



Optoelectronics Meets Optoionics: Light Storing Carbon Nitrides and Beyond

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Known for decades, Liebig's carbon nitrides have evolved into a burgeoning class of macromolecular semiconductors over the past 10+ years, front and center of many efforts revolving around the discovery of resource-efficient and high-performance photocatalysts for solar fuel generation. The recent discovery of a new class of "ionic" 2D carbon nitrides—poly(heptazine imide) (PHI)—has given new momentum to this field, driven both by unconventional properties and the prospect of new applications at the intersection between solar energy conversion and electrochemical energy storage. In this essay, key concepts of the emerging field of optoionics are delineated and the "light storing" ability of PHI-type carbon nitrides is rationalized by an intricate interplay between their optoelectronic and optoionic properties. Based on these insights, key characteristics and general principles for the de novo design of optoionic materials across the periodic table are derived, opening up new research avenues such as "dark photocatalysis", direct solar batteries, light-driven autonomous systems, and photomemristive devices.

1. Introduction

Over the last decade, carbon nitrides have lived through a renaissance triggered by a unique combination of semiconducting properties, earth-abundance, and chemical robustness, putting them at the forefront of sustainable energy research. While known for centuries,^[1] carbon nitrides have long been lab curiosities until the prediction that the C–N system may host novel ultrahard phases, represented by the cubic and, more recently, an orthorhombic polymorph of C₃N₄.^[2] Although this prospect sparked a flurry of interest at the end of the 1990s, complications associated with metastability and complexity of the carbon nitride phase space, but also with precursor selection

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DOI: 10.1002/aenm.202003049

and accessible pressure range have so far precluded the unambiguous realization of ultrahard carbon nitride phases. The next, and lasting, surge of interest in carbon nitrides dates back to the discovery of light-driven water splitting by the prototype carbon nitride (Melon) in 2008.^[3] The rapid growth of carbon nitride research seen over the past 10 years has arguably been a main driver of sustainable materials research for photocatalysis ever since.

Often collectively and simplistically viewed as 2D materials, the family of carbon nitrides is substantially more diverse, with the prototype material Melon being actually a 1D heptazine-based polymer.^[4] Over the past years, a new generation of "true" 2D carbon nitrides featuring a covalently bonded 2D backbone has emerged, represented by poly(triazine imide) (PTI), and poly(heptazine imide) (PHI).^[5] Intriguingly, the advent of 2D

carbon nitrides marks a cornerstone not only regarding the enlarged phase space, but also regarding the property space that is available to carbon nitride research. While "classic" Melon-type carbon nitrides, the products of conventional high-temperature solid-state synthesis, often suffer from ill-defined structures and high levels of disorder that preclude detailed structural insights, the new generation of 2D carbon nitrides is obtained by ionothermal routes from salt melts and characterized by a high level of crystallinity, hence structural definition.^[5d,6] While the first PHI-type carbon nitride has been discovered in 2009,^[7] it was not until recently that the richness in unconventional properties of PHI and its congeners (i.e., structurally similar compounds) had been realized.^[8] PHI-type carbon nitrides open up an "ionic" dimension, unknown in Melon-type carbon nitrides: Alkali metal ions—remnants of the ionothermal synthesis in salt melts—reside in the channel-type structural pores of PHI, compensating the net negative charge of the anionic carbon nitride backbone due to deprotonation. This additional layer of compositional complexity—and tunability—imbues such carbon nitride semiconductors with a plethora of unexpected properties, which are determined by the subtle interplay of optoelectronic and optoionic degrees of freedom, as we will show below.

In this essay, we will revisit recent developments in the design of optoionic carbon nitrides—a term we use to distinguish ionic 2D carbon nitrides from their non-ionic 1D counterparts—and contextualize their properties in terms of the recently emerging field of optoionics.^[9]

We will first describe the essentials that define optoionic solid-state systems and adapt the existing terminology to photoelectrochemical systems. We will then discuss synergies arising from the interplay between optoelectronics and optoionics in “light storing” carbon nitrides and demonstrate how they can be utilized for the design of hybrid light-harvesting and storing devices, bridging solar energy conversion and ion transport with energy storage. Finally, we generalize our observations on carbon nitrides and delineate design principles for the de novo design of new optoionic materials across the periodic table.

