

Metal-Free Photocatalysis: Two-Dimensional Nanomaterial Connection toward Advanced Organic Synthesis

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ABSTRACT: Two-dimensional (2D) nanostructures are a frontier in materials chemistry as a result of their extraordinary properties. Metal-free 2D nanomaterials possess extra appeal due to their improved cost-effectiveness and lower toxicity with respect to many inorganic structures. The outstanding electronic characteristics of some metal-free 2D semiconductors have projected them into the world of organic synthesis, where they can function as high-performance photocatalysts to drive the sustainable synthesis of high-value organic molecules. Recent reports on this topic have inspired a stream of research and opened up a theme that we believe will become one of the most dominant trends in the forthcoming years.



Although research on two-dimensional (2D) materials traces back several decades, its renaissance can be pinpointed to when single-layer graphene was isolated and characterized by Geim and Novoselov, who were awarded the Nobel Prize in Physics for their discoveries.^{1,2} Since then, graphene's incredible properties have inspired many researchers investigating a wide range of possible applications. The recognition that such distinct properties go hand in hand with the 2D arrangement motivated and accelerated the exploration of other 2D materials, which include both metal-based and metal-free materials. In recent years, research on 2D metal-free materials has become increasingly broad because of the lower materials cost of metal-free materials, as compared to that of metal-based structures. Among the various applications for such materials, photocatalysis is an exceptionally attractive field, fitting most of the aspects of the “green chemistry” modern philosophy, where integrating sustainability criteria into chemical production is the core mission. In this context, exploiting the energy of solar light to trigger chemical transformations in lieu of more energy-intensive and less ecological production schemes represents a big step forward toward sustainability.^{3,4} Despite the promising findings and the high expectations for the use of 2D metal-free materials as photocatalysts for organic transformations, the full potential of these intriguing structures has yet to be uncovered, and understanding the structure/activity relationship still requires a

great deal of investigation. In this Perspective, we identify the critical points of 2D metal-free materials and discuss their success as photocatalysts for advanced organic synthesis. We also offer critical discussion on the areas to be improved to extend applicability and increase industrial appeal. Finally, we present emerging trends in 2D materials photocatalysis leading toward richer organic synthesis.

TYPES OF TWO-DIMENSIONAL MATERIALS

Although different classes of 2D materials exist, 2D materials are often described as layered solids with a high in-plane bond strength but weak interplanar interactions, typically deriving from van der Waals forces.⁵ The layered structure can be exfoliated into thinner, few-layer structures with relative ease.^{6–8} A more stringent definition of 2D materials is restricted to those featuring single-atom-thick layers, whereby the resemblance with relativistic Dirac particles makes them unique.⁹ In contrast with monolayered 2D species, few-layered

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2D materials are more accessible and versatile, explaining their popularity from an application-focused point of view. The flexibility in defining 2D materials has led to a “gray area”, where the arrangement of chemical species organized in sheets has been taken as an indicator to claim the 2D nature, even when multilayered structures are the subject of the reported study. It is important to keep in mind that the two situations (thin, few-layered *vs* multilayered bulk solids) usually generate dramatic changes in the material properties.

Among two-dimensional structures, the carbon nitrides represent the most popular choice for photocatalytic applications, including organic transformations, because of their visible-light absorption, facile synthesis, stability, and versatility for structural modifications.

WHY FOCUS ON TWO-DIMENSIONAL STRUCTURES FOR PHOTOCATALYSIS?

The properties of 2D photocatalysts match some photocatalysis requirements well. The planar sizes in 2D materials can reach the micron scale, with concomitant enhancement of the specific surface area.¹⁰ In addition, thicknesses can be reduced to a few nanometers, or even, in some cases, to monatomic sizes, using modern synthetic approaches.¹¹ These geometric features are notably correlated with quantum and dielectric confinement effects, which modify the band structure and, consequently, the band gap.¹² Typically, the band gap widens due to quantum confinement, and upshifts of the conduction band (CB) are observed, enhancing both the potential energy of the photogenerated electrons and their reduction ability.¹³ The 2D geometry also improves the separation and migration of the charge carriers, which are prerequisites for efficient photocatalysis, and higher densities of surface active sites. Moreover, the chemical and morphological structures can be locally modified, enabling tunability of the defect density.^{14,15} It is also possible to adjust the electronic states by doping the lattice with various elements, either metals or nonmetals. Although doping is a versatile approach that has also been adopted for bulk catalytic materials, this strategy notably benefits from the 2D arrangement for reaching (i) higher per-mass relative dopant concentrations and (ii) superior control over the dopant environment. The former aspect capitalizes on the easier diffusion of the dopant through a thinner structure (as compared to bulk materials), whereas the latter benefits from the usually higher homogeneity of 2D layered materials.¹⁵ Finally, great opportunities arise from creating interfaced 2D structures by combining two different phases. This combination results in the creation of heterojunctions (p–n) or Z-schemes, which are two of the most modern approaches for achieving significant enhancement of catalytic performance.¹⁶ Metal-free interfaces are also a rapidly emerging field, with 2D hybrid structures offering various advantages.¹⁷ It is evident that the effectiveness of the interface is maximized in 2D structures for geometric reasons,

which also enables the construction of devices with higher mechanical flexibilities (Figure 1).¹⁸

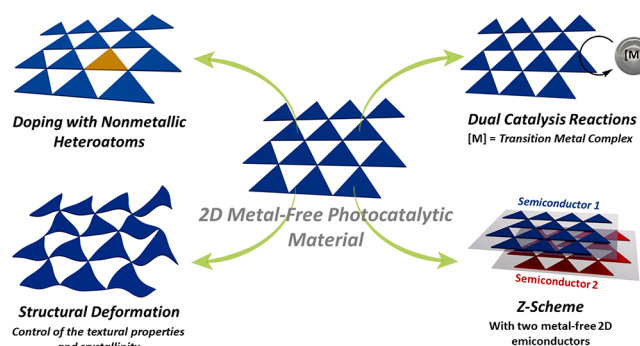


Figure 1. Graphical representation of the foreseen major avenues to organic photocatalysis by metal-free two-dimensional (2D) materials.

Although metal-free 2D materials can be based on several elements including Si, Se, P, S, B, or Te, carbon has been investigated the most for the design and synthesis of photocatalysts. Carbon has been preferred to date because of its easy availability and the rich arsenal of available morphologies of carbon materials, particularly at the nanoscale, which enables tailoring of the physicochemical and electronic properties.¹⁹ For instance, these properties can be tuned by simple chemical modification of graphene *via* introduction of functional groups or dopants.^{20–25} Apart from carbon, other nonmetal 2D materials with semiconducting properties that have emerged include hexagonal boron nitride (h-BN) and black phosphorus (BP), although their use has thus far mainly involved energy-related catalysis.^{26–28} A key issue when reporting metal-free catalysts is to ascertain that no adventitious metal impurities are incorporated within the material, as even at low parts per million (ppm) levels metals can affect the performance, thus generating false conclusions and reproducibility problems.²⁹

TWO-DIMENSIONAL METAL-FREE PHOTOCATALYSTS: PROTAGONISTS, MINOR CHARACTERS, AND RISING STARS

Among 2D structures (Figure 2), the carbon nitrides (CNs) represent the most popular choice for photocatalytic applications, including organic transformations, because of their visible-light absorption, facile synthesis, stability, and versatility for structural modifications.^{30–32}

Carbon-nitride-based materials diversify to large extents, and various structures have been reported, building a portfolio of material subclasses. From a structural point of view, the most stable and most frequently investigated allotrope, namely, graphitic-CN (g-CN), is proposed to be constituted by repeating N-bridged poly(tri-*s*-triazine) frameworks arranged into graphite-like π -conjugated planar layers (although other repeating units have been proposed, such as, for example, *s*-triazine).^{33,34} The C/N ratio in g-CN is theoretically 3/4 (as indicated by the typically used formula, C₃N₄); however, the experimental ratio deviates from this value depending on the synthetic procedure due to the formation of defective structures and incorporation of other elements (*e.g.*, O). The accurate structure of g-CN (and other CNs in general) has not been defined in detail, and often the depiction of the structure

