the primary amine and the weakly Lewis basic heptazine nitrogens to be responsible for the polymer strands being aligned into sheet-like arrays that stack together into a faux-graphitic structure. Revelation of this structure and characterization of its properties not only brings us closer to completing a map of the thermal condensation pathways, but also illustrate the challenge of attaining full condensation to the true g-C₃N₄, since further heating of melon typically leads to its decomposition to carbonaceous products and nitrogen under pressure, or to mostly gaseous products under open conditions rather than the truly 2D structure.

One avenue of thought at this point is that the condensation reaction to the graphitic phase, presumably a solid-state reaction, is kinetically hindered by diffusion of the reaction intermediates such as melam and/or melam. Hence, shortly after the structural elucidation of melon, a report was published claiming the synthesis of g-C₃N₄ based on tertiary amine linkage of heptazine units (Figure 1, 2008), following an ionicothermal route employing a eutectic of KCl and LiCl as a high temperature solvent to overcome the aforementioned limitation in reactant diffusion.[6] While the resultant product was initially thought to be the desired graphitic phase, subsequent material characterization including the use of nuclear magnetic resonance (NMR) crystallography showed the dominant phase to be the 2D network poly(triazine imide) or PTI.[26] As shown in Figure 1 (2011), this network comprises triazine units bridged by secondary amines into stacked arrays that incorporate lithium ions within the structural pores and chloride ions within the interlayers. Despite the lack of success in obtaining the stoichiometric carbon nitride in the graphitic phase, this report was influential in providing the precedent for further research in ionothermal syntheses in the 2010s, when research on the structure-directing effect of salt melts led to the synthesis of poly(heptazine imide) (abbreviated henceforth as PHI; see Figure 1, 2019), which is the heptazine analogue of PTI comprising stacked 2D arrays of heptazine units conjoined by secondary amines.[20] In other words, this work demonstrates that the synthesis environment can provide a handle on controlling the dimensionality of the compounds in the carbon nitride family, changing the connectivity of heptazine units in the 1D polymer melon as prepared using classical solid-state synthesis to the 2D networks of triazine in PTI and heptazine in PHI. At this point, we should note that PHI is not a new structure, but a melamine-intercalated PHI had been observed by electron microscopy as a side phase in melon and was structurally determined already in 2009.[10] Nevertheless, the significance in developing syntheses mediated by salt melts is the realization that 2D carbon nitrides are indeed synthetically accessible, and that their synthesis is scalable to allow for in-depth analysis of their properties.

From these developments in synthesis methods, there is a growing notion that the hydrogen-free g-C₃N₄ cannot be prepared following a simple solid-state synthesis (i.e., by heating the hydrogen and/or oxygen containing precursor in air or inert atmosphere), or at least cannot be prepared in sizeable quantity for unambiguous characterization. In fact, our recent computational study suggests that this hydrogen-free graphitic phase would be difficult to obtain by such synthesis procedure, a conclusion based on the energy of formation of this phase as a function of the chemical potential of ammonia, which is the by-product in the synthesis equilibrium (Scheme 1).[13] Indeed, fully condensed, heptazine-based g-C₃N₄ was found to become stable only at very low ammonia partial pressures and high temperatures, conditions that are not met in standard ampoule syntheses targeted at crystalline carbon nitride phases. However, synthesis under extreme conditions[32] or using unconventional methods, such as the ionothermal approach as discussed above for PTI and PHI, may circumvent some of these thermodynamic limitations. To exemplify such possibility, upon re-examination of the liquid/gas interface of the salt melt synthesis, Cooper, Bojdys, and coworkers identified a material with crystallographic and spectroscopic properties consistent with those of the triazine-based, hydrogen-free g-C₃N₄ (Figure 1, 2014).[19] Spectroscopic evidence consistent with this (fully condensed, hydrogen-free) phase was reported for the product obtained by the thermal decomposition of Hg(SCN)₂, the precursor of the original “Pharaoh's serpent” as originally conducted by Wöhler and revisited by McMillan and coworkers. However, interpretation of the results was inevitably complicated by the lack of crystallinity and other phases present in the product (e.g., HgS), leading the authors to converge on a HgS-containing porous carbon nitride species that may contain triazine or heptazine units, or both.[14] The preparation of the fully condensed heptazine-based carbon nitride has also recently been claimed using a dynamic vacuum synthesis route,[33] based on our aforementioned computational work suggesting that an extremely low ammonia partial pressure is required to form this phase.[14] In any case, unambiguous assignment of a particular structural model requires rigorous material characterization, a subject addressed in the next section. Likewise, interpretation or inference of experimental or computational results based on fully condensed g-C₃N₄ should be critically assessed, especially those related to (photo-/electro-)chemical properties, as subtle structural details such as full versus partial condensation, or more obvious differences in terms of dimensionality of the carbon nitride backbone, may alter the (opto)electronic characteristics of g-C₃N₄ significantly.

As a final remark to this section, considering how our understanding of their structure evolved from these historic contexts, it is no surprise that misleading appellations such as “graphitic carbon nitride” or “g-C₃N₄” have become so widespread in the literature that these terms have entered common usage. Perhaps in the future, when a true g-C₃N₄ has been reproducibly synthesized and structurally verified unambiguously, there will be a standardization of nomenclature. For now, considering their pervasiveness, researchers including ourselves have used these misnomers in line with contemporary literature as a convenient means to establish the subject matter with the audience in scientific communications. However, our preference is
to use the term “melon,” Liebig’s original appellation, to refer to the final condensation product under autogenous pressure, and the phrase “(graphitic) carbon nitrides” as a more general categorization of 1D or 2D materials based on the triazine and heptazine building blocks.

3. Characterization Methodologies from Molecular Structure to One-Dimensional/Two-Dimensional Periodicity and Stacking in the Third Dimension

That nearly two centuries elapsed between the first report of melon and its structure solution illustrates the difficulty of structurally characterizing this and related carbon nitride materials. Their amorphous or semicrystalline nature makes structure solution by diffraction methods challenging, and to date no solvent exists that can solubilize melon without a chemical reaction, thus preventing straightforward recrystallization or solution-based analytical methods like chromatography, GC-MS, or solution nuclear magnetic resonance (NMR). This leaves only direct characterization in the solid-state the sole option, although this again is complicated by the inherent disorder of polymeric melon, which can lead to significant signal broadening in bulk-averaged characterization techniques, necessitating the sample to be of highest possible quality for structure solution. Fortunately, sufficiently crystalline products can be obtained by following the closed synthesis mentioned above, and has been applied for synthesizing melem,[18] melon,[5] PTI,[28] and PHI[29d] for structure solution. This section thus uses these examples as case studies for how these materials (and related “carbon nitride” materials) should be characterized as part of scientific rigor. At this point, we should remark that oftentimes less crystalline product is desirable, especially in the case of heterogeneous catalysis, since catalytic reactivity generally originates from high energy species such as surface states or defects. For this reason, most syntheses of melon in the literature were conducted in what term “open synthesis” (e.g., in an open vessel placed in a standard tube/muffle furnace), which is more scalable than the closed synthesis. The choice of synthetic protocol—closed versus open—depends essentially on the aim of the experiment, whether it is for structure solution or for applications. One may question whether the structures solved using highly crystalline materials are relevant to the poorly crystalline materials used in catalytic (and other) applications. In fact, this problem draws parallel to the famous “pressure gap” conundrum in heterogeneous catalysis: whether the active sites determined from highly ordered model catalysts at low temperature and low pressure are identical to real catalysts operating at high temperature and pressure. We will describe our approach to this ongoing problem for melon photocatalysis below.