1.1. Optoelectronics Meets Optoionics

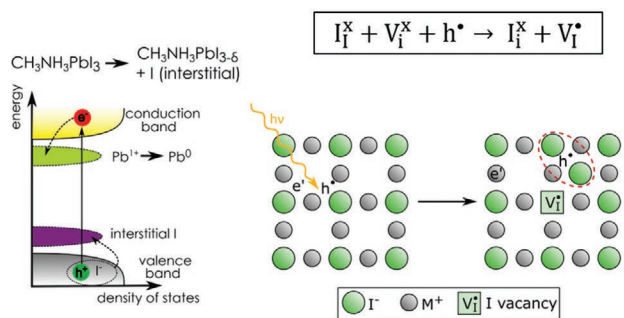
Tailored light-matter interactions are the basis for most energy-converting processes occurring in nature, thus enabling life as it has evolved on our planet. Taking the natural photosystem—the photosynthetic machinery of cyanobacteria, algae, and higher plants—as an example, light energy is absorbed, converted, and stored in the form of chemical bonds. Using nature as a blueprint, this process—as a whole or parts of it—has been adapted to enable artificial photosynthesis, catalyzed by a uniquely diverse range of light-absorbing materials, and as such forms the basis of essentially all man-made solar energy converting technologies from photovoltaics (PV) to photo(electro)catalysis. And yet, just like in natural photosynthesis itself, most processes are strictly divided into light conversion (PV, photocatalysis) and (electro)chemical energy storage, exemplified by the two-step conversion and storage of solar energy via PV coupled to batteries. The underlying cause for this division lies in the practical difficulties associated with the direct and reversible storage of solar energy in the form of (electro)chemical energy, as the materials requirements for efficient light absorption and energy storage are commonly disjunct. While this inherent dichotomy poses severe challenges to any large scale solar energy storage system such as direct solar batteries, the synergistic coupling of light-harvesting and electrochemical storage functions in either a single material or across suitably engineered interfaces may nevertheless open up an essentially uncharted field of hybrid, that is, combined, energy conversion and storage systems.^[10] We will use the terms “direct solar energy storage” or “light storage” to capture this dual functionality, which is enabled through a subtle interplay between light-absorbing, that is, optoelectronic functions, and (faradaic or non-faradaic) charge storage functions on a single material, which appears to be crucially dependent on optoionic contributions, as we will show below. Let us first clarify our use of the term “optoionic” before we proceed with exemplifying possible optoelectronic–optoionic synergies in carbon nitrides.

As for any emerging field, the meaning of optoionics, as it stands, is currently rather diffuse. Optoionic effects *stricto sensu*, as defined by Maier and co-workers,^[9b,11] imply light-induced changes in the ionic conductivity, either through changes in ionic mobility (e.g., phonon-mediated changes in the activation energy of ion diffusion) or ionic carrier concentration (e.g., via the formation of point defects). Depending on the energy of the exciting radiation, light–ion interactions are mediated either through lattice distortions (phononic mechanism), or via electronic excitation (excitonic mechanism), typically

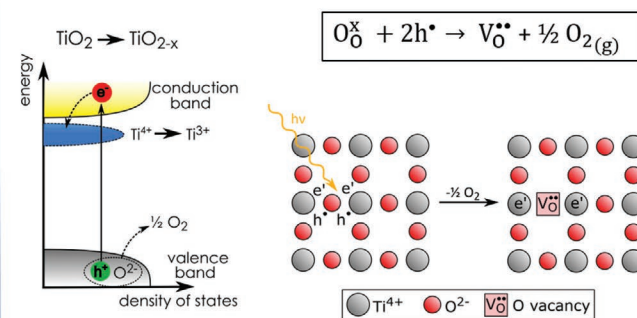
accompanied by polaron formation. The excitonic mechanism is expected to be enabled when radiation with energies above the band gap of the light absorber is involved. Exciton-mediated light–matter interactions have long been known to operate in ionic halide crystals such as alkali metal halides,^[11,12] first giving rise to localized, that is, self-trapped excitons. These are the precursors of photochemically generated lattice defects such as electrons trapped in anion vacancies, so-called F-centers (Farbzentrum, color center), and holes trapped as complementary H-centers (interstitial halogen atoms, often giving rise to X_2^- pairs with significant covalent bonding).^[12b,13] Self-trapping of holes is relatively common in metal halides as a consequence of the narrow valence bandwidth, which is primarily formed by halogen *p* states, and the consequently strong localization of the hole, as well as the high binding strength of the molecular dimer X_2^- . The light-induced formation of H-centers has recently been shown to be at the heart not only of the observed photodecomposition in methylammonium lead iodide (MAPI), the archetypical photoabsorber in halide perovskite PV, but also of the observed orders-of-magnitude increase in ionic conductivity upon above-band gap illumination.^[9a] Here, trapping of photo-induced holes on I^- is proposed to result in the formation of neutral I^0 and its displacement into interstitials, boosting in turn the concentration of mobile iodine vacancies (Figure 1a). Similar effects have been observed in oxides, where UV irradiation can lead to hole trapping on the oxygen sublattice, followed by the removal of oxygen into the gas-phase and concomitant formation of oxygen vacancies, and electron trapping in the form of Ti^{3+} , as observed in TiO_{2-x} (Figure 1b).^[14] Conversely, electron trapping has been described by UV-induced oxygen incorporation into the bulk lattice in $SrTiO_3$, resulting in the filling of oxygen vacancies (Figure 1c).^[15] In all cases, the interaction between photogenerated charge carriers and ionic lattice constituents is balanced, giving rise to coupled changes in electronic and ionic conductivities of the photoabsorber whilst maintaining the overall electroneutrality of the system. Such systems, therefore, classify as “optoionic”.