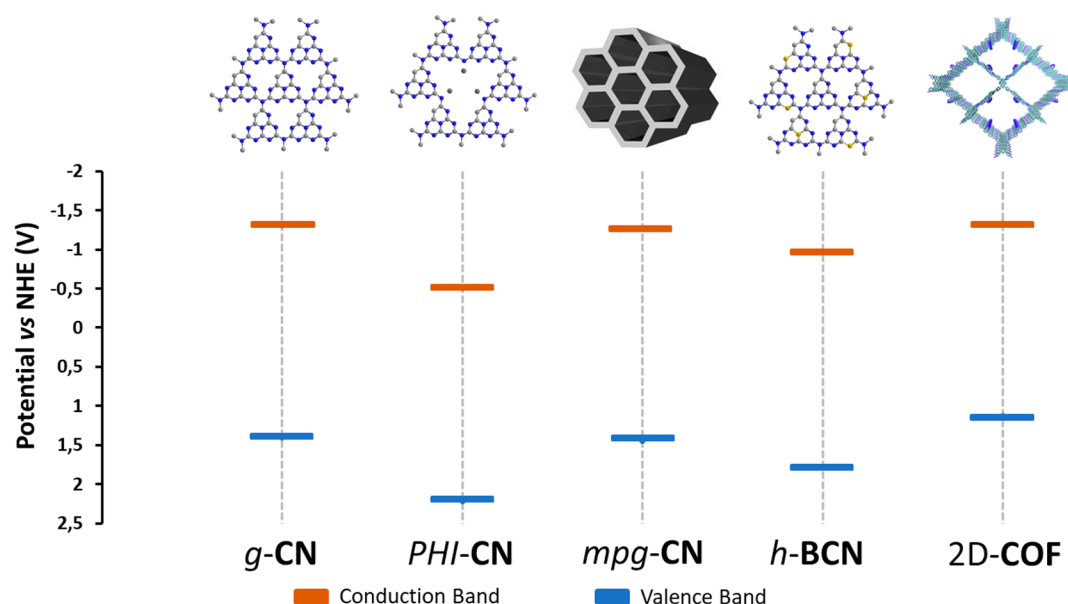


Figure 2. Typical band edge potentials of the two-dimensional metal-free semiconductors graphitic-CN (g-CN), poly(heptazine imides) (PHI-CN), mesoporous carbon nitride (mpg-CN), hexagonal boron carbon nitride (h-BCN), and two-dimensional covalent organic frameworks (2D-COFs) discussed herein.

is merely a simplification for guiding the reader. Because conventional preparation protocols (which are also the simplest ones) based on pyrolysis of solid precursors do not enable easy control on the final structure, detailed knowledge of the entire structure is not accessible in most cases. This lack of knowledge poses an extra challenge for theoretical studies on CN catalysts, as the observed activity may rely on definite structural features (defects, specific moieties, or others) that could be overlooked during computational analyses, thus generating erroneous conclusions. To mitigate this problem, diligent and in-depth characterization of the materials should become a routine part of the work, even when materials syntheses are replicated from previously published articles, because marginal differences in conditions may lead to alterations of the final structures. Fortunately, rapid progress is being made, leading to next generations of materials with improved performance and better-defined structures.³⁵ The position of both valence and conduction bands (VB and CB, respectively) can be modulated on the basis of the C/N ratio, polymerization degree, crystallinity, and the presence of doping agents (e.g., boron, sulfur, phosphorus, organic additives).^{30,34,36} The textural properties can also be tailored for better photocatalytic performance, as shown by the development of mesoporous carbon nitride (mpg-CN), which possesses surface areas much higher than those of g-CN.^{37,38} Indeed, mpg-CN has recently emerged in organic reactions for the synthetically relevant functionalization of arenes and heteroarenes (Figure 3).³⁹

Although CN materials are conventionally prepared as bulk, appropriate protocols for 2D structures have been proposed. For example, Zhao and Antonietti showed that, starting from melamine and cyanuric acid, a g-CN consisting of thin, multisheet structures (thicknesses in the range of 15–20 nm) could be prepared. This catalyst effectively promoted a photocatalyzed Diels–Alder reactions under visible light irradiation,⁴⁰ being one of the milestones in 2D CN-based photocatalytic organic synthesis (Figure 4).

Understanding the textural properties of this material could have provided additional information related to activity, and we propose that future studies should carefully consider the contributions of surface area and pore size distributions.⁴¹ A similar g-CN prepared by pyrolysis of guanidine was employed to carry out photo-oxidative additions of aminoalkyl radical precursors to unsaturated acceptors.⁴² Researchers have demonstrated that exfoliation of CN bulk materials into thin 2D nanosheets is one main contributing factors to the much enhanced photocatalytic activity, as a result of the increased active site density.^{43,44} Graphitic CN in its pristine form generally exhibits moderate catalytic activity because of the sluggish conductivity and low surface area. A great deal of research has focused on strategies to modify the pristine material in order to boost the resulting photocatalytic activity.³⁵ In this direction, our group recently investigated how postsynthetic modifications of g-CN can influence the outcome of a photocatalytic process, namely, perfluoroalkylation reactions of electron-rich organic molecules (Figure 5).⁴⁵

Important insights into the mechanistic features were gathered by advanced ¹⁹F nuclear magnetic resonance techniques, revealing the criticality of the fluorinated substrate's affinity toward the CN surface. In our opinion, studies that couple the screening of new organic reactions with investigations (theoretical and experimental) on the related mechanism could considerably accelerate the development of 2D photocatalysts toward industrial feasibility.

One subclass of CN that is flourishing in photocatalytic applications are poly(heptazine imides) (PHI-CN). These materials are conventionally prepared by eutectic molten salts methods, giving rise to a nanometer-size layered structure with continuous channels. The synthesis generates some negatively charged N sites, which bind the cation of the employed metal salt (usually K⁺ or Na⁺).⁴⁶ Although most of the CN photocatalysts have always been linked to electron-transfer processes, PHI-CN is also capable of driving energy-transfer reactions. This ability can translate into the generation of excited-state molecules other than charged radicals, paving the