With sufficiently pure and/or crystalline carbon nitride samples, determining their molecular structure is relatively straightforward by spectroscopic methods, especially by Fourier transform infrared (FTIR) and solid-state magic angle spinning NMR spectroscopy. These characterization methods are aided in large part by the aforementioned works from the groups of Schnick[28,72,20] and Kroke,[17,13,26] whose structure solutions of heptazine- and triazine-based compounds provide the references for spectroscopic signal assignment. The triazine and heptazine core can be identified by the FTIR signals at around 800–850 cm\(^{-1}\) and in the region 1400–1600 cm\(^{-1}\) (Figure 2c), and can be corroborated by \(^{15}\)C NMR (Figure 2a), which in the absence of ring protonation would exhibit the single carbon environment of triazine at around 165–170 ppm and the two carbon environments of heptazine at 155–160 and >164 ppm of similar intensity (the latter depending on the functional groups present on the 2-, 5-, 8-position). It should be noted, however, that tautomerism and additional ring protonation can lead to multiple carbon signals or signal shifts in triazine-based PTI,[28b] hence rendering the distinction between triazine and heptazine-based carbon nitrides somewhat error-prone. Similarly, to differentiate monomeric (melem) from polymeric species, the secondary amine (\(\sim\)NH\(\sim\)) bridging the triazine/heptazine units can be identified by the strong FTIR signals in the region 1200–1400 cm\(^{-1}\) that are present in melam[27] (triazine dimer) but not in melamine nor melem, and corroborated by the presence of its corresponding \(^{15}\)N NMR signal at around ~245 ppm (Figure 2b). The \(^{15}\)N chemical shift for the central heptazine nitrogen may also act as an indirect evidence differentiating monomeric, oligomeric, and polymeric structure, since this shift is around ~234 ppm for melem, ~225 ppm for melon, and in-between for oligomers.[34] The primary amines in melon manifest as broad signals in the 3000–3500 cm\(^{-1}\) region, while they are seen as sharp signals in melem and melamine, and also in the \(^{15}\)N NMR spectrum as signals in the range ~250 to ~275 ppm as observed for melamine, melam, and in melem. It should be noted that absence of the primary amine FTIR signal is a poor indicator of a higher degree of condensation, since either the signal for secondary amine also appears sharp signals in this region despite having only low amounts of primary amine groups at the edges), or the O\(\sim\)H stretch from water (e.g., in melem hydrate[27]) can mask these amine signals. Another widely used characterization method that may distinguish the various nitrogen environments is X-ray photoelectron spectroscopy (XPS), of which the spectrum in the N1s region is shown in Figure 2d for melon as an often studied material.[35] Here, based on a recent spectral reassigment[36] for better consistency of signal intensity with crystallographic structure, the spectrum can be deconvoluted into four signals—heptazine nitrogen at 398.7 eV, NH\(_3\) at 399.4 eV, NH at 400.3 eV and N\(\sim\)(C\(_3\)) at 401.4 eV—although corroboration with the other spectroscopic methods mentioned above is recommended due to possible observational bias in the deconvolution process especially for strongly overlapped signals (Figure 2d). Nevertheless, as illustrated here, characterization of the basic building blocks of carbon nitrides is relatively straightforward, given their robust spectroscopic fingerprint. However, mapping out their connectivity and their spatial arrangement in 2D and 3D so as to obtain complete structure solutions, including the differentiation between monomeric and polymeric species as well as between quasi-2D and true 2D structure, relies on the use of more advanced local and long-range structural probes spanning several length scales. In the following, we will discuss selected examples of less frequently applied methodologies that have proven particularly useful in structural carbon nitride chemistry.
Solid-state NMR spectroscopy is a powerful tool to resolve the local structure, bonding arrangements and connectivity of carbon nitrides. The $^1$H→$^15$N cross polarization with polarization inversion (CPPI) sequence has been successfully applied to resolve the ambiguity surrounding the assignment of amine signals as alluded to above. This technique discriminates nitrogen nuclei according to the number of hydrogen directly attached, based on the different polarization transfer dynamics of primary, secondary, and tertiary amine groups.[37] The CPPI sequence applies a phase inversion step to the rare spin system with varying duration (the inversion time) such that the signal amplitude decreases toward or below zero (i.e., negative amplitude) depending on the number of hydrogen directly bonded to the nuclei. This is illustrated in Figure 3a, which plots the inversion time versus the normalized intensity of each nitrogen signal, and shows how nitrogen atoms that are not bonded to hydrogen (i.e., triazine/heptazine nitrogens) will have an invariant signal intensity, whereas the signals for hydrogen-bearing nitrogens will decrease with a distinct time behavior. The crossover point of this decay curve is dependent on the number of hydrogen attached, with a value of $-\frac{1}{3}$ if the nitrogen is a primary amine, and 0 for secondary amine, thus distinguishing the various amine functional groups.

Crystal structure solution in carbon nitrides suffers not only from low crystallinity and high defect levels, but also from the fact that carbon nitrides are exclusively composed of light scatterers which interact only weakly with X-rays and often have large unit cells, thus often requiring additional information from complementary techniques. In this context, two literature case studies illustrate the methodological approach to structure solution in spite of these challenges, the first being the structure solution of cyameluric acid in terms of differentiating the acid-oxo tautomer, and the second being the elucidation of hydrogen and lithium crystallographic sites in PTI. In the former, for identifying the prevalent tautomer in cyameluric acid,[41] Senker and coworkers compared the experimental $^{13}$C and $^{15}$N NMR spectra with those from quantum chemical calculations, from which the tri-oxo rather than hydroxyl tautomer was identified to be the likeliest. This motif, with its geometry optimized by molecular modeling, could then be used as input for structure solution.
solution based on direct-space methods and subsequent Rietveld refinement of the powder X-ray data. Regarding PTI in the second example, although the connectivity of the triazine building blocks has already been determined,\textsuperscript{28a,43} to determine the H/Li positions unambiguously,\textsuperscript{28b} the same group approached this problem using 2D NMR to first determine the covalently bonded and non-covalently-bonded neighbors of the NMR active nuclei (\textsuperscript{1}H, \textsuperscript{7}Li, \textsuperscript{13}C, and \textsuperscript{15}N), from which suitable structure models were proposed. After narrowing down the number of models based on calculated energetics and consistency between predicted and measured interatomic distances as determined by NMR crystallography, the crystal model was refined with electron diffraction data and corroborated by X-ray pair distribution function (PDF) analysis. The final structure, based on an orthorhombic unit cell with space group \textit{P2}_1\textit{2}_1\textit{2}_1, has two lithium ions and two protons within the cavity surrounded by six triazine units, with the protons residing on both the bridging nitrogen and the triazine nitrogen. It should be mentioned that, following recent developments in transmission electron microscopy, direct visualization of these light elements has been recently reported\textsuperscript{39} based on aberration-corrected integrated differential phase contrast imaging using an extremely low electron dose rate, which is especially suitable for carbon nitrides and other soft crystals considering their propensity to suffer from beam damage. Provided the PTI sample is sufficiently crystalline as obtained from closed synthesis, the 2D triazine network with the chloride and even the lithium cations could be imaged with near atomic resolution (though with low contrast for the lithium sites), as shown in Figure 3c.

Beyond the local structure, scattering techniques have proven invaluable to determine how the molecular motifs are arranged in the 2D as 1D, quasi-layered (i.e., melon) and truly layered materials (PTI and PHI), and how these layers are stacked together in the 3D. For melon, its powder X-ray diffraction (XRD) pattern as shown in Figure 3d presents only two prominent reflections corresponding to the in-plane (7.02 Å, (210)) and interlayer (3.19 Å, (002)) periodicity, while other reflections are too weak and broad to allow for ab initio structure analysis from X-ray powder diffraction (though contain sufficient information to rule out the hydrogen-free, fully condensed 2D carbon nitride as a structure model\textsuperscript{36-40}). However, structure elucidation was possible in conjunction with solid-state NMR spectroscopy and electron diffraction of the nanocrystalline sample. The electron diffraction (ED) pattern of melon shows pseudo-hexagonal symmetry reminiscent of, yet distinct from, graphite or the hypothetical g-C\textsubscript{3}N\textsubscript{4}, and can be indexed to the \textit{p2gg} plane group (Figure 3b).\textsuperscript{35} Structure solution in projection revealed the in-plane structure of melon, which is composed of NH-bridged heptazine units arranged into a planar and tightly hydrogen-bonded 2D array. Since only information on the \textit{k\textsubscript{0}l0} plane was available by ED, details of the layer stacking remained unresolved though several approaches to this problem have been undertaken as discussed below. Nevertheless, ED has become an indispensable tool in the subsequent elucidation of crystal structures, namely of PTI and PHI, as a standalone characterization technique or for corroboration of structure solution determined from their powder XRD patterns.\textsuperscript{28a,29d}

Determining the periodicity of melon in the 3D is challenging due to its layered character and inherent stacking disorder, which had led to conflicting conclusions (AA\textsuperscript{40b} vs AB stacking\textsuperscript{40a}) in the earlier analyses of powder diffraction results. Senker and coworkers\textsuperscript{43} approached this problem using NMR crystallography by combining diffraction techniques with heteronuclear cross polarization experiments and force field calculations to verify the structure model. Here, for signals in the 1\textsuperscript{D} and 1\textsuperscript{5}N spectra assigned to identical crystallographic sites based on the melon plane group (2D structure), peak splitting for one nitrogen and a peak shoulder for one carbon environment were observed. After ruling out impurity phases based on NMR correlation experiments, the authors concluded that this splitting and shoulder arose due to inequivalent crystallographic sites when considering the 3D structure (i.e., stacking of the pseudo layers). This then allowed the estimation of interatomic distances between layers of heptazine units based on magnetization build-up, from which structure models could be proposed and verified on account of their energetics calculated from computational methods. Two models were proposed which are at the energetic minima and fitted the experimental data, both showing shifts in adjacent layers (shifted along the \textit{b}-axis only or along the \textit{a}-axis) to minimize the eclipsed arrangement of stacked heptazine units.