Three features of the above optoionic systems are noteworthy: First, light-induced stoichiometry changes may be desired (oxygen non-stoichiometries in TiO_2 and $SrTiO_3$) or detrimental effects (iodine loss in MAPI), and in the worst-case scenario, can lead to complete photodecomposition of the material. Second, light-induced changes in stoichiometry can result from annihilation of electronic charge carriers (e.g., quenching of photoinduced holes through oxygen loss in TiO_{2-x} , or through the formation of lattice O^{2-} by reaction between oxygen and light-induced electrons in $SrTiO_3$), hence preventing charge carrier recombination and leading to a stabilization of the overall system. By acting as a source or sink for the mobile ionic species, the surrounding environment—whether gaseous, liquid, or even solid—is thus of critical relevance. Besides enabling compositional and structural changes, the environment determines the chemical potential difference across the surface or interface, and hence the driving force for the uptake or release of the mobile ionic species. Third, the fate of the counter-charge carrier—electrons in MAPI and TiO_2 , holes in $SrTiO_3$ —and their degree of localization can affect the overall stability of the system and its transient behavior. In particular, the ability to co-localize the counter-charge carrier

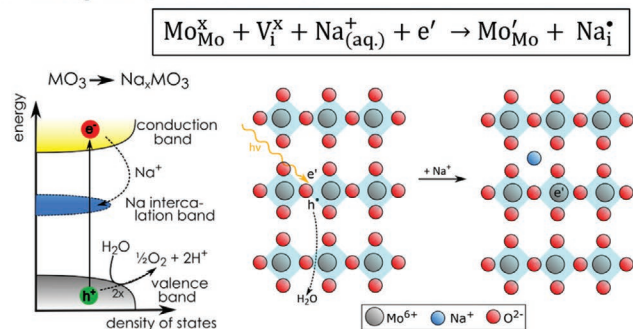
a) MAPI: Iodine vacancy formation



b) TiO₂: Oxygen vacancy formation



d) MoO₃: Na⁺ photointercalation



c) SrTiO₃: Oxygen incorporation

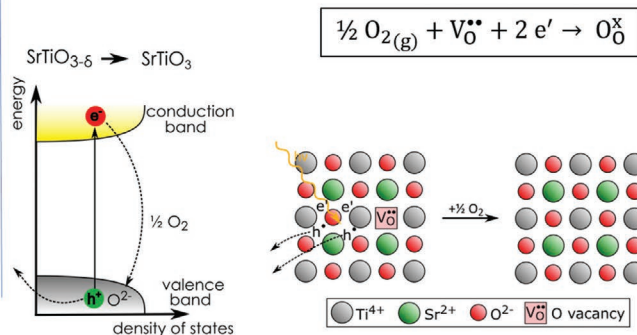


Figure 1. Manifestations of optoionic effects in different inorganic materials illustrating the equivalence of photogenerated and ionic charge carriers. a) Holes are trapped in methyl ammonium lead iodide (MAPI) by forming iodine interstitials. Electrons are either removed via the external circuit or by reducing Pb²⁺ to Pb⁰. Adapted under the terms of the CC BY-NC-ND 4.0 license.^[9b] Copyright 2020, The authors. b) UV-induced holes are trapped in TiO₂ by forming oxygen vacancies. Adapted under the terms of the CC BY-NC-ND 4.0 license.^[9b] Copyright 2020, The authors. c) SrTiO₃ shows light-induced oxygen incorporation (vacancy filling), thus trapping the light-induced electrons. Adapted under the terms of the CC BY 3.0 license.^[15b] Copyright 2017, The authors. d) Photointercalation of aqueous Na⁺ occurs in MoO₃, accompanied by reduction of Mo⁶⁺. Water acts as hole quencher. Adapted with permission.^[19] Copyright 2017, Wiley & Sons. For all display items, the Kröger–Vink notation shows the reactions of the relevant photogenerated charge carriers.^[36] Band structures illustrate the energetics of the respective reactions. Schematic crystal structures show the trapping of charge carriers and the stoichiometry changes occurring in the crystal lattice.

(e.g., the electron as Pb⁰ in MAPI or as Ti³⁺ in TiO₂), or even entirely remove it (e.g., through reaction with a gas-phase or solution species in the surrounding electrolyte, or by extraction via an external circuit) is crucial for the possible mode of operation in practical devices and long-term stability of the system. To extend the scope of optoionic systems and render it useful for applications, the surrounding gaseous or liquid phase should therefore be considered part of the overall system, which puts the spotlight on photoelectrochemical systems, for which optoionic effects may take on a different shape due to involvement of the solid–solution interface.

In fact, the process termed “photointercalation” (PI) by Tributsch captures the essentials of optoionic photoelectrochemical systems.^[16] We will exemplify this process based on the photo-assisted intercalation of cationic species (H⁺, Li⁺, Cu²⁺, etc.) into p-type transition metal dichalcogenides such as MSe₂ (M = Zr, Hf),^[17] or of Cu⁺ into Cu_{6-x}PS₅I.^[18] Here, photo-excited electrons diffuse towards the surface, where they react with cations from the electrolyte, driving their intercalation into the host electrode. This electron localization process is driven by the formation of an intercalation band within the material’s band gap, which effectively lowers the energy of the excited charge carriers. Kinetically, the process is assisted by the field effect in p-type systems, manifested by downwards