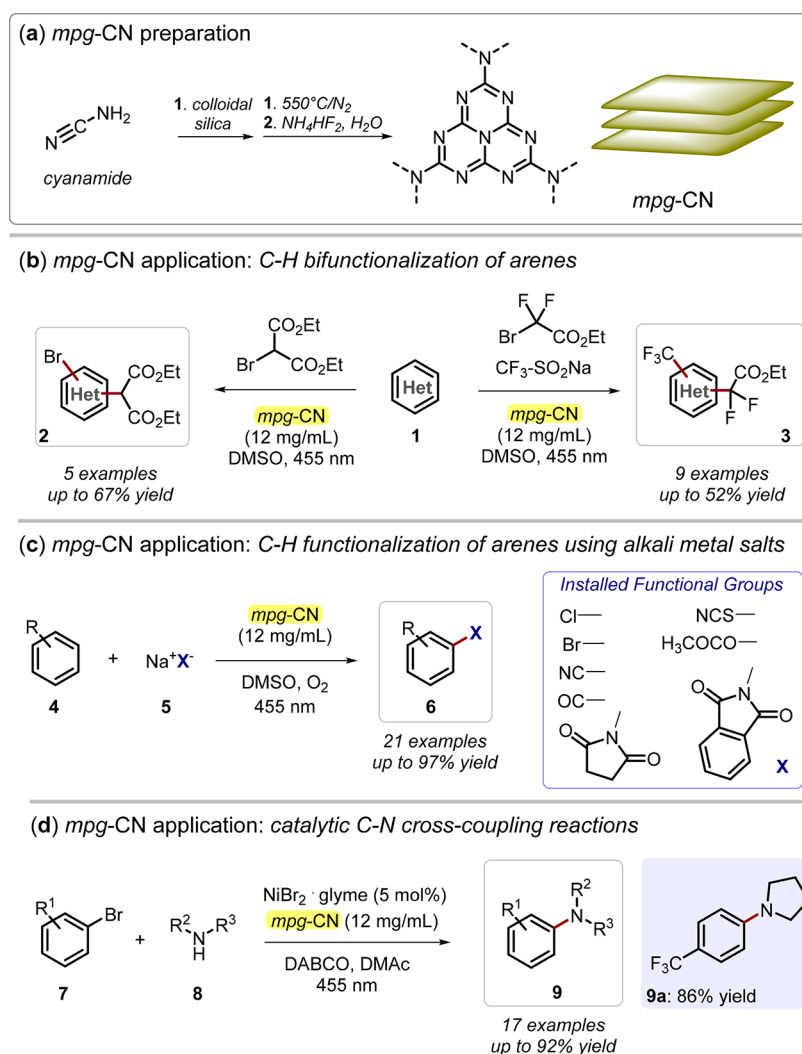


Figure 3. (a) Mesoporous carbon nitride (mpg-CN) preparation from cyanamide through thermal treatment. (b) mpg-CN application in C–H bifunctionalization of arenes and heteroarenes. (c) mpg-CN application in C–H functionalization of arenes using alkali metal salts. (d) mpg-CN application in C–N cross-coupling reactions. DMSO: dimethyl sulfoxide.

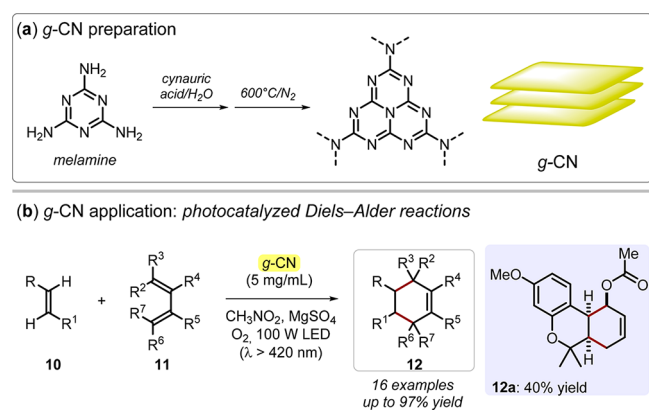


Figure 4. (a) Graphitic carbon nitride (g-CN) preparation from melamine and cyanuric acid through pyrolysis. (b) g-CN application in photocatalyzed Diels–Alder reactions. LED: light-emitting diode.

way for new reactivities.^{47–51} Moreover, PHI-CN materials offer another interesting opportunity in that the alkaline metals could be replaced by other transition metals through cation

exchange strategies, thus potentially leading to CN–single atom materials.⁵²

One subclass of carbon nitrides that is flourishing in photocatalytic applications are poly(heptazine imides).

Although they have been less investigated to date, boron carbon nitrides (BCNs) also offer interesting potential applications. Boron CNs are ternary-component materials made of carbon, nitrogen, and boron that can be formed with cubic (c-BCN) or hexagonal (h-BCN) crystal structures. In particular, h-BCN synthesis resulted from interest in combining graphene with hexagonal boron nitride (h-BN) to amend the 0 band gap of graphene (G) and the wide band gap of h-BN (typically above 5 eV) simultaneously. As theoretical studies have confirmed,⁵³ the resulting material (h-BCN) shows an intermediate optical behavior with absorption energy that can be adjusted in the visible range (e.g., by varying the BCN stoichiometry),⁵⁴ with the possibility of forming segregated domains of one of the three elements (typically C).^{55,56} As a result, h-BCN is an appealing option for

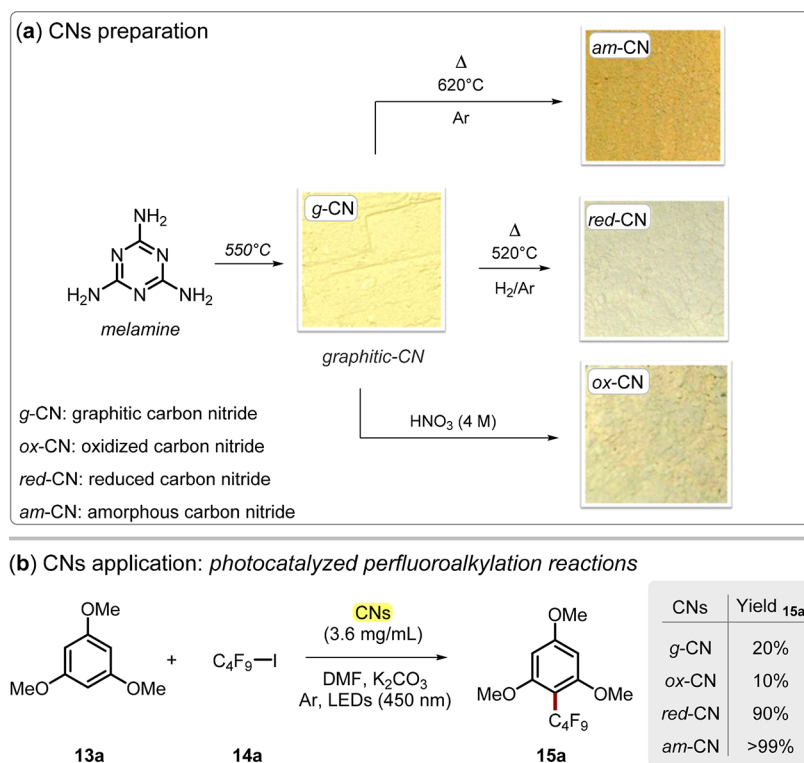


Figure 5. (a) Carbon nitride (CN) preparation from melamine and related postsynthetic modifications. (b) CN applications in photocatalyzed perfluoroalkylation reactions.

photocatalytic applications,⁵⁷ and, apart from water splitting evolution and CO₂ reduction,^{56,57} h-BCN has recently attracted attention as a catalyst for synthetically relevant photoredox reactions.^{58,59} König, Wang, and co-workers studied the photochemical C–H functionalization of electron-rich arenes catalyzed by an h-BCN with notable activity,⁶⁰ whereas other photo-oxidation and photoreduction reactions were possible by simply tuning the relative content of the h-BCN precursors (typically glucose and boric acid, Figure 6).^{61–63} Despite the above-mentioned encouraging case studies, organic photocatalysis by BCN is still in its infancy; therefore, there is fertile soil for future developments.

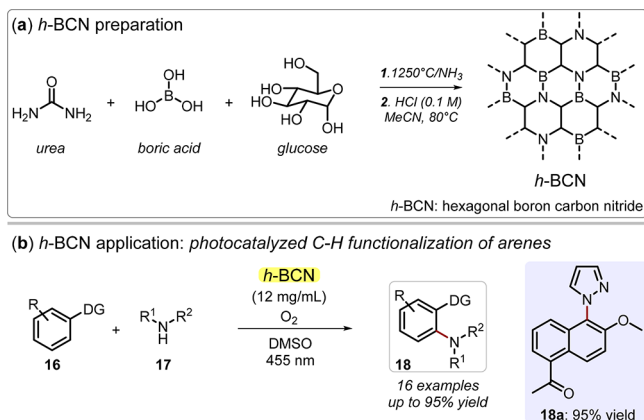


Figure 6. (a) Hexagonal boron carbon nitride (h-BCN) preparation from urea, boric acid, and glucose through calcination. (b) h-BCN application in photocatalyzed C–H functionalization of arenes. DG: directing group.