As an alternative to combined computational modeling and NMR crystallography above, Irvine and coworkers\textsuperscript{40b} approached the stacking problem using a combination of XRD and neutron scattering. They first narrowed down the number of structural models of melon by examining the X-ray powder diffraction pattern in terms of reflection positions and intensities, and then collected the neutron total scattering data. The crucial methodology in the neutron experiment is the comparison of deuterated and non-deuterated melon, since the neutron scattering lengths of hydrogen and deuterium have opposite signs, and their coherent scattering cross sections differ substantially (Figure 3e). This then will produce opposite intensities for hydrogen sites in the differential correlation function, which reveals the atomic pair distances involving hydrogen, thus enabling the identification of peaks corresponding to the hydrogen positions in melon. From these PDF analyses, the bonding arrangement of the structure model of melon was confirmed in the short-range (0–2 Å) region, while results in the medium-range (2–6 Å) region provide atomic distances of both the second- or third-nearest atomic intralayer neighbors

Figure 3. a) \textsuperscript{1}H-\textsuperscript{15}N CPPI experiment for differentiating primary, secondary, and tertiary amines (note that this example is taken from urea-terminated PHI). b) Experimental (left) and simulated (right) selected area electron diffraction pattern of crystalline melon. c) Prismatic PTI crystals observed in SEM (top left) and its crystallographic representations (top right), and direct visualization of its structure with near-atomic resolution by transmission electron microscopy using aberration-corrected integrated differential phase contrast (AC-iDPC) imaging (bottom). d) XRD pattern of melon and analysis thereof based on unit cell shown in inset. e) Neutron scattering differential correlation function analysis of melon and its deuterated counterpart. a) Reproduced with permission.\textsuperscript{34b} Copyright 2017, John Wiley & Sons. b) Reproduced with permission.\textsuperscript{15} Copyright 2007, John Wiley & Sons. c) Reproduced with permission.\textsuperscript{19b} Copyright 2020, Nature Springer. d,e) Reproduced with permission.\textsuperscript{40b} Copyright 2015, Royal Society of Chemistry.
and distances in the stacking direction (c.f. interlayer \(d\)-spacing of 3.26 Å from XRD). Based on fitting the structural models to experimental data, the best match was obtained for a model based on an orthorhombic unit cell with the melon layers in an AB stacking arrangement (rather than AA\(^{[40b]}\)), where the layers stack with a shift in the \(x\)- and \(y\)-directions to minimize heptazine overlap. One interesting aspect of their neutron scattering results is the absence of interatomic distance in the range of \(C_{sp^2}-N_{sp^3}\) bonding, which is expected if the heptazine units are bridged by \(sp^1\)-hybridised amine. From this absence, the authors inferred that the bridging nitrogen must have \(sp^2\) character similar to the nitrogen atoms in the heptazine itself. This inference is significant because it implies a planar structure which may allow for a degree of electron delocalization across bonded heptazine units and will have implications to our understanding in the dimensionality of charge transport (vide infra), although this matter is yet to be settled. These findings also illustrate PDF from total scattering data as an emerging technique for investigating the local structure of carbon nitrides, especially in providing subtle yet important structural details based on atom–pair distances, including stacking sequence and real structure effects such as defects and strain, complementing diffraction techniques, which yield information on the average structure only. Using PTI as one example, PDF analyses up to 20 Å can show that the triazine layers are not strictly planar but are slightly buckled as caused by the residual dipole moments generated by the distribution of hydrogen and lithium ions within the triazine cavity\(^{[28b]}\), a structural feature that would be difficult to discern using conventional characterization methods. This buckling was later corroborated in a re-examination of PTI’s powder diffraction pattern collected using synchrotron X-ray at a low temperature of 100 K, at which overlapped peaks become resolved due to anisotropic thermal expansion.\(^{[42]}\) As is indeed the case in this study, cooling the sample splits the reflection corresponding to \(d = 1.65\) Å into two peaks as indicative of symmetry being reduced from a strictly planar hexagonal space group, and the best structural model from subsequent Rietveld refinement shows slight non-planarity in the triazine layers. For PHI as another example, describing the stacking structure is one problem\(^{[44]}\) that can be tackled by combined PDF and XRD analyses, which show how its pore constituents—the water molecules and potassium ions—mediate the stacking of the PHI layers in the 3D.\(^{[29d]}\) Here, within the pores of the PHI, the water-solvated potassium cations as incorporated from the salt melt synthesis strongly interact with the PHI layers, providing a directing effect on the layer stacking resulting in slip-stacked layers; conversely, removal of these cations (e.g., by exchange with protons) leads to more defective stacking owing to the weaker interactions between the PHI layers.

The above examples illustrate how one can achieve an increasing level of precision for structure elucidation of the carbon nitrides, from the molecular level to higher dimensions in terms of the arrangement of periodic motifs within the (quasi-)layers in the 2D, and their stacking order in the 3D. Given that the physicochemical and (photo)catalytic properties as well as the reactivity and opto–electronic behavior of the carbon nitrides are governed by their structure at all dimensions, in the next sections where we examine these properties and characteristics, the discussion will take place from a structural perspective.

4. Reactivity of Graphitic Carbon Nitride: From Molecular Constituents to One-Dimensional Polymers and Two-Dimensional Networks

The properties of g-C\(_3\)N\(_4\) materials largely reflect those of their constituent heptazine or triazine motif, and thus it is instructive to briefly review some of the properties of these nitrogen-bearing aromatic heterocycles. The triazine unit is historically well-known and has thus been extensively studied. Synthesis involving this unit has been well-developed and its derivatives have found uses in pharmaceutical, biological, and industrial applications.\(^{[45]}\) On the other hand, the heptazine unit has been far less studied, and publications on its derivatives have been sporadic in the decades since Pauling and Sturdivant proposed its structure until around 2000, when Kroke and coworkers proposed heptazine to be more energetically stable than triazine at high temperature. As mentioned earlier, the triazine and heptazine cores are both aromatic in that they conform to all of Hückel rules, having, respectively, 6 and 14 \(\pi\)-electrons inclusive of the electron pair in heptazine’s central nitrogen, which in its bonding with the neighboring three carbons was estimated by Pauling and Sturdivant to have 28% double-bond character.\(^{[13]}\) Considering the chemical similarities of triazine and heptazine compounds, we will discuss them together in the following.

Analogous to other nitrogen-containing aromatic heterocycles, owing to the inductive and mesomeric effect of the nitrogen, triazine is electron deficient, particularly more so than pyridine and pyrimidine due to its three ring nitrogens forming part of the pi system.\(^{[35c]}\) This mesomeric effect was illustrated in the work of Pfaff et al.\(^{[46]}\) who synthesized triferrocenyl benzene/pyridine/triazine where the ferrocene units act as redox probe for the electron-withdrawing effect of the aromatic center. Here, the electrochemical experiments show a progressive oxidative shift of the ferrocene redox potential with increasing number of nitrogen in the central aromatic unit, the largest anodic shift being observed for the triazine compound. Electronically, the triazine core is similar to heptazine based on their ionization potential as determined from their photoelectron spectra. Specifically, both are ionized above \(+9\) eV, with the main difference between the two being the highest occupied orbitals, which is the lone-pair orbital for triazine and the \(\pi\) orbital for heptazine.\(^{[47]}\) Furthermore, calculations show that the lone electron pairs in heptazine and triazine are delocalized into the aromatic heterocycle to a greater extent than in pyridine. As such, both these motifs are resistant to oxidation and are extremely weak as base, thus conferring exceptional chemical stability to melon, PTI, and other related compounds like melem and the cyamelurates, mirrored by their generally high synthesis temperatures. This stability, while advantageous for applications such as catalysis, can be problematic if one wishes to attach specific functional groups to the triazine/heptazine core. To exemplify the harsh conditions required, the melonate anion is obtained by reacting melon in a cyanate or thiocyanate melt above 300 °C,\(^{[23,48]}\) while the cyamelurate anion is
synthesized by boiling melon in a highly concentrated alkaline solution.\[24]\ For this reason, activation of the triazine and heptazine unit is necessary to make them amendable for functionalization. For triazine-based compounds, most synthetic routes begin with cyanuric chloride (trichlorotriazine), a commercially available and inexpensive precursor. As mentioned above, the numerous applications of triazine compounds have led to numerous reaction protocols being developed, including nucleophilic addition, Friedel–Crafts arylation, and Suzuki coupling.\[40,45] Analogously, functionalization of heptazine by nucleophilic substitution typically starts with trichlorohexazine, which is obtained by chlorinating cyamelurate with PCl₅ either as a solid-state reaction\[57] or in POCl₃ as solvent.\[69]\ Though far less studied, trichlorohexazine can presumably undergo the same reactions as cyanuric chloride, with nucleophilic addition\[50] and Friedel–Crafts arylation\[51] being reported. The fact that functionalization reactions for both triazine and heptazine are largely confined to nucleophilic substitution reiterates the electron deficiency of these centers, contrasting other nitrogen-based hetero-aromatic compounds such as pyridine where electrophilic substitution would still be possible. To control the number of substitutions in the triazine core, an empirical rule of thumb states that mono-substitution of cyanuric chloride takes place at 0 °C, di-substitution at ambient temperature and tri-substitution at 60 °C.\[43]\ In the case of trichlorohexazine, Zambon et al. performed its nucleophilic di-substitution at ~95 °C, with the third substitution taking place at room temperature.\[52]\ In fact, as observed in the nucleophilic reaction between trichlorohexazine and diphenylamine, after two substitutions, the remaining chloride on the heptazine has sufficient stability to resist hydrolysis at ambient conditions.\[53]\ Hence, it is evident that the reactivity of the triazine/heptazine center decreases with each nucleophilic substitution, and that trichlorohexazine is seemingly more reactive than cyanuric chloride when comparing these synthetic protocols. These reactions are summarized in Scheme 2.

In addition to resisting oxidation and general chemical inertness, the electron deficiency and weak basicity of the triazine/heptazine core also affect other properties of g-C₃N₄ materials in subtle ways, particularly in terms of the reactivity of the functional groups attached. This is exemplified by the (lack of) basicity in the 2° amine in PTI and the 1° and 2° amines in melon. Despite the presence of these amine functional groups, the sites with the greatest (Brensted) basicity are instead the triazine or heptazine nitrogens as evidenced by the structures of salts of melamine and melem. In melamine salts\[54] and in tricyanomelaminates,\[38c,55] protonation occurs on the triazine ring rather than the peripheral group, −NH₂ or −NCN, as illustrated in the pyrophosphate salt of melamine in Figure 4a. Similarly for salts of melem,\[56] and as implied in the cyamelurate tautomerism\[43] discussed above, protonation also occurs on the heptazine ring rather than the groups on the 2-, 5-, 8-position; an example is shown in Figure 4b for the hydrogen sulfate salt of melem. In spite of these examples illustrating their basicity, the pKa of melamine and related compounds such as amidine and ammelide have been measured to be ≤5, that is, on a similar order of magnitude as organic acids.\[57]\ In the case of heptazine compounds as exemplified by melem, its three −NH₂ moieties do not undergo the typical reactions expected for nucleophilic primary amines, and of the reactions reported (examples including reaction with hydrazine\[58]\ and phthaloyl dichloride but not phthalic anhydride\[59]—see Scheme 2), harsh reaction conditions are necessary. Hence, we expect melon to also display resistance against typical reactions involving primary and secondary amines, more so considering that it is a quasi-2D material with these functional groups being locked up in interpolymer hydrogen bonding and buried within the layer stacking, making post-synthetic derivatization of melon a difficult prospect. This is in contrast to the higher nucleophilic reactivity of the primary amine groups in melamine, which condense readily with electrophiles such as formaldehyde to form melamine formaldehyde resin.