band bending, which separates the photogenerated charges and accumulates electrons at the surface, giving rise to attractive Coulombic interactions between the electrons and electrolyte ions. The new intercalative electronic states in the band gap lie sufficiently positive of the quasi-Fermi level of the electrons, thus giving rise to a gain in the free energy of the overall system. The counter-charge (holes) is removed through contact with the counter electrode. The process is illustrated in Figure 1d by a recent PI example based on MoO₃ interacting with Na⁺.^[19] Like in the solid-state systems discussed above, photoexcitation gives rise to a light-induced change in stoichiometry, here via the electrolyte, which acts to counter-balance and stabilize the light-induced charge carriers, similar to the situation in SrTiO₃ discussed above. Note, however, that the photointercalated species in these two cases are different: while in SrTiO₃ the incorporated (neutral) gas-phase species becomes itself part of the anionic (oxygen) sublattice, Tributsch’s concept of PI implies the uptake of an external guest species distinct from both anion and cation sublattices. Therefore, in the latter case, directional ionic transport is enabled by the PI process of a guest species, whereas in the examples above, the ionic conductivity of an intrinsic lattice species is modified.

We have now set the stage for understanding the light response of ionic carbon nitrides, taking K⁺-intercalated PHI as

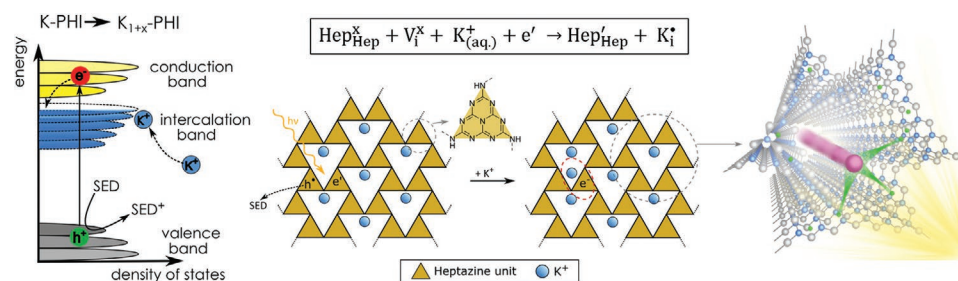


Figure 2. Process and energetics of PI of K^+ in PHI. Solvated alkali metal ions (blue) located in the structural pores of PHI and entering the pores from the solution are charge-balanced by light-induced electrons trapped on the heptazine units (Hep). The holes are quenched by a SED. The channel-like pore structure enables efficient diffusion of alkali metal ions, which screen the light-induced electrons located on the heptazine backbone.

an example (Figure 2). When illuminated with light above the band gap (>2.7 eV), an electron-hole pair is formed. Next, the photogenerated hole is either quenched by a sacrificial electron donor (SED) in solution (e.g., methanol), or—in a photoelectrochemical configuration—extracted at the contact by applying a potential. Intriguingly, the electron remains trapped on the material for up to several hours, as seen by transient absorption spectroscopy.^[8a] This electron storage process is accompanied by a color change from yellow to blue, reminiscent of F-centers in metal halides, but also stable radicals of molecular compounds,^[20] and directly indicates a temporally stable change in the optoelectronic properties of the material, reminiscent of photochromic systems such as alkali metal intercalated WO_3 bronzes (same process as in Figure 1d, but driven electrically).^[21] The fact that this behavior is not seen in Melon-type carbon nitrides further suggests the involvement of ions in the electron trapping process, pointing to an interplay between the electronic and ionic properties of PHI.^[22] Similar to the PI scenario, electron storage is mediated by cations, which are either constituents of the lattice itself (i.e., hydrated K^+ ions in the structural pores) or part of the electrolyte, or both. Contrary to PI, where external ions are taken up by the host lattice, however, PHI already hosts structural ions in its channels, hence rendering its optoionic response more intrinsic. Moreover, it does not show significant dimensional changes upon additional K^+ uptake from the electrolyte, as the ions are intercalated into the structural pores already present in the material.^[22]

We hypothesize that the primary optoionic effect in K-PHI can be understood as a field-effect arising from the build-up of a photopotential in PHI, due to the accumulation of electrons after sacrificial hole extraction at the illumination site. Mobile K^+ ions residing in the channels of PHI and at the PHI–solution interface then relocate, that is, move along the electric field towards the electron accumulation site where they screen and, hence, stabilize the negative charge by lowering the system's overall energy. In parallel, there is an influx of additional cations from the solution, which are incorporated to balance the overall charge (Figure 2). Photoelectrochemical studies suggest that this process has both pseudocapacitive and capacitive contributions,^[22] pointing to the formation of “intercalative” electronic states in the band gap of PHI, in addition to capacitive screening by ions from the surrounding electrolyte on the surface of the nanosheets. Importantly, the PI process observed in PHI maintains the material's semiconducting properties. This is different from most other PI systems, which transition

towards the metallic state, as described by Tributsch and stated as problematic, since the ability to absorb light vanishes.^[17a,23]

We have seen that the ionic carbon nitride backbone and the presence of mobile counter ions impart charge storage properties to PHI, which not only set it apart from Melon-type carbon nitrides, but open up the unique possibility to combine light absorption with charge storage in a single, earth-abundant material. This property of PHI opens up new perspectives for applications, in which solar energy conversion and storage are intimately linked. In the following, we will show that the first steps in this direction have already been made and highlight potential development areas.