Finally, covalent organic frameworks (COFs) are a popular class of single-phase 2D metal-free candidates for photocatalytic organic synthesis. Covalent organic frameworks are covalent, porous crystalline polymers that enable the integration of organic motifs into an ordered structure.^{64,65} The better-defined structures of COFs, as compared to those of CN or BCN, make this class of materials distinctive. In particular, 2D-COFs possess extended π -conjugated frameworks and eclipsed stacked sheets with regularly aligned columns, where the ordered columns in 2D-COFs provide ideal channels for charge carrier transport in the stacking direction.⁶⁶ In addition, despite their heterogeneity, the controlled, high porosity of 2D-COFs ensures great accessibility to active sites, offering excellent catalytic performance and the potential for higher reaction selectivity by means of pore size tailoring.^{65,67} Thus, 2D-COFs could lead to the development of photoactive materials for optoelectronics, photovoltaics, and visible light photocatalysis.^{67–70} For COFs, the 2D versus 3D distinction is easier to define because it evolves from the simplified symmetry of the specific building blocks used to construct the framework.⁶⁴ In general, 2D-COFs exhibit a richer topology than other 2D materials (*i.e.*, hexagonal or tetragonal geometries of different sizes), leading to increasing interest in the development of synthetic strategies for the next generation of materials.⁷¹ For catalytic applications, there are additional opportunities for introducing organic groups within specific channel positions, endowing COFs with enhanced functionality.⁷² Wang and co-workers illustrated the photochemical oxidation of boronic acids using three different 2D-COFs having different shapes and channel dimensions (hexagonal or rhombic repetitive units with dimensions of 1.4–2.8 nm).⁷³ Recently, Yang and co-workers envisaged the use of a hydrazone-based 2D-COF with a

hexagonal pore system with dimensions of 2.2 nm for carrying out photochemical alkylation of N-heterocyclic compounds (Figure 7).⁷⁴ In addition to these examples, many other

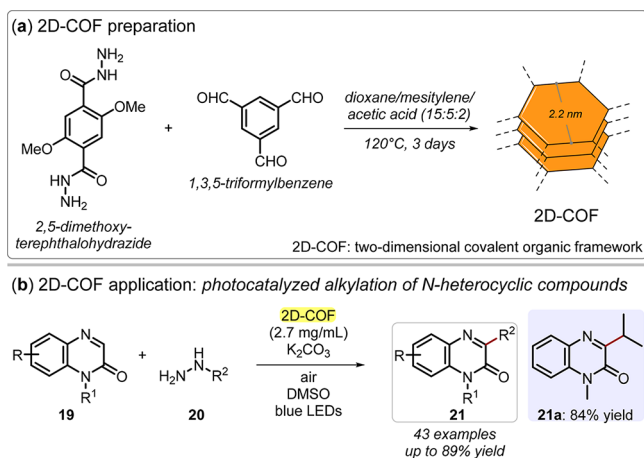


Figure 7. (a) Two-dimensional covalent-organic framework (2D-COF) preparation from 2,5-dimethoxyterephthalohydrazide and 1,3,5-triformylbenzene through solvothermal treatment. (b) 2D-COF application in photocatalyzed alkylation of N-heterocyclic compounds.

photocatalytic procedures have been reported, some of which deal with photo-oxidation reactions of simple organic substrates such as alcohols, amines, and sulfides.^{75–77} Nevertheless, more complex reactions such as photodehalogenations, cross-couplings, and cyclizations have demonstrated and proven the great versatility of 2D-COFs.^{78–82} Therefore, we expect rapid proliferation of more challenging organic transformations by 2D-COF photocatalysts.

EMERGING DIRECTIONS AND VISION FOR THE FUTURE

Despite the great progress in photocatalytic organic synthesis by metal-free 2D single-phase catalysts, the parallelism with 2D inorganic hybrids, which, through creation of suitable heterojunctions, can remarkably enhance photocatalytic performance, has naturally provided a new direction for metal-free analogues. Specifically, one frontier is combining two metal-free phases and suitably interfacing them, thus preparing 2D metal-free nanohybrids to combine their catalytic behavior while exploiting the resulting new features. One objective is to replicate the well-known inorganic Z-schemes by relying on only nonmetal 2D structures. This method retards electron–hole recombination rates while exploiting the higher CB energy level and the lower VB energy level to enable coupled energetically demanding redox processes (Figure 8).⁸³

The synergism in 2D metal-free nanohybrids for photocatalysis has thus far been confined to energy-related processes. A notable achievement was reported by He *et al.*, who prepared a 2D CN/h-BN nanohybrid by the direct growth of CN on h-BN nanosheets, which they successfully used for photocatalytic H₂ and H₂O₂ synthesis. Enhanced activity originated from the suitable interfacial domain between CN and h-BN, causing physical separation of the charge carriers and prolonging their lifetime, although, in this case, the potential energy of the photoexcited electrons was reduced following the CN to h-BN injection.⁸⁴ Two-dimensional BP/CN catalytic heterostructure for H₂ evolution is another remarkable example of interfacial

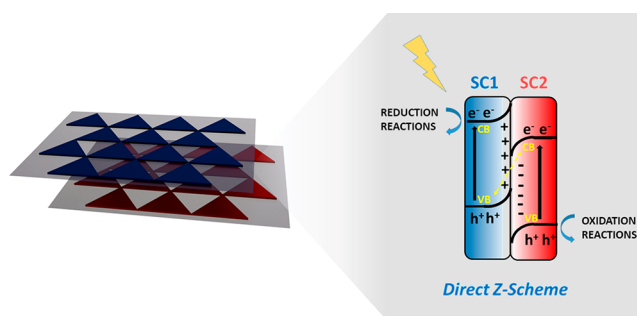


Figure 8. Graphical sketch of a Z-scheme and its function. Two semiconductors (SCs) opportunely interfaced and with staggered band configuration (and suitable band Fermi levels and work functions) give rise to band bending. The built-in internal electric field and the band bending cause coupling of the photogenerated holes and electrons of SC1 and SC2, respectively, whereas the electrons and holes in SC1 and SC2 are maintained and spatially separated, able to function for reduction and oxidation reactions.

synergism, whereby charge transfer inhibited charge recombination, making catalysis possible, even under infrared irradiation.⁸⁵ Other interesting examples with graphene/CN and BP/covalent triazine frameworks used for water splitting or decontamination of organic pollutants indicate the great potential of this type of heterostructure.^{17,86,87} We anticipate that their use in photocatalytic organic synthesis will soon take off, making the synthesis of high-value organic compounds with good solar-to-chemical efficiency possible. A thorough evaluation of the band structures and Fermi levels of the two phases will be critical to establish truly cooperative mechanisms, possibly by means of the Z-scheme configuration, and synthetic efforts must look at the phase connection, maximizing interfacial domains with strong interactions.

Two-dimensional covalent organic frameworks could lead to the development of photoactive materials for optoelectronics, photovoltaics, and visible light photocatalysis.

Another recent trend that we expect to flourish in the near future is coupling 2D metal-free materials with metal complexes. The concept is to make use of transition metal complexes for combining photocatalysis with conventional organic catalysis. More specifically, the photocatalyst is intended to serve as a single-electron-transfer (SET) shuttle to harness the metal complex with specific oxidation states and the coordination environment to perform the tasks required by the mechanism. Although not purely metal-free overall, this strategy still builds on the ability of metal-free materials to absorb light, to generate the separated excited charges, and to transfer the charges. Pioneering work by Durrant, Reisner, and co-workers coupled CN photocatalysts with Ni diphospine complexes to achieve the dual function of H₂ solar generation and the simultaneous oxidation of benzyl alcohol.⁸⁸ This work also inspires studies of more challenging purely organic reactions. Pieber and co-workers exploited this metal/OA-CN (oxamide-based carbon nitride) dual mechanism to enable a variety of organic reactions such as esterifications, (thio)-etherifications, and aminations under white light irradiation (Figure 9),^{89–92} while Ghosh *et al.* used dual catalysis by Ni

derivatives and mpg-CN to drive coupling of aryl halides with aliphatic/aromatic amines and sulfamides (Figure 3).³⁹