In terms of metal coordination, we are unaware of any melamine/melem complexes with structure solutions other than a copper complex of melamine\[60] and a zinc complex of melam (melamine dimer),\[74]\ both of which coordinate to the metal center through the triazine nitrogen rather than the pendant amine (Figure 4c). The lack of metal complexes reported is likely due to their poor Lewis basicity from delocalization of the lone electron pairs into the triazine or heptazine center as mentioned above. It is also noteworthy that, in some related compounds such as (alkali or alkali earth) metal salts of tricyanomelaminates (Figure 4d),\[93]\ cyamelurates\[24,64]\ and melonates,\[63]\ the triazine/heptazine nitrogens generally participate in the coordination even in the presence of the strongly coordinating cyamide or oxo group (Figure 4e), though we are aware of one exception where melonate coordinates to the transition metal copper solely through the cyamide (Figure 4e, middle).\[62]\ We may further surmise that, given the (few) metal complexes available and the extent of aromaticity, melamine (triazine) has slightly better coordination ability than melem (heptazine). Regardless, the fact that triazine/heptazine compounds have difficulties forming transition metal complexes is of paramount significance to their catalytic applications, especially for reactions requiring metal cocatalysts, since a strong interaction between the components in a catalytic system (i.e., through coordination interactions) is essential for fast kinetics. Another important aspect to consider is the directionality of the coordination, since the sp²-hybridised Lewis basic electron pairs on the triazine/heptazine nitrogens are coplanar with the triazine/heptazine unit, and thus would likely ligate to the metal cocatalyst in the parallel direction (i.e., in the same plane as the aromatic center). Based on this consideration, the dimensionality of both melon and PTI presents one limit toward their catalytic applicability in terms of the low number of available docking sites for the cocatalysts and accessibility of the layers to more bulky substrates such as the hole quenchers, since the majority of these ligating electron pairs are either inaccessibly buried in the bulk of the material or locked up in intermolecular bonding, for example, hydrogen bonding between neighboring polymeric strands in melon. Nevertheless, recent reports on grafting metal complexes onto melon suggest that it may be feasible for the heptazine nitrogens to coordinate with, for example, metal complexes of iridium\[66]\ and rhenium.\[67]\ Several strategies based on rational modification of the carbon nitride structure and/or morphology can also be pursued to overcome these
Figure 4. Crystal structures of salts and metal complexes: a) melaminium dihydrogenpyrophosphate, b) melemium hydrogensulfate, c) a copper(II) melamine complex (top) and a zinc melam complex (bottom); d) potassium tricyanomelaminate (potassium shown as white circles); and e) copper melonate (top), lanthanum melonate (middle) and zinc cyamelurate (bottom). a) Reproduced with permission. Copyright 2004, American Chemical Society. b) Reproduced with permission. Copyright 2010, John Wiley & Sons. c) Reproduced with permission. Copyright 2007 and 1999, John Wiley & Sons and Royal Society of Chemistry. d) Reproduced with permission. Copyright 2001, John Wiley & Sons. e) Reproduced with permission. Copyright 2011, 2012 and 2009, John Wiley & Sons.
limitations for catalytic applications, as will be presented further down.

Likewise, hydrogen bonding affects the material’s ability to disperse in water, directs supramolecular assembly as exemplified by the classic melamine-cyanuric acid rosette structure, and is of special significance to catalytic reactions in the aqueous phase (e.g., photocatalytic water splitting). Neither of the monomeric constituents of melon and PTI, melem and melamine, is particularly soluble in water despite the three primary amine groups and the triazine/heptazine nitrogen sites. Dimethyl sulfoxide is one of the few solvents that exhibits decent solubility (or at least solubilize without causing a chemical reaction, as in the case with acidic media). Nevertheless, their interaction with water is still observable based on the crystal structures of their hydrates. For the case of melem, recrystallization from water rearranges the dense helical patterns of planar melem molecules, held by hydrogen bonding between the amine and the heptazine nitrogens of neighboring molecules, into a pseudo porous structure with water trapped in the pores (Figure 5b). These trapped water molecules interact through hydrogen-bonding solely to the primary amines, since the heptazine nitrogens are occupied by hydrogen bonding between neighboring melem molecules. As such, the water molecules are weakly held by the surrounding melem units, as evidenced by the release of water at temperature well below 100 °C based on thermogravimetric analysis. From this, we can infer from the partial water solubility of melon (or at least interaction through hydrogen bonding) that melon must also have some interaction with water, however weak, at its polymeric terminations. As for melamine, no hydrate has been reported other than those of melaminium (salts of melamine), although a hydrate of melam has been reported and studied in detail (Figure 5a). Identical to the case of melem, recrystallization in water rearranged the packing of melam units into a pseudo porous structure, but with ellipsoidal pores rather than circular ones in melem hydrate. Here, water molecules are hydrogen bonded to both the amine and triazine nitrogens, and are held tightly within the melam pores until

*Figure 5. Crystal structures of the hydrates: a) hydrogen-bonded, rosette-like network of melam hydrate showing the ellipsoidal void (top) and the water molecules within the void (bottom); adapted from ref. [26]. b) Melam hydrate from ref. [25] showing the hexagonal network with 1D pore and the melem units hydrogen-bonded in a helical arrangement along the c-axis (bottom left); water molecules are incorporated within the pores (bottom right). a) Reproduced with permission.[26] Copyright 2013, John Wiley & Sons. b) Reproduced with permission.[25] Copyright 2012, John Wiley & Sons.*
the hydrate is heated well above 100 °C based on thermogravimetric analysis. Based on these crystal structures of hydrates for melem and melamine-based molecules, we can surmise that both melon and PTI have a certain degree of interaction with water despite the poor water solubility of their monomeric constituents, melem and melamine. As one case in point, intercalant-free and freshly dried PTI, prepared by long Soxhlet extraction (20 days) followed by vacuum drying at 150 °C, can spontaneously adsorb around 10 wt% water from ambient atmosphere, which is approximately equivalent to one water molecule for each void within the triazine lattice.[71] For PHI, its voids hold two types of water molecules, one that is relatively free and one strongly bound to the heptazine network, as evidenced by NMR and the two-step thermogravimetric profile.[29c] The strength of the water–network interaction is demonstrated by the high temperature required for their removal, above 75 °C for the loosely held water molecules and above 200 °C for the strongly bound ones, the latter well above the temperatures in the previous examples of melon and melam hydrates. These water molecules bound within the planes of PHI appear not to be simply incorporated into the network as part of the synthesis process, but may be involved in directing layer stacking in the 3D through direct or indirect (via solvation of potassium ions in the potassium form of PHI) interactions with the neighboring layers based on combined results from XRD and PDF analysis as well as simulation of stacking faults. Hence, one may assume PHI to be quite hydrophilic and may have, for example, a higher extent of affinity for polar substrates compared to melon in catalytic reactions, a point that will be addressed in a later section below. Nevertheless, the structural origin of this hydrophilicity is yet to be fully investigated, especially in terms of dimensional transition from the monomer melamine and melem to the 1D polymer melon and finally to the truly 2D PTI and PHI. The ability to control this parameter by structural modification will be essential for performance enhancement in various applications, especially for aqueous phase reactions.

5. Opto–Electronic Properties of Graphitic Carbon Nitrides

Considering that the most published application of g-C₃N₄ is in solar-to-chemical energy conversion, the study of how this class of materials interacts with light, the energetics of the excited states, and the transport mechanism of charge carriers are of particular importance. While these topics have been reviewed recently from a spectroscopic standpoint[72] and in terms of how these properties are affected by intermolecular interactions,[73] our discussion in this and the next section will be from a structural basis especially in terms of the dimensionality of the materials. Even though these properties have yet to be unambiguously delineated from the materials' structural features, we anticipate the possibility of manipulating the materials' opto-electronic properties and carrier dynamics through structural modification for improved performance in solar-to-chemical energy conversion.

