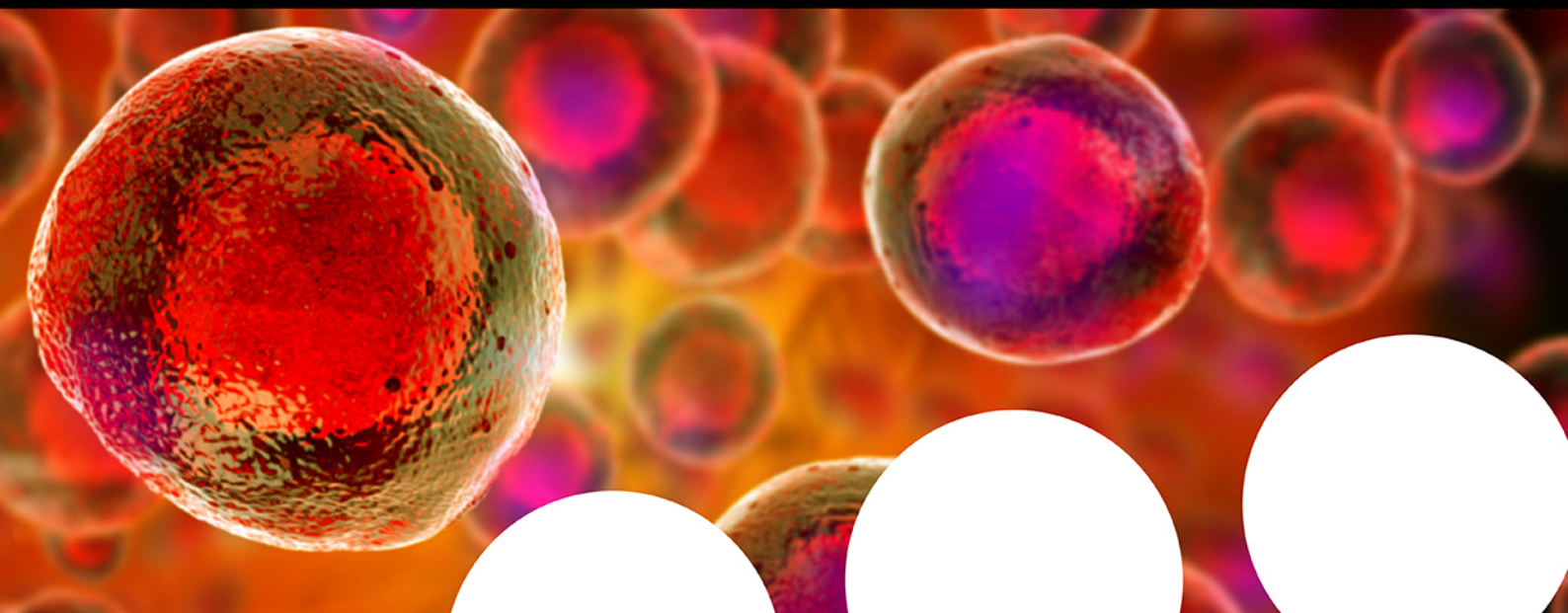


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Use of Carbon Nitrides as Photoactive Supports in Single-Atom Heterogeneous Catalysis for Synthetic Purposes

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In recent years, the field of dual photocatalysis has become an increasingly popular tool for the functionalization of organic substrates under mild operative conditions. Single-atom heterogeneous catalysts (SACs), where the metal atoms are stabilized by means of properly structured photoactive supports, are currently one of the frontiers of this research field. To this end, Carbon Nitrides (CNs) have emerged as ideal two-dimensional

semiconducting supports, capable of stabilizing single metal sites (for instance: nickel, iron, among other) through nitrogen-rich structures. This Concept highlights the recent advances in the synthesis of carbon nitride-based SACs and their applications in light-driven dual-catalytic processes, also providing forward-looking opportunities within this research area.