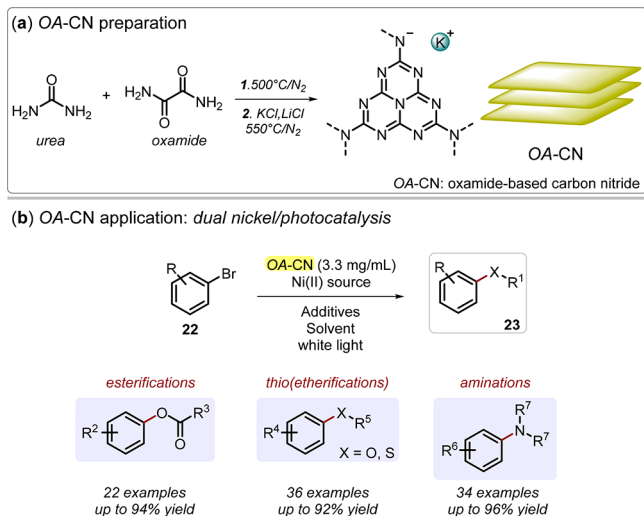


Figure 9. (a) OA-CN (oxamide-based carbon nitride) preparation from urea and oxamide through calcination. (b) OA-CN application in photocatalyzed esterification, (thio)etherification, and amination reactions by means of dual nickel/photocatalysis.

Such examples are quite recent and exclusively include CN as the 2D photocatalyst. The key mechanistic aspects are not yet well understood and require further exploration, but it is likely that the specific steps will differentiate according to the type of reaction and catalytic system.⁹³ Nevertheless, these examples highlight the immense potential for organic synthesis, possibly encompassing a wide range of reactivity. Future developments will depend on the study and definition of the main features of the catalytic cycle for each class of investigated reactions, such as, for example, the dynamics of the SET steps (whether it is a direct transfer, a second coordination sphere transfer, or a solvent-mediated transfer) and the nature of the metal active site.

To sum up, several examples of non-metal-based 2D materials beyond graphene have all the qualifications to satisfy the strict requirements of photocatalysis. Thus far, a great effort has focused on their use as components in hybrid catalytic systems, with widespread use in energy-related photocatalysis. However, photocatalytic organic synthesis is experiencing a great deal of attention, and we expect that it will take a central role for future applications of this class of materials. Future avenues of development of 2D metal-free catalysts will converge toward (i) the ability to control and to modify the structure by synthetic schemes; (ii) the appropriate advanced characterization tools and methods required to reveal the substructure/functionality relationships in photocatalysis; (iii) nonreliance on high metal loadings (*i.e.*, exploring possible introduction of low fractions of single metal atoms); and (iv) the possibility of interfacing different 2D nonmetal phases with suitable contacts and interactions, both to extend the possible applicability to more demanding classes of reactions and to improve photocatalytic activity. More complex catalytic systems, such as the inclusion of metal species for performing traditional organic steps also represent an attractive opportunity, driving organic transformations of higher complexity.

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Notes

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REFERENCES

- (1) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. Electric Field Effect in Atomically Thin Carbon Films. *Science* **2004**, *306*, 666–669.
- (2) Geim, A. K.; Novoselov, K. S. The Rise of Graphene. *Nat. Mater.* **2007**, *6*, 183–191.
- (3) Liu, G.; Zhen, C.; Kang, Y.; Wang, L.; Cheng, H. M. Unique Physicochemical Properties of Two-Dimensional Light Absorbers Facilitating Photocatalysis. *Chem. Soc. Rev.* **2018**, *47*, 6410–6444.
- (4) Zhu, Y.; Peng, L.; Fang, Z.; Yan, C.; Zhang, X.; Yu, G. Structural Engineering of 2D Nanomaterials for Energy Storage and Catalysis. *Adv. Mater.* **2018**, *30*, 1706347.