Relevant to all photo(electro)chemical applications is the electronic or band structure of the material, which determines which reactions are thermodynamically possible. Here, one already encounters a point of contention: whether the different forms of g-C₃N₄ are direct[74] or indirect semiconductors.[75] To date, the majority of experiments determine the electronic structure of carbon nitrides using optical spectroscopy performed on polycrystalline powder, though efforts have been made to prepare highly crystalline thin films for spectroscopic investigations.[33,76] Characterization based on powder may lead to conflicting results if sample quality is not carefully controlled. As a case in point, the UV–vis spectrum of melon shows an absorption onset at around 450 nm (2.8 eV transition) and, depending on how the sample had been prepared, a tail near the absorption onset may be visible at higher wavelengths. One interpretation of this tailing is that the transition is indirect, leading to the conclusion that melon is an indirect semiconductor. Alternatively, this tailing may be the so-called “Urbach tail,” which arises from disordered states with energies in the interband region. Given that melon, and most carbon nitride materials for that matter, is poorly crystalline under standard synthetic protocols, especially in open synthesis, the latter interpretation cannot be ruled out, necessitating alternative approaches to determining band structure. Computationally, melon is a direct semiconductor with an (underestimated) band gap of around 2.6 eV[1,74c] while the hypothetical heptazine-based g-C₃N₄ has an indirect transition of 2.1 eV[72] Note that, here, we have used semiconductor terminology to facilitate discussion, although it is uncertain whether the energy states are sufficiently dense to be treated as a continuum (bands) or if they are better treated as molecular orbitals (i.e., highest occupied molecular orbitals [HOMO] and lowest unoccupied molecular orbitals [LUMO]). Given that many publications assume the fully condensed hypothetical 2D structure, tailing in the optical spectrum has been interpreted as an indirect transition even though there is no unambiguous evidence for this structure as elaborated above, thus demonstrating again the importance of unambiguous structure elucidation for analysis of experimental results. Complicating matters further, a recent spectroscopic study gave a band gap value of 3.4 eV for melon film grown on conductive substrate (gold or highly oriented pyrolytic graphite), as calculated from their valence band maximum (2.7 eV vs Fermi level) as determined by ultraviolet photoemission spectroscopy, and from the conductance band minimum (~0.7 eV vs Fermi level) as determined by inverse photoemission spectroscopy.[33] Resolving this inconsistency in the value of band gap as originating from various experimental factors (i.e., controlling sample quality, measurement methods, etc.) is thus a prerequisite for elucidating the band structure of the carbon nitrides.

While the mode of electronic transition is contentious, the band potentials are largely in consensus in the literature, at least in terms of providing sufficient driving force for photocatalytic hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), as well as carbon dioxide reduction and nitrogen fixation. Experimental determination of band energies, however, present some challenges, mostly owing to the very low electric conductivity of carbon nitride materials. In one estimation using the four-point probe technique on a pressed pellet of melon, a conductivity upper-bound value of 10⁻² S cm⁻¹ was obtained[78] for a compact sample, while other measurements have either obtained a much lower estimate (e.g., the same
authors in a separate work obtained <10^{-12} \text{ S cm}^{-1} using a two-electrode measurement\cite{80} or failed to obtain any observable conductivity in thin films (see below). The Mott–Schottky method is another approach and relies on determining the double layer capacitance by performing impedance spectroscopy. The complication with this method, however, is that the capacitance of both the carbon nitride material and the substrate it was deposited on must be accounted for when analyzing and fitting the impedance spectrum, which may present difficulties given the negligible electric conductivity of the former and the typically large conductivity of substrates used for electrochemical experiments. An alternative is the photocurrent method, which focuses on identifying the onset potentials for photocurrent as an indicator for band energies. Even for this technique, melon requires some texturization to form a homogeneous film of sufficient conductivity to yield a photocurrent in the absence of further additives. With this method, the valence and conduction band energies were, respectively, measured to be around 1.83 and −0.83 V versus NHE (pH 0).\cite{80} thus straddling the redox potentials required for water splitting and CO₂ reduction. Computational modeling of the band energies is largely consistent with these experimental results, and shows that the valence band of melon comprises nitrogen pₓ-zorbitals from the melem monomer, and the conduction band constitutes mainly of carbon p-orbitals but mixed with some nitrogen p-orbitals.\cite{81} By a similar method, the valence and conduction band energies of PHI was measured to be around 2.2 and −0.5 V versus NHE (pH 6.3).\cite{81} For comparison with the triazine-based material, one estimation for PTI is 1.96 and −0.70 V versus NHE (pH not stated) for the valence and conduction band, respectively, based on Mott–Schottky analysis.\cite{82} Hence, as a photo(electro)catalyst, melon (and related carbon nitride materials) satisfies the minimum thermodynamic criteria for water splitting and CO₂ reduction, minimum in the sense that no over-potential is required. Realistically, to overcome the reaction barrier and accelerate the reaction kinetics, cocatalysts are employed together with the carbon nitride, most often platinum for hydrogen evolution (overpotential required \( \eta \approx 0 \text{ mV} \)).\cite{83} and iridium or ruthenium oxide for oxygen evolution (\( \eta > 300 \text{ mV} \)).\cite{84} This additional component adds a layer of complexity to the catalytic system, since all components must function in conjunction with each other for the overall reaction to proceed. Nevertheless, an understanding of how the photocatalyst and cocatalyst cooperate, as well as uncoupling the reaction bottleneck(s), is necessary to devise suitable counter-strategies for improving their catalytic performance.

6. Carrier Dynamics of Graphitic Carbon Nitride—Dimensionality in Carrier Transport and Interfacial Charge-Transfer

The processes that occur in the subsecond timespan following irradiation—exciton transport or dissociation, recombination, charge trapping, and charge transfer to catalytic sites—are typically tracked by time-resolved emission or absorption spectroscopy, predominantly as liquid suspension. While this sampling method can replicate the photocatalytic environment, excessive scattering and difficulties in keeping the carbon nitride particulates suspended during the experiment reduce the quality of the results obtained. For this reason, recent spectroscopic works have employed carbon nitride samples that have been processed for colloidal stability, although whether this processing affects the intrinsic material properties is as-yet uncertain. Another consideration relates to sample preparation, as varying synthetic parameters can modify the local molecular structures of the carbon nitride in subtle ways that can heavily impact its carrier dynamics. As part of scientific rigor, given that the spectroscopic conclusions drawn are pertinent to the sample analyzed and require critical analyses before generalization to all carbon nitride systems, the following review of published results will attempt to relate the findings to the types of samples used and, where possible, their molecular structure.

Early results from photoluminescence spectroscopy by Merschmied and coworkers\cite{86a,86a} based on spectral peak shape and decay dynamics in the nanosecond regime suggested that the photo-generated exciton remains tightly bound and confined (presumably) to the individual heptazine units—a quasi-monomer model—contrary to previous assumptions that g-C₃N₄ shows semiconductor-like behavior. This conclusion has some consistencies with previous computational studies, which calculated the dielectric constant and charge carrier mobility to be so low in PTI and melon that exciton dissociation is inhibited,\cite{86a} and that transport along the 1D polymer chain is hindered by the high energetic barrier of ~1 eV of the bridging amines, a value modeled based on a cyclic heptazine trimer.\cite{86a} However, in the neutron scattering experiments mentioned above, shorter-than-expected bond length of the bridging nitrogen suggests significant sp² character that may (or not) give rise to conjugation along the polymer chain, which in turn suggests a lower-than-expected energy barrier for charge carriers to percolate in the direction along the polymer strands. Nevertheless, combined with later results from transient absorption spectroscopy (TAS) in the picosecond timescale showing signal invariance up to 1600 ps, the authors proposed that excitons could be dissociated either by entropy or by excitation above the energy gap (i.e., hot carriers), and are transported as polaron pairs analogous to conjugated polymers. To construct their transport model shown in Figure 6a, they combined the transient absorption results in the picosecond timescale with the emission spectra in the nanosecond timescale, effectively assuming that the two methods describe an identical process (which may not be a valid assumption as discussed below). Fitting the absorption and emissive decay to a mathematical model for carrier density based on Brownian recombination of the polaron, the authors found that polaron movement in 1D gave the best fit, a finding that they verified by comparing the experimental and calculated absorption coefficient of the material, the latter calculated based on polaron-pair density. Since the 2D transport model produced a poorer fit to the decay kinetics and to the experimental absorption coefficient, they concluded that transport takes place mainly out-of-plane, that is, along the stacking direction, invoking also the previous computational studies regarding the large energy barrier for intraplanar transport. In fact, this transport model does have some experimental consistencies. Since hopping is highly distance dependent, the authors found a high correlation between
hopping rate and interlayer distance in a series of melon samples produced by varying the synthesis temperature. In a separate study by Corp and Schlenker,[87] exfoliated melon yielded lower signal intensity than its bulk counterpart in the transient absorption spectra, from which the authors inferred that fewer exciton dissociations took place in the mono-/few-layer material necessary to give rise to long-lived charges, as consistent with the out-of-plane transport model. Similar observations have recently been made for PHI, where particle sizes below a certain threshold lead to decreasing photocatalytic activity, in line with inefficient out-of-plane charge carrier separation in PHI stacks with only few layers.[88] Corp and Schlenker also found that the dissociated electrons can transfer effectively from the bulk to the exfoliated melon, an effect that also translated to a
near doubling of photocatalytic hydrogen evolution rate in the mixed bulk and exfoliated system, though the authors could not conclude whether the transfer is in the perpendicular or in the intraplanar direction. Should this out-of-plane transport model prove to be correct, one performance-limiting process may be related to charge transport as governed by the hopping rate, which is inversely correlated to the hopping distance. For the quasi-2D melon, hopping distance here would thus be given by the interlayer separation and the layer stacking vector as indicated by the 00l reflection, from which one may argue that a structural parameter in the 3D is one determinant in terms of charge transport efficiency, thus again highlighting the importance of dimensionality—both in terms of structure and properties—in photo-electro-chemical energy conversion.