1. Introduction

Metal-free semiconductors (SCs) are a popular class of photocatalytic systems for several synthetic applications.^[1,2] These photoactive materials can easily undergo charge separation by absorbing photons of sufficient energy, thus generating excited electrons and holes that can be involved, respectively, in the reduction and oxidation of suitable organic substrates.^[3] Importantly, the heterogeneous nature of SCs facilitates the recovery and reuse of the photocatalysts, therefore overcoming the classical limitations of homogeneous catalysis.^[4] Recently, organic chemists have investigated the merging of Earth-abundant metal-based catalysts

and photocatalysts, establishing what is today called dual photocatalysis, which synergistically exploits the separate functions of the metal species and the photocatalyst to obtain an overall more complex synthetic scheme.^[5–7] In this context, an emerging class of heterogeneous catalysts is represented by single-atom catalysts (SACs), where isolated metal atoms are finely dispersed and stabilized onto various supporting host materials.^[8] SACs overcome the intrinsic limitation of traditional heterogeneous catalysts, in which the aggregation of metal atoms limits the metal exposure to reactants. Consequently, the number of successful application of SACs in several catalytic processes has risen in the last decade.^[9] In specific cases, SACs can be also addressed as ideal examples of fully heterogeneous dual catalytic systems, where the photoactive scaffold and the metal (M) are integrated into a “one-package” material. The ideality arises from several appealing features including (i) the maximum level of metal atom economy in relation to the catalysis, therefore securing best turnover frequencies (TOF); (ii) an increase in robustness; (iii) a direct handle on the metal atom properties by choosing the suitable coordinative environment, without the complicacy of adjacent metal atoms (as happens in nanoparticles).^[10]

The appropriate choice of supports for the formulation of SACs is pivotal to avoid common drawbacks, above all the instability or metal aggregation into clusters or nanoparticles.^[11] For this purpose, carbon nitrides (CNs) are rising as excellent photoactive hosts for the preparation of SACs, due to a firmer metal anchorage by their nitrogen-rich two-dimensional polymeric scaffolds. As an example, graphitic carbon nitride (g-CN), which is the most stable and most frequently investigated allotrope, consists of graphitic layers of N-bridged triazine or heptazine units, with a C/N ratio of about 3:4 (Figure 1).^[11]

In recent years, CNs have been employed as heterogeneous catalysts due to their environmental-friendliness, low

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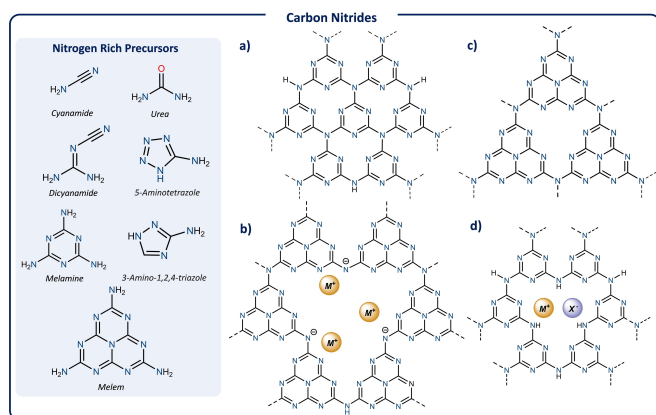
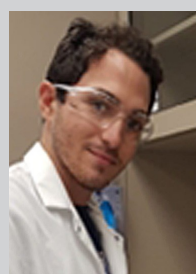


Figure 1. Left: commonly employed precursors in CNs synthesis. Right: a) Fully condensed triazine-based *g*-CN. b) metal-poly(heptazine imide) M-PHI. c) Fully condensed heptazine-based *g*-CN. d) poly(triazine imide) PTI/M⁺X⁻.