- (5) Gupta, A.; Sakthivel, T.; Seal, S. Recent Development in 2D Materials beyond Graphene. *Prog. Mater. Sci.* **2015**, *73*, 44–126.
- (6) Novoselov, K. S.; Jiang, D.; Schedin, F.; Booth, T. J.; Khotkevich, V. V.; Morozov, S. V.; Geim, A. K. Two-Dimensional Atomic Crystals. *Proc. Natl. Acad. Sci. U. S. A.* **2005**, *102*, 10451–10453.
- (7) Yang, H.; Hernandez, Y.; Schlierf, A.; Felten, A.; Eckmann, A.; Johal, S.; Louette, P.; Pireaux, J. J.; Feng, X.; Mullen, K.; Palermo, V.; Casiraghi, C. A Simple Method for Graphene Production Based on Exfoliation of Graphite in Water Using 1-Pyrenesulfonic Acid Sodium Salt. *Carbon* **2013**, *53*, 357–365.
- (8) Hu, C.-X.; Shin, Y.; Read, O.; Casiraghi, C. Dispersant-Assisted Liquid-Phase Exfoliation of 2D Materials beyond Graphene. *Nano-scale* **2021**, *13*, 460.
- (9) Geim, A. K. Graphene: Status and Prospects. *Science* **2009**, *324*, 1530–1535.
- (10) Zhang, X.; Yuan, X.; Jiang, L.; Zhang, J.; Yu, H.; Wang, H.; Zeng, G. Powerful Combination of 2D G-C₃N₄ and 2D Nanomaterials for Photocatalysis: Recent Advances. *Chem. Eng. J.* **2020**, *390*, 124475.
- (11) Hu, S.; Zhu, M. Ultrathin Two-Dimensional Semiconductors for Photocatalysis in Energy and Environment Applications. *ChemCatChem* **2019**, *11*, 6147–6165.
- (12) Katan, C.; Mercier, N.; Even, J. Quantum and Dielectric Confinement Effects in Lower-Dimensional Hybrid Perovskite Semiconductors. *Chem. Rev.* **2019**, *119*, 3140–3192.
- (13) She, X.; Wu, J.; Zhong, J.; Xu, H.; Yang, Y.; Vajtai, R.; Lou, J.; Liu, Y.; Du, D.; Li, H.; Ajayan, P. M. Oxygenated Monolayer Carbon Nitride for Excellent Photocatalytic Hydrogen Evolution and External Quantum Efficiency. *Nano Energy* **2016**, *27*, 138–146.
- (14) Zhang, Y.; Wang, Y.; Di, M.; Zhou, B.; Xu, W.; Wu, N.; Wu, Y.; Du, Y.; Zhong, W. Synergy of Dopants and Defects in Ultrathin 2D Carbon Nitride Sheets to Significantly Boost the Photocatalytic Hydrogen Evolution. *Chem. Eng. J.* **2020**, *385*, 123938.
- (15) Di, J.; Xiong, J.; Li, H.; Liu, Z. Ultrathin 2D Photocatalysts: Electronic-Structure Tailoring, Hybridization, and Applications. *Adv. Mater.* **2018**, *30*, 1704548.
- (16) Xu, Q.; Zhang, L.; Yu, J.; Wageh, S.; Al-Ghamdi, A. A.; Jaroniec, M. Direct Z-Scheme Photocatalysts: Principles, Synthesis, and Applications. *Mater. Today* **2018**, *21*, 1042–1063.
- (17) Han, Q.; Chen, N.; Zhang, J.; Qu, L. Graphene/Graphitic Carbon Nitride Hybrids for Catalysis. *Mater. Horiz.* **2017**, *4*, 832–850.
- (18) Britnell, L.; Ribeiro, R. M.; Eckmann, A.; Jalil, R.; Belle, B. D.; Mishchenko, A.; Kim, Y.; Gorbachev, R. V.; Georgiou, T.; Morozov, S. V.; Grigorenko, A. N.; Geim, A. K.; Casiraghi, C.; Neto, A. H. C.; Novoselov, K. S. Strong Light-Matter Interactions Thin Films. *Science* **2013**, *340*, 1311–1315.
- (19) Li, C.; Xu, Y.; Tu, W.; Chen, G.; Xu, R. Metal-Free Photocatalysts for Various Applications in Energy Conversion and Environmental Purification. *Green Chem.* **2017**, *19*, 882–899.
- (20) Sreeprasad, T. S.; Berry, V. How Do the Electrical Properties of Graphene Change with Its Functionalization? *Small* **2013**, *9*, 341–350.
- (21) Criado, A.; Melchionna, M.; Marchesan, S.; Prato, M. The Covalent Functionalization of Graphene on Substrates. *Angew. Chem., Int. Ed.* **2015**, *54*, 10734–10750.
- (22) Li, X.; Yu, J.; Wageh, S.; Al-Ghamdi, A. A.; Xie, J. Graphene in Photocatalysis: A Review. *Small* **2016**, *12*, 6640–6696.
- (23) Tuci, G.; Zafferoni, C.; D'Ambrosio, P.; Caporali, S.; Ceppatelli, M.; Rossin, A.; Tsoufis, T.; Innocenti, M.; Giambastiani, G. Tailoring Carbon Nanotube N-Dopants While Designing Metal-Free Electrocatalysts for the Oxygen Reduction Reaction in Alkaline Medium. *ACS Catal.* **2013**, *3*, 2108–2111.
- (24) Iglesias, D.; Giuliani, A.; Melchionna, M.; Marchesan, S.; Criado, A.; Nasi, L.; Bevilacqua, M.; Tavagnacco, C.; Vizza, F.; Prato, M.; Fornasiero, P. N-Doped Graphitized Carbon Nanohorns as a Forefront Electrocatalyst in Highly Selective O₂ Reduction to H₂O₂. *Chem.* **2018**, *4*, 106–123.
- (25) Li, X.; Zhou, J.; Zhang, J.; Li, M.; Bi, X.; Liu, T.; He, T.; Cheng, J.; Zhang, F.; Li, Y.; Mu, X.; Lu, J.; Wang, B. Bamboo-Like Nitrogen-Doped Carbon Nanotube Forests as Durable Metal-Free Catalysts for Self-Powered Flexible Li–CO₂ Batteries. *Adv. Mater.* **2019**, *31*, 1903852.
- (26) Lai, C.; An, N.; Li, B.; Zhang, M.; Yi, H.; Liu, S.; Qin, L.; Liu, X.; Li, L.; Fu, Y.; Xu, F.; Wang, Z.; Shi, X.; An, Z.; Zhou, X. Future Roadmap on Nonmetal-Based 2D Ultrathin Nanomaterials for Photocatalysis. *Chem. Eng. J.* **2021**, *406*, 126780.
- (27) Li, B.; Lai, C.; Zeng, G.; Huang, D.; Qin, L.; Zhang, M.; Cheng, M.; Liu, X.; Yi, H.; Zhou, C.; Huang, F.; Liu, S.; Fu, Y. Black Phosphorus, a Rising Star 2D Nanomaterial in the Post-Graphene Era: Synthesis, Properties, Modifications, and Photocatalysis Applications. *Small* **2019**, *15*, e1804565.
- (28) Tahir, M. B.; Fatima, N.; Fatima, U.; Sagir, M. A Review on the 2D Black Phosphorus Materials for Energy Applications. *Inorg. Chem. Commun.* **2021**, *124*, 108242.
- (29) Kiciński, W.; Dyjak, S. Transition Metal Impurities in Carbon-Based Materials: Pitfalls, Artifacts and Deleterious Effects. *Carbon* **2020**, *168*, 748–845.
- (30) Cao, S.; Low, J.; Yu, J.; Jaroniec, M. Polymeric Photocatalysts Based on Graphitic Carbon Nitride. *Adv. Mater.* **2015**, *27*, 2150–2176.
- (31) Liu, J.; Wang, H.; Antonietti, M. Graphitic Carbon Nitride “Reloaded”: Emerging Applications beyond (Photo)Catalysis. *Chem. Soc. Rev.* **2016**, *45*, 2308–2326.
- (32) Zhang, J.; Chen, Y.; Wang, X. Two-Dimensional Covalent Carbon Nitride Nanosheets: Synthesis, Functionalization, and Applications. *Energy Environ. Sci.* **2015**, *8*, 3092–3108.
- (33) Wang, X.; Blechert, S.; Antonietti, M. Polymeric Graphitic Carbon Nitride for Heterogeneous Photocatalysis. *ACS Catal.* **2012**, *2*, 1596–1606.
- (34) Markushyna, Y.; Smith, C. A.; Savateev, A. Organic Photocatalysis: Carbon Nitride Semiconductors vs. Molecular Catalysts. *Eur. J. Org. Chem.* **2019**, 1294–1309.
- (35) Luo, Y.; Yan, Y.; Zheng, S.; Xue, H.; Pang, H. Graphitic Carbon Nitride Based Materials for Electrochemical Energy Storage. *J. Mater. Chem. A* **2019**, *7*, 901–924.
- (36) Savateev, A.; Ghosh, I.; König, B.; Antonietti, M. Photoredox Catalytic Organic Transformations Using Heterogeneous Carbon Nitriles. *Angew. Chem., Int. Ed.* **2018**, *57*, 15936–15947.
- (37) Vinu, A.; Ariga, K.; Mori, T.; Nakanishi, T.; Hishita, S.; Golberg, D.; Bando, Y. Preparation and Characterization of Well-Ordered Hexagonal Mesoporous Carbon Nitride. *Adv. Mater.* **2005**, *17*, 1648–1652.
- (38) Han, Q.; Wang, B.; Gao, J.; Cheng, Z.; Zhao, Y.; Zhang, Z.; Qu, L. Atomically Thin Mesoporous Nanomesh of Graphitic C₃N₄ for High-Efficiency Photocatalytic Hydrogen Evolution. *ACS Nano* **2016**, *10*, 2745–2751.
- (39) Ghosh, I.; Khamrai, J.; Savateev, A.; Shlapakov, N.; Antonietti, M.; König, B. Organic Semiconductor Photocatalyst Can Bifunctionalize Arenes and Heteroarenes. *Science* **2019**, *365*, 360–366.
- (40) Zhang, G.; Li, G.; Lan, Z.; Lin, L.; Savateev, A.; Heil, T.; Zafeiratos, S.; Wang, X.; Antonietti, M. Optimizing Optical Absorption, Exciton Dissociation, and Charge Transfer of a Polymeric Carbon Nitride with Ultrahigh Solar Hydrogen Production Activity. *Angew. Chem., Int. Ed.* **2017**, *56*, 13445–13449.
- (41) Melchionna, M.; Fornasiero, P. Updates on the Roadmap for Photocatalysis. *ACS Catal.* **2020**, *10*, 5493–5501.
- (42) Cai, Y.; Tang, Y.; Fan, L.; Lefebvre, Q.; Hou, H.; Rueping, M. Heterogeneous Visible-Light Photoredox Catalysis with Graphitic Carbon Nitride for α -Aminoalkyl Radical Additions, Allylations, and Heteroarylations. *ACS Catal.* **2018**, *8*, 9471–9476.
- (43) Wang, Y.; Hou, X.; Zhang, J.; Xu, T.; Liu, S.; Liu, B. Highly Crystalline Carbon Nitride Nanosheets for Ultrahigh Photocatalytic Hydrogen Evolution. *ChemPhotoChem* **2018**, *2*, 490–497.
- (44) Schwinghammer, K.; Mesch, M. B.; Duppel, V.; Ziegler, C.; Senker, J.; Lotsch, B. V. Crystalline Carbon Nitride Nanosheets for