Notwithstanding the experimental supports of the out-of-plane transport model, it needs to be pointed out that the complexity of the experimental data leaves room for alternative interpretations. The systematic variation in interlayer spacing of melon was achieved by changing the synthesis temperature from 490 to 610 °C to correlate hopping rate and interlayer distance. However, at the higher temperature where the interlayer spacing of melon decreases, there is a concomitant increase in melon polymerization and/or crystallinity, and even distortion of the quasi-2D melon layers such that the otherwise forbidden n→π* transition in the visible region manifests, all of which can alter carrier dynamics due to structural changes. Regarding the inhibition of exciton dissociation in mono-/few-layer melon, the bulk melon was prepared by urea thermolysis and contained already 7% oxygen by XPS analyses, a figure which then increased to 17% upon exfoliation. As expounded below, introduction of such oxygen-bearing species can also affect the carrier dynamics of the native material, especially in exciton dissociation and charge transfer. These considerations illustrate the challenges in untangling the various structural features of melon from their effects on the transport mechanism, owing to the difficulties (or even unfeasibility) of systematically varying its structure without introducing other secondary changes. Another assumption regarding the data treatment is whether the TAS and photoluminescence spectroscopy describe the same process, given that the former tracks all (emissive and non-emissive) states within experimental/instrumental limits whereas the latter cannot detect non-emissive states. This issue was raised in several publications, which found that the photoluminescence of melon is unaffected by the presence of electron/hole acceptors, regardless of whether they are chemical oxidant/reductant or metal particulates (e.g., platinum cocatalyst). Since these observations were for melon prepared following various routes as well as for melon derivatives, the generalized conclusion from these studies is that the emissive state(s) as probed by photoluminescence spectroscopy do not capture the charge transfer processes of the photo-generated charges relevant for catalysis, requiring TAS to “complete the picture.” When Durrant and coworkers measured the transient absorption and emissive spectra across ten orders of timescale of melon prepared by heating urea to 600 °C, they found the emissive and absorptive behavior begin to deviate from 10^{-5} s onward (Figure 6b, left). The photoluminescence signal decays rapidly with a large power law exponential, a result also observed by Corp and Schlenker and is akin to quasi-molecular systems as consistent with the aforementioned conclusions of Merschjann and coworkers. On the other hand, the absorption signal is (relatively) long-lived and decays with a much smaller power law exponential, reminiscent of charge separation and trapping in inorganic semiconductors, leading the authors to conclude that melon has photophysical characteristics more similar to inorganic semiconductors than conjugated polymers; their model for carrier dynamics is depicted in the center of Figure 6b. However, charge separation (and subsequent trapping) would require either large energy input to overcome both the band gap and the exciton binding energy, or that separated charges must be energetically stabilized. The proponents for the out-of-plane transport model described above suggest exciton dissociation to be driven either by excess photon energy or by entropic effects. The likelihood of the former depends on the magnitude of the exciton binding energy, which may be dependent on the nature of the material itself. One measurement based on Arrhenius-type analysis of variable temperature photoluminescence gave an estimate of 74 meV which, being within the range of inorganic semiconductors (e.g., 47 meV for CdTe, 150 meV for GaN), is small enough for electron–hole separation by visible light irradiation. Note that this measurement was undertaken for melon synthesized under open condition at 550 °C for a somewhat short duration of 2 h, which may lead to kinetically trapped defects (see sections above regarding closed and open synthesis) that may affect exciton binding energy, a point elaborated below. Nevertheless, this estimate has some credence in light of recent measurement of the exciton binding energy of highly crystalline PTI/LiCl using an identical method, which gave a value of around 50 meV. On the other hand, Sautet and coworkers calculated the exciton binding energy to be above 800 meV, which would then require an irradiation energy input of >3.4 eV (band gap ≈ 2.6 eV + 800 meV binding energy) to dissociate the exciton. They also calculated the dielectric constant of melon to be 6.1, much lower than those of inorganic semiconductors (c.f. ≈80 for rutile TiO2 and ≫300 for cubic perovskite SrTiO3) and found the excited states to be localized, thus disfavoring exciton separation. Exciton dissociation by excess photon energy would thus be unlikely if the binding energy from Sautet calculations were used, though charge separation with energy input below 3 eV is clearly possible, since the transient spectroscopy studies above utilizes excitation in the visible region (≈400 nm), not to mention the numerous demonstration of visible-light photocatalysis of melon.

The other cause for exciton separation is proposed to be entropic effects, which may be associated with material disorder. Considering that charge separation in melon is weakly affected by highly polar solvents, Durrant and coworkers concluded that exciton separation is likelier to be driven by something inherent to the material. To identify such driver for charge separation, they performed calculations on a heptazine hexamer without and with a pendant urea, a structure based on our findings that show melon prepared from urea contains residual urea groups as a structural defect. As shown in the right part of Figure 6b, incorporation of this urea group in melon leads to separation of the HOMO and LUMO, respectively, away and toward the urea moiety, stabilizing the separated electron and hole by ≈150 meV each. In further support of
this finding and the idea of entropically driven exciton separation, recent calculations\(^{92}\) have suggested that, in highly disordered material as is often the case for the carbon nitrides, structural defects can significantly contribute to the entropic term in the Gibbs free energy of separated electron–hole pairs, decreasing the separation barrier to the order of \(k_B T\), that is, charge separation is possible with thermal energy. The significance of the modeling with the pendant urea group is that a structural feature has been causally suggested to alter the photophysics of melon in terms of the mechanism for exciton dissociation and stabilization of separated charges, pointing to defect engineering as a potent strategy that we will elaborate upon for controlling the carrier dynamics in \(\text{g-C}_3\text{N}_4\).

As mentioned above, since the emissive states, which have been assigned to the \(\pi^*\) and \(\pi\) transitions in the heptazine units by McMillan and coworkers,\(^{93}\) are unaffected by electron donors/acceptors, the energy states involved in charge transfer (and ideally their corresponding molecular structures) for photocatalytic reactions or extraction of photo-generated electrons require probing by TAS, studies of which have been done by Maeda and coworkers\(^{38b,c}\) and Durrant and coworkers.\(^{74a,94}\) In the former group, transient infrared spectroscopy was performed on molecular ruthenium electrocatalysts for \(\text{CO}_2\) reduction together with Ag-modified mesoporous melon, which was prepared by silica templating. Here, we should note that this melon sample may have intrinsically different surface reactivity caused by the silica porogen,\(^{95}\) since heating silica at high temperature (i.e., at the synthesis temperature of melon) can produce strained siloxanes and defects at the surface,\(^{96}\) which are high energy species that have been shown to induce radical formation in molecules such as anthracene.\(^{97}\) In the latter group, transient UV–vis and near-infrared spectroscopy were performed on urea-derived melon together with sacrificial reductant and metal cocatalysts (Pt and Ag); of note here is that, melon obtained from urea contains significant amounts of oxygen as mentioned above. For these experiments, photo-induced absorption signals above 700 nm were assigned to photo-generated electrons, based on how signal lifetime changed in the presence of electron donors and acceptors in the reaction system. The authors further separated these signals into photo-generated electrons that are either in shallow traps (3000–1000 cm\(^{-1}\), 3333–10 000 nm) or deep traps (20 000–1000 cm\(^{-1}\), 500–3333 nm) based on comparison with similar studies carried out for \(\text{TiO}_2\), \(\text{SrTiO}_3\), and nitrogen-doped \(\text{Ta}_2\text{O}_5\), so as to differentiate their propensity for interfacial transfer. With these signals assigned, in two separate studies, photo-generated electrons on mesoporous melon transfer to Ag cocatalyst within a few microseconds when analyzed in the 10\(^{-6}\)–10\(^{-3}\) s timescale, while transfer to the molecular ruthenium catalyst occurs within a few picoseconds based on experiments on this timescale. The former result was partially corroborated by Durrant and coworkers, who found that signal decay did not change in the fs–ns timescale upon Pt deposition, nor was there decay change in the µs–s regime other than a decrease in initial signal amplitude. From these results the authors concluded that electron transfer in urea-derived melon to the Pt cocatalyst takes place in the ns–µs timescale (middle of plot in left-most panel of Figure 6b). Whether the timescale difference is attributable to the nature of the cocatalyst or to experimental limitations was not clarified, though one commonality in these studies is that shallowly trapped electrons can be transferred at much faster kinetics than deeply trapped ones. One rationale is the loss of thermodynamic driving force for deeply trapped electrons to transfer to the cocatalyst due to loss of potential energy. However, based on the conduction band potential of melon (−1.3 V vs NHE at pH 10) and the redox potential of the electron acceptor Ag\(^+\) (+0.8 V vs NHE) used in these experiments, sufficient driving force should remain even with up to 2 eV loss in photoelectron energy. These considerations led the authors to suggest the weak interaction between the melon and Ag\(^+\) to be one limiter to charge transfer kinetics (as mentioned above), and another limiter could be the spatial confinement and localization of the deeply trapped electrons to inhibit their charge transfer. The physical meanings of these shallow and deep traps, or in other words their molecular identity, are however not discussed, and their elucidation is a necessary next step for rational design of carbon nitrides. Last, we note here in regards to the other half reaction, the kinetics of hole transfer to the electron donor, hole quenching by benzyl alcohol in PHI takes place in the submicrosecond timescale, and is much faster than the electron transfer, which is in the second timescale and thus seemingly much slower than that of melon.\(^{94}\) In fact, this slow electron transfer kinetics in PHI coupled with fast photo-oxidation can lead to electron accumulation so much that the recombination kinetics can be accelerated.\(^{98}\) Similar situations were later reported for melon, where electron accumulation was cited as one bottleneck for photocatalytic hydrogen reduct.\(^{99}\) In terms of the photo-holes as probed by femtosecond TAS, the methoxy species on melon’s surface produced from the photo-oxidation of methanol as electron donor can re-introduce the (photo-)holes back into melon, that is, re-oxidize melon in a reverse hole transfer process on a timescale of a few hundred picosecond, where these holes can eventually recombine with the trapped electrons.\(^{99}\) While the aforementioned observations suggest the electron transfer to the catalytic center (i.e., cocatalyst) to be an even more drastic photocatalytic bottleneck in PHI than in melon—an effect that may be attributed to the electron-deficient and more conjugated 2D structure of PHI and/or peripheral functionalities but yet to be clearly delineated—this slow kinetics also presents an alternative paradigm of storing photochemical energy as photo-generated, (quasi) stabilized electrons within PHI, which we will elaborate upon in the next section.