cost, outstanding catalytic performances and tuneable structure.^[4,13] Specifically, CNs have found applications in

several areas of catalysis, such as photo-, organo- and electrocatalysis (e.g., H₂ production, water oxidation, organic synthesis, CO₂ reduction).^[14,15] CNs can be obtained through simple and up-scalable calcination processes using abundant nitrogen-containing precursors, such as cyanamide, urea and melamine (Figure 1). Depending on the preparation protocols, CNs with different degrees of condensation, morphology and chemical nature can be produced.^[16] Due to the variety of synthetic approaches, the family of CN-based materials is extremely broad, spanning from *g*-CN and mesoporous *g*-CN (*mpg*-CN) to ionic CNs, such as potassium poly(heptazine imide), namely K-PHI, which bears negatively charged nitrogen atoms within their polymeric structures.^[13,15] Moreover, CNs' electronic and optical properties can be further tuned through other methodologies, including doping or post-synthetic modifications, that allow the *ad hoc* introduction of functionalities/defects in the structure,^[17–19] which can suitable anchor metal atoms.^[10,18,19] It is worth noting that the metal-support interactions, between the anchored single atoms and the CNs, lead to the formation of new electronic states, which modify the photocatalytic properties of the material.^[22] Although the use of



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carbon nitrides in organic photocatalysis is fairly recent, examples describing the applications of CN-based SACs for the effective production of relevant organic molecules have been reported in the last few years.^[20,23–26] Mechanistically, visible-light irradiation may induce electron transfer processes within the photocatalytic system, thus altering the oxidation state of surface metal atoms. Subsequently, these metal sites become capable of activating organic substrates eventually evolving in the formation of the desired products. Nevertheless, it is important to emphasize that the reaction mechanisms are still debated, and a better understanding of these photocatalytic processes is required. Moreover, it is likely that the actual mechanism strictly depends on the chemical nature of the reaction components and operative conditions. It is also important to highlight that in many cases, CN-based SACs show lower catalytic efficiencies when compared with homogeneous dual photocatalytic systems based on noble metal-complexes. Thus, a higher catalytic loading of the SACs is often necessary to achieve a satisfactory reactivity level.^[7] This Concept aims to illustrate the potential of carbon nitrides as hosts for non-precious metal-based SACs to drive organic transformations.

2. CN-Based SACs Preparation

The synthetic strategies for the production of CN derivatives containing surface metal atoms can be divided into two main classes: (i) “*in situ*” routes, where a the incorporation of the single metal occurs directly during CN synthesis (e.g., copolymerization, “*in situ*” doping), and (ii) “*ex situ*” methods, in which the metal ions are introduced in a second stage after the CN synthesis (e.g., wet chemical route) such as impregnation, optionally followed by thermal treatment (by heat or microwave), atomic layer deposition and photo-deposition (Figure 2).^[22,27–29]

A general comparison between the two approaches was attempted in a seminal work by Chen *et al.*, who studied the formation mechanisms of different CN-based SACs produced using five metals (Pd, Ag, Ir, Pt and Au).^[30] These materials were synthesized by “*in situ*” protocols that use co-polymerizable metal precursors or by employing “*ex situ*” approaches, namely wet deposition-reduction of suitable metal species. The authors showed that the “*in situ*” routes enable better flexibility for embedding different metals, whereas the post-synthetic approach allows enhanced control over the metal loading but it led in part to undesired nanoparticles formation.^[31] Interestingly, this comparison was carried out using different types of CNs (graphitic, mesoporous and exfoliated) to evaluate the role of the host morphology. In particular, the high surface areas of the mesoporous and exfoliated CNs increased the coordination and stabilization of single metal atoms on the supports.

In 2018, Perez-Ramirez and collaborators studied the production of SACs based on different carbon nitrides, providing relevant insights on the metal deposition step. Graphitic carbon nitride (*g*-CN), poly(triazine imide) (PTI),