- Improved Visible-Light Hydrogen Evolution. *J. Am. Chem. Soc.* **2014**, *136*, 1730–1733.
- (45) Filippini, G.; Longobardo, F.; Forster, L.; Criado, A.; Di Carmine, G.; Nasi, L.; D'Agostino, C.; Melchionna, M.; Fornasiero, P.; Prato, M. Light-Driven, Heterogeneous Organocatalysts for C–C Bond Formation toward Valuable Perfluoroalkylated Intermediates. *Sci. Adv.* **2020**, *6*, No. eabc9923.
- (46) Savateev, A.; Tarakina, N. V.; Strauss, V.; Hussain, T.; ten Brummelhuis, K.; Sánchez Vadillo, J. M.; Markushyna, Y.; Mazzanti, S.; Tyutyunnik, A. P.; Walczak, R.; Oschatz, M.; Guldi, D. M.; Karton, A.; Antonietti, M. Potassium Poly(Heptazine Imide): Transition Metal-Free Solid-State Triplet Sensitizer in Cascade Energy Transfer and [3 + 2]-Cycloadditions. *Angew. Chem., Int. Ed.* **2020**, *59*, 15061–15068.
- (47) Kurpil, B.; Otte, K.; Mishchenko, A.; Lamagni, P.; Lipiński, W.; Lock, N.; Antonietti, M.; Savateev, A. Carbon Nitride Photocatalyzes Regioselective Aminium Radical Addition to the Carbonyl Bond and Yields N-Fused Pyrroles. *Nat. Commun.* **2019**, *10*, 945.
- (48) Savateev, A.; Kurpil, B.; Mishchenko, A.; Zhang, G.; Antonietti, M. A “Waiting” Carbon Nitride Radical Anion: A Charge Storage Material and Key Intermediate in Direct C–H Thiolation of Methylarenes Using Elemental Sulfur as the “s”-Source. *Chem. Sci.* **2018**, *9*, 3584–3591.
- (49) Markushyna, Y.; Lamagni, P.; Catalano, J.; Lock, N.; Zhang, G.; Antonietti, M.; Savateev, A. Advantages in Using Inexpensive CO₂ to Favor Photocatalytic Oxidation of Benzylamines. *ACS Catal.* **2020**, *10*, 7336–7342.
- (50) Mazzanti, S.; Kurpil, B.; Pieber, B.; Antonietti, M.; Savateev, A. Dichloromethylation of Enones by Carbon Nitride Photocatalysis. *Nat. Commun.* **2020**, *11*, 1387.
- (51) Kurpil, B.; Markushyna, Y.; Savateev, A. Visible-Light-Driven Reductive (Cyclo)Dimerization of Chalcones over Heterogeneous Carbon Nitride Photocatalyst. *ACS Catal.* **2019**, *9*, 1531–1538.
- (52) Colombari, F. M.; da Silva, M. A. R.; Homsí, M. S.; de Souza, B. R. L.; Araujo, M.; Francisco, J. L.; da Silva, G. T. S. T.; Silva, I. F.; de Moura, A. F.; Teixeira, I. F. Graphitic Carbon Nitrides as Platforms for Single-Atom Photocatalysis. *Faraday Discuss.* **2021**, DOI: 10.1039/C9FD00112C.
- (53) Zhou, M.; Wang, S.; Yang, P.; Huang, C.; Wang, X. Boron Carbon Nitride Semiconductors Decorated with CdS Nanoparticles for Photocatalytic Reduction of CO₂. *ACS Catal.* **2018**, *8*, 4928–4936.
- (54) Wan, Q.; Wei, F.; Ma, Z.; Anpo, M.; Lin, S. Novel Porous Boron Nitride Nanosheet with Carbon Doping: Potential Metal-Free Photocatalyst for Visible-Light-Driven Overall Water Splitting. *Adv. Theory Simulations* **2019**, *2*, 1800174.
- (55) Da Rocha Martins, J.; Chacham, H. Disorder and Segregation in B–C–N Graphene-Type Layers and Nanotubes: Tuning the Band Gap. *ACS Nano* **2011**, *5*, 385–393.
- (56) Guilhon, I.; Marques, M.; Teles, L. K.; Bechstedt, F. Optical Absorbance and Band-Gap Engineering of (BN)_{1-x}(C₂)_x Two-Dimensional Alloys: Phase Separation and Composition Fluctuation Effects. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2017**, *95*, 035407.
- (57) Zheng, M.; Cai, W.; Fang, Y.; Wang, X. Nanoscale Boron Carbonitride Semiconductors for Photoredox Catalysis. *Nanoscale* **2020**, *12*, 3593–3604.
- (58) Shi, W.; Cao, L.; Zhang, H.; Zhou, X.; An, B.; Lin, Z.; Dai, R.; Li, J.; Wang, C.; Lin, W. Surface Modification of Two-Dimensional Metal–Organic Layers Creates Biomimetic Catalytic Microenvironments for Selective Oxidation. *Angew. Chem., Int. Ed.* **2017**, *56*, 9704–9709.
- (59) Ghosh, I.; Marzo, L.; Das, A.; Shaikh, R.; König, B. Visible Light Mediated Photoredox Catalytic Arylation Reactions. *Acc. Chem. Res.* **2016**, *49*, 1566–1577.
- (60) Zheng, M.; Ghosh, I.; König, B.; Wang, X. Metal-Free Semiconductor Photocatalysis for Sp² C–H Functionalization with Molecular Oxygen. *ChemCatChem* **2019**, *11*, 703–706.
- (61) Wang, B.; Anpo, M.; Lin, J.; Yang, C.; Zhang, Y.; Wang, X. Direct Hydroxylation of Benzene to Phenol on H-BCN Nanosheets in the Presence of FeCl₃ and H₂O₂ under Visible Light. *Catal. Today* **2019**, *324*, 73–82.
- (62) Zheng, M.; Shi, J.; Yuan, T.; Wang, X. Metal-Free Dehydrogenation of N-Heterocycles by Ternary h-BCN Nanosheets with Visible Light. *Angew. Chem., Int. Ed.* **2018**, *57*, 5487–5491.
- (63) Zheng, M.; Yuan, T.; Shi, J.; Cai, W.; Wang, X. Photocatalytic Oxygenation and Deoxygenation Transformations over BCN Nanosheets. *ACS Catal.* **2019**, *9*, 8068–8072.
- (64) Feng, X.; Ding, X.; Jiang, D. Covalent Organic Frameworks. *Chem. Soc. Rev.* **2012**, *41*, 6010–6022.
- (65) Waller, P. J.; Gándara, F.; Yaghi, O. M. Chemistry of Covalent Organic Frameworks. *Acc. Chem. Res.* **2015**, *48*, 3053–3063.
- (66) Chen, L.; Furukawa, K.; Gao, J.; Nagai, A.; Nakamura, T.; Dong, Y.; Jiang, D. Photoelectric Covalent Organic Frameworks: Converting Open Lattices into Ordered Donor-Acceptor Heterojunctions. *J. Am. Chem. Soc.* **2014**, *136*, 9806–9809.
- (67) Wang, G. B.; Li, S.; Yan, C. X.; Zhu, F. C.; Lin, Q. Q.; Xie, K. H.; Geng, Y.; Dong, Y. B. Covalent Organic Frameworks: Emerging High-Performance Platforms for Efficient Photocatalytic Applications. *J. Mater. Chem. A* **2020**, *8*, 6957–6983.
- (68) Ding, S. Y.; Wang, W. Covalent Organic Frameworks (COFs): From Design to Applications. *Chem. Soc. Rev.* **2013**, *42*, 548–568.
- (69) Zhi, Y.; Wang, Z.; Zhang, H. L.; Zhang, Q. Recent Progress in Metal-Free Covalent Organic Frameworks as Heterogeneous Catalysts. *Small* **2020**, *16*, 2001070.
- (70) Lopez-Magano, A.; Jiménez-Almarza, A.; Aleman, J.; Mas-Ballesté, R. Metal–Organic Frameworks (MOFs) and Covalent Organic Frameworks (COFs) Applied to Photocatalytic Organic Transformations. *Catalysts* **2020**, *10*, 720.
- (71) Nguyen, H. L.; Gropp, C.; Yaghi, O. M. Reticulating 1D Ribbons into 2D Covalent Organic Frameworks by Imine and Imide Linkages. *J. Am. Chem. Soc.* **2020**, *142*, 2771–2776.
- (72) Nagai, A.; Guo, Z.; Feng, X.; Jin, S.; Chen, X.; Ding, X.; Jiang, D. Pore Surface Engineering in Covalent Organic Frameworks. *Nat. Commun.* **2011**, *2*, 536.
- (73) Wei, P. F.; Qi, M. Z.; Wang, Z. P.; Ding, S. Y.; Yu, W.; Liu, Q.; Wang, L. K.; Wang, H. Z.; An, W. K.; Wang, W. Benzoxazole-Linked Ultrastable Covalent Organic Frameworks for Photocatalysis. *J. Am. Chem. Soc.* **2018**, *140*, 4623–4631.
- (74) Tian, M.; Liu, S.; Bu, X.; Yu, J.; Yang, X. Covalent Organic Frameworks: A Sustainable Photocatalyst toward Visible-Light-Accelerated C₃ Arylation and Alkylation of Quinoxalin-2(1H)-ones. *Chem. - Eur. J.* **2020**, *26*, 369–373.
- (75) Abednatanzi, S.; Derakhshandeh, P. G.; Leus, K.; Vrielinck, H.; Callens, F.; Schmidt, J.; Savateev, A.; van der Voort, P. Metal-Free Activation of Molecular Oxygen by Covalent Triazine Frameworks for Selective Aerobic Oxidation. *Sci. Adv.* **2020**, *6*, eaaz2310.
- (76) Chen, R.; Shi, J. L.; Ma, Y.; Lin, G.; Lang, X.; Wang, C. Designed Synthesis of a 2D Porphyrin-Based Sp² Carbon-Conjugated Covalent Organic Framework for Heterogeneous Photocatalysis. *Angew. Chem., Int. Ed.* **2019**, *58*, 6430–6434.
- (77) Li, Q.; Lan, X.; An, G.; Ricardez-Sandoval, L.; Wang, Z.; Bai, G. Visible-Light-Responsive Anthraquinone Functionalized Covalent Organic Frameworks for Metal-Free Selective Oxidation of Sulfides: Effects of Morphology and Structure. *ACS Catal.* **2020**, *10*, 6664–6675.
- (78) Li, Z.; Zhi, Y.; Shao, P.; Xia, H.; Li, G.; Feng, X.; Chen, X.; Shi, Z.; Liu, X. Covalent Organic Framework as an Efficient, Metal-Free, Heterogeneous Photocatalyst for Organic Transformations under Visible Light. *Appl. Catal., B* **2019**, *245*, 334–342.
- (79) Liu, W.; Su, Q.; Ju, P.; Guo, B.; Zhou, H.; Li, G.; Wu, Q. A Hydrazone-Based Covalent Organic Framework as an Efficient and Reusable Photocatalyst for the Cross-Dehydrogenative Coupling Reaction of N-Aryltetrahydroisoquinolines. *ChemSusChem* **2017**, *10*, 664–669.
- (80) Liu, S.; Pan, W.; Wu, S.; Bu, X.; Xin, S.; Yu, J.; Xu, H.; Yang, X. Visible-Light-Induced Tandem Radical Addition-Cyclization of 2-Aryl Phenyl Isocyanides Catalysed by Recyclable Covalent Organic Frameworks. *Green Chem.* **2019**, *21*, 2905–2910.