7. From Dimensionality to Applicability in Photo(electro)chemical Energy Conversion and Storage

It is evident from the above discussions why the \(\text{g-C}_3\text{N}_4\) class of materials has attracted widespread research interests, especially in the photocatalytic production of fuel chemicals. Unlike the earlier wonder materials (i.e., titanium dioxide, cadmium sulfide, tungsten trioxide, and iron oxide), the carbon nitrides are unique in that they have appropriate band energies that straddle the potentials for many redox reactions (e.g., the hydrogen and oxygen evolution reactions) yet having a band gap sufficiently narrow for visible light activity, all the while having
One typical route to directly resolve one of the primary performance limiters—poor exciton separation and carrier transport and interfacial transfer into the catalytic/reaction sites—is to miniaturize the photocatalyst into micro-/nano-particles such that the charge carriers can reach the surface within their diffusion length for interfacial transfer to the catalytic active centers that are typically metal-based cocatalyst(s). Indeed, as (quasi) 2D materials, melon and PTI can be exfoliated following solvent-assisted, chemical or ultrasonic routes (Figure 7a). Yielding dispersions comprising stacks of few or single triazine/heptazine layers (i.e., several nanometers in thickness), some of which showing an up to ninefold increase in photocatalytic activity for sacrificial hydrogen evolution. Note that these results are not necessarily inconsistent with the aforementioned out-of-plane transport mechanism (c.f. Figure 6a) or other publications showing reduced activity in exfoliated nano-sheets/stacks since photocatalysis involves a series of processes that are sensitive to a complex interplay of several factors which are themselves not independent from each other, such as particle size and band gap, surface terminations, and trap states. Despite this apparent ambiguity regarding the influence of particle size and morphology on the photocatalytic activity of carbon nitrides, we emphasize the importance of method development for their exfoliation in providing new processing routes that may, for example, lead to thin films for advanced characterization and device assembly. Substantial progress along these lines has recently been made by Howard, McMillan, and coworkers who have demonstrated spontaneous dissolution of PTI in polar aprotic solvents such as NMP, DMSO, or DMF without chemical or physical intervention, while large scale production of PTI nanosheets was achieved by Agrawal and coworkers by a hot exfoliation route using anhydrous dimethylacetamide as solvent. Contrasting this top–down miniaturization by exfoliating into (quasi) 2D stacks, one example of a bottom–up approach is to synthesize the carbon nitride from a supramolecular assembly of pre-organized precursors such as the aforementioned melamine–cyanuric acid assembly pioneered by Whiteside and coworkers. By varying the parameters used to prepare this supramolecular assembly (e.g., solvent, dopants that have molecular structure complementary to melamine such as barbituric acid, benzoguanamine, and even caffeine) followed by subsequent annealing, melon can be obtained with a spectrum of morphologies ranging from fibers and tubes to platelets and sheets (Figure 7b), which are considered to be conducive to improved photocatalytic activity for solar fuel production and dye/organic degradation. One particular advantage of this synthesis approach is that textured melon can be uniformly deposited onto substrates with tight adhesion, which thus enables the preparation of photo-electrode with excellent performance metrics for photoelectrochemical water-splitting, attributable to efficient exciton separation and carrier extraction.

Other than miniaturizing the particle size along specific dimensions from a material basis, an analogous approach may be taken on a molecular basis, given that melon is a 1D polymer. Here, reducing the polymer length by lowering the synthesis temperature is anticipated to accelerate interfacial charge transfer by increasing the relative amount of polymer terminations that are considered to be the site of reactivity and/or charge transfer, based on the notion that high energy sites such as terminations and defects are the active sites analogous to the general situation for heterogeneous catalysis. Indeed, heptazine oligomers as structurally verified by spectroscopic methods including matrix-assisted laser desorption/ionization time-of-flight are five times more active than the polymer on a per-gram basis and more than twice as active on a per-(BE)surface area basis for visible light (>420 nm) photocatalytic hydrogen evolution using methanol as sacrificial reductant and platinum as cocatalyst (Figure 7c). This larger photocatalytic activity is observed although the oligomers have a blue-shifted UV–vis absorption onset and thus absorb a smaller range of photons than the polymers, indicating the better incident photon utilization of the oligomers by facilitating interfacial charge transfer—the slowest (up to millisecond timescale depending on photocatalyst system; see above) and therefore rate-limiting process in photocatalytic reactions—across the larger amount of catalytically relevant surface. Similar enhancement in photocatalytic activity, attributed to an increase in the amount of active site/defect, was observed when melon polymerization was physically restricted using porous silica. Another contribution to the improved activity of the oligomers is improved charge separation/transfer between the separate oligomers themselves as suggested by Corp and Schlenker mentioned above, whose ultrafast spectroscopy work found that exfoliated melon quenches the photinduced electrons in bulk melon at timescales similar to those of diffusion-controlled kinetics. Hence, molecular and/or oligomeric heptazine species may act in a similar manner to shuttle charge by effectively providing/extracting and transferring photo-generated charges from the
light-harvesting species to the reaction center or cocatalyst (in their example, bulk and exfoliated melon used in conjunction with platinum cocatalyst). While the conformation (perpendicular, edge-to-edge etc.) for charge transfer is unknown, determining the characteristics of the molecular/oligomeric species for efficacious photoelectron acceptance/transfer, such as their band positions relative to the polymeric species, may lead to improved photocatalytic performance through better charge separation and charge steering to the active sites.

Instead of the indiscriminate increase in the surface area of the carbon nitride through particle miniaturization or oligomerization, a more productive approach is to selectively increase the structural features that are the catalytic active sites, though achieving this is predicated on identifying molecular moiety associated with interfacial charge transfer with the reaction substrate(s). For this, the methodology employed in the field of heterogeneous catalysis is to use model catalysts that are both structurally defined and can replicate the function of the investigated catalyst so as to circumvent material heterogeneity and identify and characterize the atomic/molecular structure of surface species relevant to catalysis that cannot be otherwise detected by bulk-averaged characterization techniques. Hence, this methodology is especially suited for the carbon nitride photocatalysts, which have complex terminating species originating from incomplete condensation/cyclization of the triazine precursor to the heptazine-based product, though with unknown contribution to photocatalytic activity. In this investigation, photoreduction activity for hydrogen evolution was observed for the platinum complex of the melonate anion (see Scheme 2), suggesting that cyanamide may be a candidate moiety that bridges the light-harvesting component to the hydrogen evolution center for interfacial charge transfer. This suggestion is supported in a later study using incompletely condensed heptazine species which, owing to their solubility in ethanol, can be identified to have cyanamide-like moieties based on characterization with quadruple time-of-flight mass spectrometry and high-performance liquid chromatography coupled with mass spectrometry. Based on combined computational and experimental mechanistic studies for the photo-oxidation of tetracycline, the authors of this study further attributed the role of this moiety, when bonded to a heptazine unit as the main light absorber, to be predominantly involved in activating dioxygen for the photocatalytic reaction. The aforementioned fundamental insight can then be translated into improved photocatalysis by decorating the material’s termination with the cyanamide moiety by, for example, following the analogous synthesis procedure for melonate using potassium thio-cyanate as a reactive salt melt but isolating the water-insoluble product (also Scheme 2). It should be emphasized here that, rather than polymeric melon, the truly 2D PHI is obtained following this and other synthetic routes involving Na/K-based salt melts, all of which appear to have a sizable amount of cyanamide moiety based on FTIR and 13C NMR characterization independent of the exact synthesis route, as observed by other groups preparing PHI using different precursors and salt melts. Hence, there is an element of ambiguity as to whether the enhancement in photocatalytic activity observed for either sacrificial hydrogen evolution or organic transformation can be solely attributed to the function of the cyanamide moiety or whether the 2D structure of PHI also alters carrier dynamics (exciton separation and charge transfer) beneficial for photocatalysis. Another complication in delineating the structure–activity relationship is the role of the cation incorporated from the salt melt used in the synthesis, since this cation is exchangeable for proton, alkali, and alkaline earth as well as transition metals, and appears to affect photocatalytic activity in terms of sacrificial hydrogen evolution. In fact, exchanging this potassium for proton leads to a nearly sixfold increase in hydrogen evolution rate in sacrificial photocatalysis (Figure 7d). However, to add further complexity into an already complicated system, it is also possible that the terminal cyanamide undergoes acid hydrolysis to a pendant urea that may also be involved in the photocatalytic mechanism. Nevertheless, consistent with the catalytic role of this moiety, the amount of cyanamide in PHI can be varied by adjusting the synthetic parameters and was found to correlate with photocatalytic activity. Conversely, this strategy may also be adapted for enhancing photocatalytic oxidation by terminating PHI with a moiety that interacts strongly with the electron donor to improve the kinetics of hole transfer. In one example, terminating the 2D PHI with melamine leads to a less hydrophilic material compared to its NCN-terminated counterpart, as evidenced by contact angle measurement. As a result of reduced hydrophilicity, the photocatalytic activity of the melamine-terminated PHI for sacrificial hydrogen evolution is modest in aqueous methanol solution but is extremely high when the reductive surfactant triethanolamine is used as the sacrificial electron donor. Alternative to the aforementioned methodology of molecular model catalysts, Wang and coworkers identified the photo-redox sites of PTI by visualizing with electron microscopy where the hydrogen evolution cocatalyst (Pt from H2PtCl6) and water oxidation cocatalyst (CoOx from CoCl3) are photo-deposited on a highly crystalline sample. As depicted in Figure 7e, they showed that both cocatalysts were deposited, not on the (0001) basal facet as enclosed by the face of the triazine units, but on the prismatic (10-10) facet terminated by the triazines planes edge-on. Harnessing this insight, they could rationally increase the photocatalytic activity for full water-splitting by synthesizing PTI crystals with more of the latter facet expressed. These examples thus underscore