1.2. Light Storing Carbon Nitrides: Optoionic Systems and Devices

1.2.1. Time-delayed Solar-to-Chemical Energy Conversion: “Dark Photocatalysis”

Like Melon-type carbon nitrides, K-PHI and its alkali metal-containing congeners show efficient photocatalytic hydrogen evolution (HE) in the presence of a SED and a suitable co-catalyst such as Pt nanoparticles. Unlike Melon, however, the dual light absorption and charge storage ability of PHI puts a new twist on conventional photocatalysis: Photoexcitation can now be temporally decoupled from the release of the stored charge in a catalytic process, by the time-delayed addition of the co-catalyst that triggers charge release “on-demand”. This intriguing property has been cast in the concept of “dark photocatalysis”, which we have introduced for the HE reaction and which has since been used for other photocatalytic and photosynthetic reactions, specifically in photoredox catalysis (Figure 3a).^[8b,24] The benefit of this concept lies in the fact that the production of solar fuels can be temporally decoupled from the availability of fluctuating solar energy, hence effectively buffering the intermittency of solar irradiation and with it, the generation of solar fuels. As such, the material mimics the natural photosynthetic process in which the light-dependent reaction in Photosystem I (i.e., the shuttling of photoexcited electrons along the electron transport chain on the thylakoid membrane and their storage in the form of NADPH and ATP), is decoupled from the light-independent reaction (i.e., the Calvin cycle, where CO_2 is fixed as glucose), with the difference that only a single and robust material is required to drive the entire process.

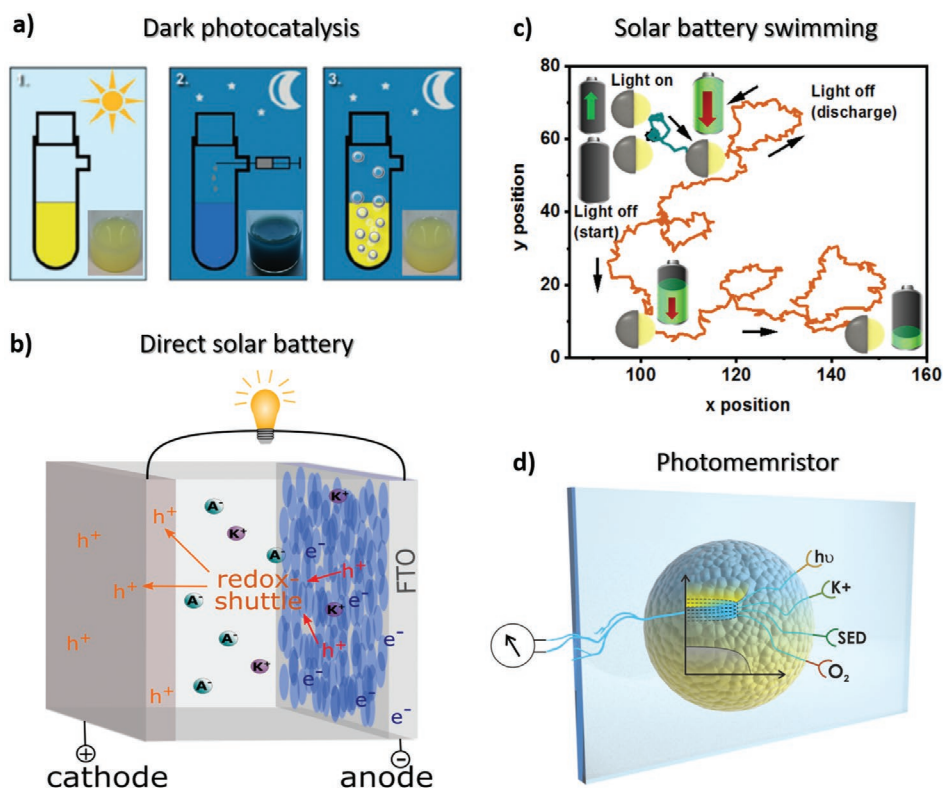


Figure 3. Illustration of direct solar energy storage in PHI enabled by coupled optoelectronic–optoionic interactions, giving rise to different applications. a) “Dark photocatalysis” illustrating the time-delayed HE in the dark. The blue color of PHI signals its photocharged state, while the material turns back yellow after giving off its electrons as H_2 . Reproduced with permission.^[8b] Copyright 2016, Wiley & Sons. b) An aqueous direct solar battery based on PHI as anode, enabling electrical discharge after photocharging. Adapted with permission.^[22] Copyright 2018, Wiley & Sons. c) “Solar battery swimming” enabling sustained ballistic propulsion of light-charged PHI-based Janus microswimmers in the dark. Reproduced under the terms of the CC BY-NC-ND license.^[25] Copyright 2020, The authors. d) Schematic illustration of a PHI particle acting as photomemristor or sensor to external stimuli which affect the presence of trapped electrons, including band gap illumination, alkali metal ions, SEDs or electron scavengers, such as oxygen.