(81) Yuan, J.; Xia, Q.; Zhu, W.; Wu, C.; Wang, B.; Liu, B.; Yang, X.; Xu, Y.; Xu, H. Sunlight-Driven Synthesis of 1,2,4-Thiadiazoles via Oxidative Construction of a Nitrogen-Sulfur Bond Catalyzed by a Reusable Covalent Organic Framework. *ChemPhotoChem*. **2020**, *4*, 445–450.

(82) Li, Z.; Han, S.; Li, C.; Shao, P.; Xia, H.; Li, H.; Chen, X.; Feng, X.; Liu, X. Screening Metal-Free Photocatalysts from Isomorphic Covalent Organic Frameworks for the C-3 Functionalization of Indoles. *J. Mater. Chem. A* **2020**, *8*, 8706–8715.

(83) Lang, J.; Hu, Y. H. Phosphorus-Based Metal-Free Z-Scheme 2D van Der Waals Heterostructures for Visible-Light Photocatalytic Water Splitting: A First-Principles Study. *Phys. Chem. Chem. Phys.* **2020**, *22*, 9250–9256.

(84) He, Z.; Kim, C.; Lin, L.; Jeon, T. H.; Lin, S.; Wang, X.; Choi, W. Formation of Heterostructures via Direct Growth CN on H-BN Porous Nanosheets for Metal-Free Photocatalysis. *Nano Energy* **2017**, *42*, 58–68.

(85) Zhu, M.; Kim, S.; Mao, L.; Fujitsuka, M.; Zhang, J.; Wang, X.; Majima, T. Metal-Free Photocatalyst for H₂ Evolution in Visible to Near-Infrared Region: Black Phosphorus/Graphitic Carbon Nitride. *J. Am. Chem. Soc.* **2017**, *139*, 13234–13242.

(86) Ai, B.; Duan, X.; Sun, H.; Qiu, X.; Wang, S. Metal-Free Graphene-Carbon Nitride Hybrids for Photodegradation of Organic Pollutants in Water. *Catal. Today* **2015**, *258*, 668–675.

(87) Zheng, Y.; Chen, Y.; Wang, L.; Tan, M.; Xiao, Y.; Gao, B.; Lin, B. Metal-Free 2D/2D Heterostructured Photocatalyst of Black Phosphorus/Covalent Triazine-Based Frameworks for Water Splitting and Pollutant Degradation. *Sustain. Energy Fuels* **2020**, *4*, 3739–3746.

(88) Kasap, H.; Caputo, C. A.; Martindale, B. C. M.; Godin, R.; Lau, V. W. H.; Lotsch, B. V.; Durrant, J. R.; Reisner, E. Solar-Driven Reduction of Aqueous Protons Coupled to Selective Alcohol Oxidation with a Carbon Nitride-Molecular Ni Catalyst System. *J. Am. Chem. Soc.* **2016**, *138*, 9183–9192.

(89) Pieber, B.; Malik, J. A.; Cavedon, C.; Gisbertz, S.; Savateev, A.; Cruz, D.; Heil, T.; Zhang, G.; Seeberger, P. H. Semi-Heterogeneous Dual Nickel/Photocatalysis Using Carbon Nitrides: Esterification of Carboxylic Acids with Aryl Halides. *Angew. Chem., Int. Ed.* **2019**, *58*, 9575–9580.

(90) Cavedon, C.; Madani, A.; Seeberger, P. H.; Pieber, B. Semiheterogeneous Dual Nickel/Photocatalytic (Thio)Etherification Using Carbon Nitrides. *Org. Lett.* **2019**, *21*, 5331–5334.

(91) Gisbertz, S.; Reischauer, S.; Pieber, B. Overcoming Limitations in Dual Photoredox/Nickel-Catalysed C–N Cross-Couplings Due to Catalyst Deactivation. *Nat. Catal.* **2020**, *3*, 611–620.

(92) Rosso, C.; Gisbertz, S.; Williams, J. D.; Gemoets, H. P. L.; Debrouwer, W.; Pieber, B.; Kappe, C. O. An Oscillatory Plug Flow Photoreactor Facilitates Semi-Heterogeneous Dual Nickel/Carbon Nitride Photocatalytic C–N Couplings. *React. Chem. Eng.* **2020**, *5*, 597–604.

(93) Zhu, C.; Yue, H.; Jia, J.; Rueping, M. Recent Advances in Nickel-Catalyzed C-Heteroatom Cross-Coupling Reactions under Mild Conditions via Facilitated Reductive Elimination. *Angew. Chem., Int. Ed.* **2020**, DOI: 10.1002/anie.202013852.