Figure 7. a) Solvent-based exfoliation of PTI—from left to right: transmission electron microscope (TEM) image at low and high magnification (scale bar 10 nm), high speed atomic force microscopy (HS-AFM) image and the corresponding height profile of dashed white line in the inset, and histogram of crystallite diameter of bulk and exfoliated PTI based on the indicated microscopy. b) Synthesis of texturized melon via supramolecular assembly of melamine and cyanuric acid (top) and with caffeine (middle), or from thiourea onto a conducting glass substrate. c) Melon oligomers and their photocatalytic activity for sacrificial H2 evolution. d) Comparison of photocatalytic sacrificial hydrogen evolution rate of PHI with incorporated K+ ions and after their exchange for protons. e) Identification of the (10-10) facet as reductive sites on a prismatic PTI crystal based on the location of photo-deposited platinum. a) Reproduced with permission. Copyright 2017, American Chemical Society. b) Reproduced with permission. Copyright 2013, 2020 and 2015, American Chemical Society, Nature Springer and John Wiley & Sons. c) Reproduced with permission. Copyright 2015, American Chemical Society. d) Reproduced with permission. Copyright 2019, American Chemical Society. e) Reproduced with permission. Copyright 2020, Nature Springer.
the importance of specific terminations at the material interface as opposed to indiscriminate increase in surface area for catalytic applications, and provide an approach to rational design by selectively functionalizing the catalyst surface with molecular moieties involved in the catalytic mechanism.

While these aforementioned developments in PHI—from its synthesis using salt melts and structural elucidation to its high photocatalytic activity—highlight some of its commonality with other members of the carbon nitride family, recent findings also show how this truly 2D heptazine-based material has unique photophysical as well as electrochemical properties. One unexpected discovery was its ability to “store” light-induced electrons whereby, following light-induced exciton generation and quenching of the holes by a reductant, the electrons are trapped on PHI and remain stable for over 10 h in aqueous solution while retaining sufficient reductive potential (≈−445 mV vs NHE at pH 7) for reduction catalysis. Here, the stored electrons are visible by a color change from the native yellow of PHI to a blue–green tinge trackable over various timescale, from seconds to hours, by UV–vis evidenced by the absorption bands in the range of 500–750 nm and by EPR at $g = 2.00246$.[81,94,98]

Hence, even well after irradiation has ceased, these stored electrons in PHI are capable of driving redox reactions, such as the hydrogen evolution reaction for use as solar fuel triggered by injecting suitable electrocatalysts such as platinum colloid (Figure 8a).[81] Alternatively, the electrons can be extracted as an electric current akin to a solar battery. Here, illumination charges the battery by storing electrons on the PHI photoanode, screened by the hydrated alkali metal ions in the pores, which can then be extracted by discharging under galvanic mode (Figure 8b).[115] Such a process is reminiscent of the light and dark reactions of natural photosynthesis, thereby offering a new paradigm in photo-energy conversion and storage alternative to the direct generation of solar fuels as described above. Recently, this effect has also been implemented in light-driven microswimmers, one (of three) embodiment of which involves Janus particles with platinum on one face and PHI on the opposite, fuelled by light-induced surface-catalytic decomposition of electron donors such as MeOH, 4-methylbenzylalcohol, or H$_2$O$_2$ (Figure 8c).[116] Under illumination, H$_2$O$_2$ as fuel is oxidized on the Pt hemisphere and the electrons generated are transferred to the Pt–PHI interface where the photo-holes of

![Figure 8. a) Storage of light-generated electrons for driving hydrogen evolution after illumination has ceased. b) Solar battery based on storage of photo-generated electrons on PHI; right shows the discharge curve at 100 mA g$^{-1}$ as a function of (prior) illumination time. c) Janus particles of PHI with a metal cap shown as schematic illustration and scanning electron microscope image (left); displacement of a Janus particle with propulsion and charging under illumination and continued propulsion in the dark (middle) based on the surface reactions shown on the right. a) Reproduced with permission.[81] Copyright 2017, John Wiley & Sons. b) Reproduced with permission.[115] Copyright 2018, John Wiley & Sons. c) Reproduced with permission.[116] Copyright 2020, National Academy of Sciences.](https://example.com/figure8)
the PHI are quenched, resulting in charge accumulation on the PHI hemisphere. When the light is turned off, the microswimmers continue to show balllastic diffusiophoretic motion for tens of minutes, a process called “solar battery swimming” that may be utilized for applications in, say, drug delivery.[107]

Considering that this electron storage phenomenon has been reproduced by different research groups[108] using different precursors and salt melts for PHI preparation, one can conclude that this effect is inherent to the PHI structure and may be related to the highly electron-deficient and at least partly conjugated 2D arrangement of heptazine units. Another key feature hypothesized to stabilize these light-generated electrons is attributed to the mobile hydrated K$^+$ ions residing in the pores of the PHI 2D network, which are incorporated from the salt melt used in the synthesis. These ions are believed to screen and thus stabilize the electrons accumulated in the material, suggesting a possible optoionic coupling between the light-induced electronic charge carriers and mobile ions in the 1D channels of PHI and the surrounding electrolyte.[115b]

In fact, the hydrated cationic species appears to play a central role in this electron stabilization phenomenon: protonated PHI obtained following K$^+$ ionic exchange for protons manifests this effect only within an (K$^+$-containing) electrolyte,[204] while the aforementioned melamine-terminated PHI synthesized by condensing the residual cyanamide groups with dicyandiamide into melamine moieties exhibits this effect presumably through the ammonium cations that charge-balance the residual anionic framework.[114] This optoionic coupling concept is not without precedent: Antonietti and coworkers demonstrated that the interaction of electrolyte ions with photo-generated charges (and asymmetric redistribution thereof) in melon can be exploited for a light-driven ion pump.[119] On the other hand, the role of these pendant groups (e.g., the cyanamide[120]) in electron/radical stabilization, if any, is also one question yet to be clarified.[81] Hence, to effectively harness this electron storage effect for applications at the interface between solar energy conversion and storage, and for propulsion of nano/micro machines as well as other applications related to, for example, photo-memristive sensing,[115b] the origin of this phenomenon from the structural basis of PHI needs to be unambiguously delineated. Nevertheless, this is very much a nascent field of research and we anticipate that advances along this research direction may uncover other phenomena that can open up new applications, reiterating our earlier message that elucidation of structure–property–activity relationships in the carbon nitrides is indeed still a work in progress.

8. Concluding Remarks

For much of its history since Liebig’s synthesis of melon in the 19th century, the g-C$_{3}$N$_{4}$ class of materials has been structurally enigmatic. However, with the establishment of characterization methodologies based on spectroscopic and diffraction techniques and recent developments in characterization techniques and instrumentations (e.g., PDF and electron microscopy) over the last two decades, we are beginning to elucidate their crystallographic features in terms of their molecular building blocks and their arrangement in 1D (melon) and 2D (PTI and PHI), as well as the stacking of their (quasi) sheet-like structure in 3D. As we uncover the structural origin to their physicochemical properties and carrier dynamics, we are also beginning to delineate the structure–property–reactivity relationship of this class of materials, so much so that we are at the cusp of rational material design, particularly for applications in solar-to-chemical energy conversion and storage as one of the world’s grand challenges. As summarized here, various strategies have been demonstrated to control their structure at the molecular level and at higher dimensions so as to improve the transport of photo-generated carriers and accelerate charge transfer kinetics for enhanced photo(electro)catalysis. Nevertheless, we have also raised here a number of unresolved aspects, especially in the case of PHI and its surprising ability to stabilize photo-generated electrons as highly reducing π-radicals for hours, effectively enabling the temporal separation of the two halves of the photo-redox reaction. We highlight some promising approaches to harness this effect for various applications, such as the delayed extraction of solar energy (as either solar fuel or electric current) drawing parallel to the light and dark reactions of natural photosynthesis, and for the design of light-driven microswimmers, which use this delayed discharge as a new propulsion mechanism which we have called “solar battery swimming.” With these proof-of-concepts for an alternative paradigm in solar energy storage and solar-powered micromachineries, it is indeed exciting that new phenomena are still being discovered even after almost two centuries since Liebig’s first report on the carbon nitrides. We anticipate further discoveries as we dig deeper into the proverbial rabbit hole, and believe there is still much to learn at the fundamental level from this fascinating yet enigmatic class of materials regarding its material chemistry, electrochemistry and photophysics, radical chemistry, and catalysis.

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Conflict of Interest

The authors declare no conflict of interest.

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