1.3. Solar Battery

The built-in charge storage capability of PHI suggests that the time-delayed photocatalytic function can be extended to discharge the photo-accumulated charge electrically, rather than by solar fuel formation. As such, PHI can act as an electrochemical storage medium rather than transforming solar to chemical energy, thus enabling also purely electrical applications that bypass the storage problem of renewable solar energy. We have demonstrated this concept by using PHI as a solar battery anode, enabling light-induced charge accumulation up to 43 C g^{-1} and time-delayed electrical discharge of the electrons accumulated on the material on the order of hours. Again, the dual function of light-harvesting and energy storage enables novel “hybrid” energy storage concepts such as solar batteries or photocapacitors, where the integration of a solar cell with a dedicated storage module can become redundant, significantly reducing the system complexity (Figure 3b). Notably, the charging process of PHI occurs in water and at potentials more negative than the reversible hydrogen electrode, which opens up new perspectives for aqueous solar batteries. In addition, it can be driven purely electrically, enabling the use of renewable electrical energy (such as wind power) for storage. On a more critical note, this storage concept comes with a number

of grand challenges, which are primarily posed by the single-component set-up and concomitant limitations in separately optimizing the intrinsic charge separation and storage ability of the material, as well as its sensitivity to electron scavengers such as oxygen. Nevertheless, such in situ storage concepts can be flexible building blocks in a sustainable energy infrastructure, where (photo)electrochemical fuel production is partially replaced or complemented by a solar battery module that can locally alleviate the large capital costs required for a solar fuel storage and distribution infrastructure, especially if based entirely on earth-abundant elements as is the case for PHI.

1.4. Light-Driven Microswimmers

The combination of instantaneous and time-delayed catalytic function of PHI does not only conceptually bridge the energy conversion and storage gap, but opens up surprising new perspectives for energy management in autonomous systems. Imagine a micron-sized, light-harvesting particle—a microswimmer—that can convert part of its energy into ballistic motion through light-driven photocatalytic surface reactions. Imagine further that this swimmer has a built-in charge storage function such that propulsion is also possible when

illumination is stopped, enabled by dark photocatalysis. This scenario is remotely reminiscent of a mitochondrion—the powerhouse of a cell—which sustains metabolic functions while storing the energy gained in the respiratory cycle as ATP. However, mitochondria neither respond to light nor are they mobile, suggesting that such motile, “artificial mitochondria” could open up new perspectives for “organismic,” autonomous systems.

In fact, we have recently shown that asymmetric PHI Janus microparticles obtained by sputtering a metal cap on one side of a PHI particle show ballistic motion when irradiated in the presence of a fuel such as methanol or 4-methyl benzyl alcohol, driven by the light-induced SED oxidation and oxygen reduction reaction, akin to mitochondrial energy conversion. Interestingly, the subtle interplay between catalytic surface reactions and internal charge transfer between the Pt cap and PHI can enable photo-charging of the microswimmers, even despite the presence of oxygen, a natural electron acceptor. After illumination has stopped, this accumulated energy can be used for sustained, ballistic propulsion for as long as 30 min in the dark (Figure 3c).^[25] Put into perspective, the storage of photocatalytically accumulated energy has immediate relevance for smart matter systems such as molecular machines and robotics, where an on-board energy storage unit allows for sustained function even in the absence of a fuel or light, just like mitochondria are able to sustain respiratory function even in the absence of oxygen, that is, under anaerobic conditions, for a certain period of time. In artificial microswimmers, the reduction of the system complexity by the intrinsic bifunctionality of light absorption and energy storage is vital for targeted applications in the “micro-world,” where complex, wired multi-material solutions fulfilling charging, power storage, and supply functions are technically challenging and of high-cost while impeding upscaling.

Another interesting aspect of PHI microswimmers concerns the mechanism of motion: while a combination of self-diffusiophoretic and self-electrophoretic motion is believed to be the underlying source of propulsion in PHI in ion-free aqueous electrolytes, “ionophoretic motion,” induced by a flow of cations towards the electron generation site, may be invoked as a new mechanism of motion when optoionic systems are employed. To induce directional movement of such a microswimmer, symmetry-breaking is necessary, which may be naturally induced by illuminating the particle from one side only, hence generating a stable photopotential across the material, originating from locally distinct photoexcitation and electron–ion interactions. Similar effects have recently been described for Melon-type carbon nitride decorated carbon nanotube membranes,^[26] which instead of generating motion of the photocatalyst particle act as light-driven ion pumps, converting light into an osmotic potential against an ionic concentration gradient. The origin of ion pumping was thought to be the generation of a photopotential in response to directional illumination and hence a modified surface band bending, which gives rise to a build-up of an asymmetric surface charge distribution across a carbon nitride membrane. This photopotential attracts ions and pumps them across two separated ion reservoirs.^[26] A similar photo-electric effect, giving rise to active proton transport, has been observed through graphene^[27] and graphene oxide membranes, where

diffusion-controlled charge carrier separation has been invoked as the origin of an electric potential gradient across an asymmetrically illuminated semiconductor structure.^[28]

1.5. Photomemristive Sensing and Photoneuromorphic Systems

It is instructive to consider the impact of light on the dielectric, optical, and electronic properties of PHI. Optoionic interactions between the semiconductor and surrounding ions as described above modify 1) its optical properties (color change), and 2) electrochemical potential; in addition, we observe 3) a significant drop in resistance in the photoreduced state as compared to the original dark state,^[22] which is likely associated with an increase in electronic conductivity due to an increased amount of mobile electrons. As such, PHI can be conceived of as a potent and possibly autonomous sensor for those stimuli that generate or diminish its optoionic response, that is, light, ions, and hole scavengers, but also oxygen, which acts as an electron acceptor, thus deactivating the photoreduced state. The presence of light and concentration of analytes, including reducing agents, readily translate into changes in color, photopotential, capacitance, and conductive properties of PHI, which already suggests its suitability for electro- or photochromic applications. While numerous photoelectrochemical sensors have been described,^[29] PHI-based sensors are distinct in that they have a built-in memory function, enabled by their optoionic properties, which integratively report on the material’s history (illumination, reduction, etc.) through the gradual and stable—that is, non-volatile—modification of PHI’s dielectric and optoelectronic properties.

This novel concept of photo-memristive sensing does not necessarily require electrical energy to drive a phase change and to sense it, in contrast to traditional memristive systems.^[30] Since no wiring is needed, such photomemristive sensors could also be operated remotely (Figure 3d). Note, however, that oxide-based memristors such as TiO_x and NbO_x are likely able to operate also in a light-driven mode, as they, too, can exhibit optoionic properties (see above and next chapter). Besides sensing, photomemristors would be innovative logic elements for next-generation information storage and neuromorphic computing, emulating neuronal activity and energy-efficient, synaptic function and plasticity, triggered or controlled by light. While such prospects are intriguing, the realization of photo-memristive devices in general and PHI-based ones in particular, is challenging. For example, stable and reversible operation under irradiation and in the presence of an electrolyte may necessitate new device concepts, the kinetic limitations due to low electrical or ionic conductivities need to be eliminated, especially for fast computational applications, and retention of the resistive states may require suitable protection from the environment.

2. Design Principles for Optoionic Systems

Using the interplay between optoelectronic and optoionic properties in carbon nitrides as a blueprint, we can now derive

general design principles for optoionic materials, irrespective of their chemical nature.

Let us first summarize criteria enabling the light-driven interaction between electronic and ionic charge carriers on a micro- and mesoscopic level, and then establish a set of features that can amplify the utility of optoionic materials.

- 1) Semiconducting properties with a suitable band gap are fundamentally needed for light-induced charge carrier generation.
- 2) “Soft” ionic lattices with a built-in tendency to form self-trapped excitons and charge carriers, as well as materials having a high tolerance to lattice defects such as certain oxides, are desirable. Such properties are typically reflected in the chemical capacitance.^[31]
- 3) Similarly, mechanisms of localizing one (or both) type of electronic charge carrier should be in place, which can most effectively be accounted for by i) band structure engineering through suitably positioned and narrow valence or conduction bands to localize holes or electrons, respectively, by ii) design of the redox properties and relative band alignments of the system, for example, via choice of a redox-active transition metal that can localize electronic charge carriers, such as the Ti^{4+}/Ti^{3+} couple, and by iii) molecular design in organic systems to enable the formation of stable radical species as hole or electron traps.
- 4) Mechanisms can be invoked to remove or annihilate the counter-charge carrier in order to stabilize the system and

prevent it from (photo)decomposition or simply recombination. Such mechanisms can operate on the systems level and as such determine the configuration of the overall device, for example, removal of the counter-charge carrier through an electrical contact in a (solid oxide) photoelectrochemical cell, or use of sacrificial agents, especially in particulate systems.

- 5) For electron(hole)–ion interactions to be effective, for example, mediated through a light-induced potential gradient, the material should either host ions as part of its structure, or be accessible to external ions (or their precursors) from the environment. In any case, energetic barriers and, hence, structural changes upon ion uptake should be minimal to prevent kinetic limitations and to maintain the semiconducting properties of the optoionic material.

From these considerations, it follows that atomistic factors (composition, structure, and (opto)electronic properties) need to be taken into account for the design of optoionic materials, along with mesoscopic features such as the microstructure and morphology, especially in systems where accessibility to ionic guest species and their mobility is of prime concern (**Figure 4**).

For photoelectrochemical systems where electron(hole)–ion interactions via field effects may be dominant, the presence of diffusion channels enabling fast ionic transport is desirable, created either by structural or textural porosity, or both. Here, porous systems with 1D channels of molecular dimensions such as Hollandites, metal-organic frameworks,

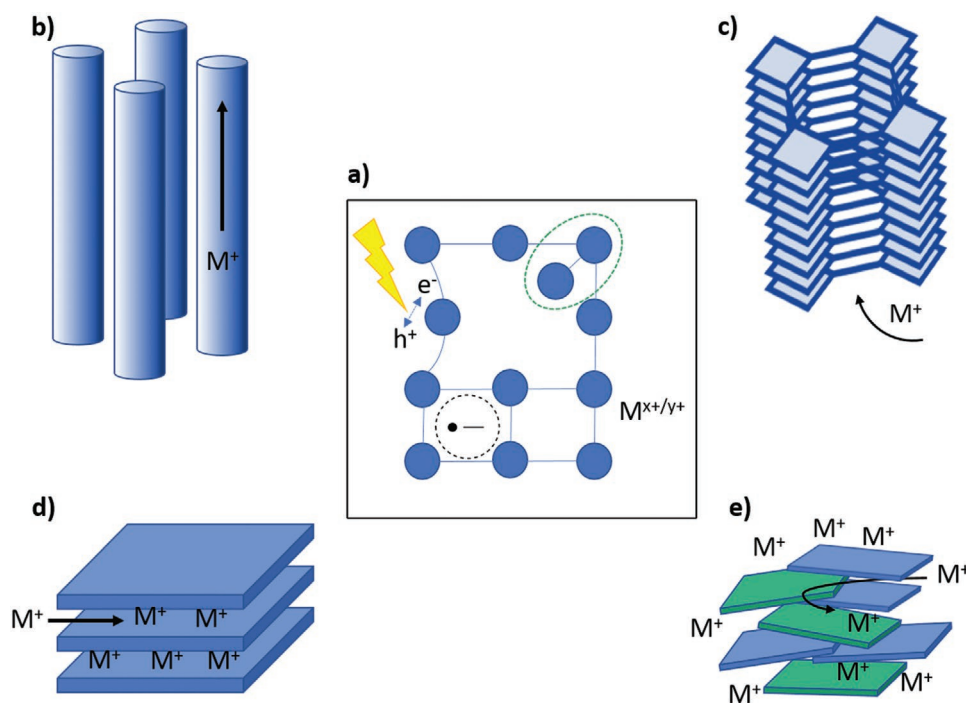


Figure 4. Design principles for optoionic materials with optimized ion transport properties across different length scales. a) Schematic representation of atomistic and optoelectronic features relevant in optoionic processes, such as light responsivity, formation of trapped excitons and charge carriers such as H-centers, electron trapping via anion radical formation or reduction of metal ions. Top panels: different morphologies and microstructures supporting ion transport and design of optoionic materials in general: 1D channels and 1D pore systems as in zeolites, mesoporous materials, MOFs or COFs (b and c). Bottom panels: ordered and turbostratically disordered layered and 2D materials such as ionic layered crystals or artificial van der Waals heterostructures (d and e). Interface-dominated, disordered 2D materials show increased accessible surface areas, lowered kinetic barriers for intercalation, and a flat energy landscape for ion diffusion.

or covalent organic frameworks would be interesting candidates (Figure 4b,c), and in fact, fast ion diffusion, partly light-induced, has recently been described in both systems.^[20c,32] Likewise, layered systems such as 2D transition metal oxides (e.g., titanates, molybdates, or tungstates) as well as dichalcogenides can provide both an intrinsic ionic component, typically hosted in the interlayer space, and be amenable to PI of electrolyte ions (Figure 4d).^[33] The dimensional flexibility of layered materials along the stacking direction can be an asset, as is the possibility of ions to be present as solvates in the interlayer space, making them more mobile. Further enhancement of ion transport is expected in turbostratically disordered 2D materials with large surface areas, providing a uniquely flat energy landscape and easy access for the diffusing ions (Figure 4e).^[34] Like in 1D channel systems, dielectric confinement effects can significantly enhance the mobility of ions sandwiched in the interlayer space, as has recently been shown in graphene, TMDs, etc., putting the spotlight on systems with channel dimensions or layer distances on the order of the hydrodynamic radius of the mobile ions.^[33,35] Intriguingly, channels of molecular dimensions play an important role also in biology, where pore-forming membrane proteins control the transduction of action potentials through trans-membrane diffusion of ions.^[32d,e] Artificial light-triggered ion channels, just like ion pumps, could be uniquely versatile elements of an optoionic toolbox for bio-inspired ionic sensory and adaptive systems.

3. Conclusion and Outlook

Meeting the global energy challenge requires innovative materials concepts. While optoelectronic systems are the backbone of solar energy conversion, electrochemical energy storage relies on the transfer of ions. Bridging the gap between the two, enabled by optoionics, is bound to evolve new hybrid “light storage” devices at the interface between solid-state ionics, photoelectrochemistry, and bio-electronics.

Here, we have shown that PHI-type carbon nitrides already serve as a blueprint in this endeavor by synergistically coupling optoelectronic and optoionic properties, cast in an earth-abundant backbone. Seizing the unique design space provided by the periodic table, combined with our ability to engineer and control optoionic features across multiple length scales, opens up new horizons for the development of direct solar energy storage systems. Extending the realm of light-matter interactions from optoelectronics to optoionics is thus bound to enable fundamentally new concepts, functions, and devices, including time-delayed photocatalysis, solar battery swimming, osmotic energy storage, optically controlled sensing and actuation, all the way to novel photomemristive devices for “photoneuromorphic” computing, or light-triggered autonomous systems.

Acknowledgements

The authors acknowledge Alberto Jiménez-Solano and Julia Kröger for assistance in the preparation of figures. The authors further thank Julia Kröger and especially Joachim Maier for fruitful discussions. Financial support by the Max Planck Society, the European Research Council (ERC) under the European Union’s Horizon 2020 Research

and Innovation Program (grant agreement no. 639233, COFLeaf), the Deutsche Forschungsgemeinschaft (DFG) via the cluster of excellence “e-conversion” (project number EXC2089/1–390776260), and by the Center for NanoScience is gratefully acknowledged.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

carbon nitride, dark photocatalysis, microswimmers, optoionic, photomemristors, solar batteries, solar energy conversion

Received: September 24, 2020

Revised: November 2, 2020

Published online:

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