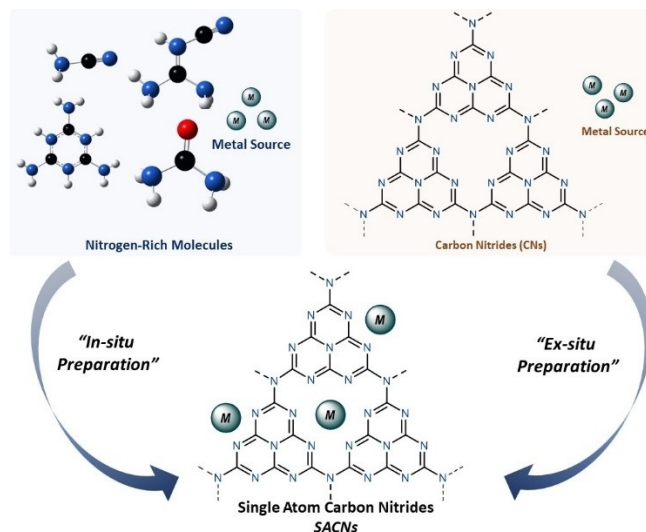


Figure 2. Schematic representation of “*in-situ*” and “*ex-situ*” strategies for SACNs preparation.

poly(heptazine imide) (PHI) were employed as supports for the introduction of palladium atoms through a microwave-assisted deposition protocol.^[20] It has been proved that a facilitated metal accommodation, observed for PTI and PHI, can be attributed to their larger cavity size and the presence of chloride ions, which results in higher resistance to sintering. Instead, palladium atoms bind weakly to *g*-CN, and their instability leads to the formation of undesired Pd nanoparticles. Another emerging “*ex situ*” strategy consists in the cation exchange method to embed metal single atoms using poly(heptazine imides).^[20,32] As an example, Colombari *et al.* reported Ru³⁺, Pt²⁺ and Ni²⁺ single-atom catalysts obtained through ion exchange of PHI.^[33] The incorporation of these transition metals allowed the tunability of various properties of the resulting materials, such as an altered lattice spacing between PHI layers and a change in the absorption bands.

These examples show the importance of engineering the host to improve the single atom formation and to modulate its loading and stability. In the case of CNs, this aspect needs to be investigated in depth, considering that the presence of suitable chemical functionalities on CN surface can be effective binding sites for the desired metal species. The *N*-rich structure of CNs is itself highly advantageous as host, exhibiting different nitrogen configuration, including graphitic-*N* and pyridinic-*N*. In addition, metals can be firmly entrapped on the edges and not homogeneously distributed on the entire materials due to the more accessible uncondensed –NH₂ moieties.^[34] To this regard, an appealing strategy could be represented by the amorphization of the CN material to make binding sites more available, following a disruption of the H bond that keep together the poly(heptazine) strands.^[18,35] The tuning of CN structure also includes the introduction of new functional groups on the surface by post-synthetic modifications. A common approach

is the chemical oxidation by strong acids and/or strong oxidants to install oxygenated moieties on the surface of the conjugated polymer and at the same time accomplish exfoliation of the CN material.^[36,37] Such oxygenated groups may also be deprotonated to form anionic basic sites and alter the binding energy.^[38] Besides, the addition of polar chemical functionalities can modulate the solvent and reactants affinity towards the CN surface, allowing for higher catalytic efficiency. Within this framework, an important challenge is the detailed understanding of the CN structure and the resulting metal-support interaction. It has become conventional to use atomic resolution electron microscopy, combined with extended X-ray absorption fine structure (EXAFS) studies, to claim the truly single atom nature of the metal.^[39–41] However, little experimental evidence is often provided to understand the exact interaction between the CN and the metal atoms. The specific CN moiety-M interaction deserves better attention, and state-of-the-art spectroscopic techniques such as nanoscale infrared spectroscopy (nanoIR), electron paramagnetic resonance (EPR), nuclear magnetic resonance (NMR) spectroscopy, X-ray photoelectron spectroscopy (XPS), aided by computational investigations, could bring an important contribution to elucidate the type of functional group, the M coordinative environment, and the electronic distribution within the material. In particular, density functional theory (DFT) calculations, using both periodic and molecular approaches, could help in providing useful insights on the chemical nature of defect and functionalities present on the CN surfaces, linking them to the photocatalytic features of the materials.^[42–44] All these conveying techniques will help a rational and purpose driven approach to the development of CN-based SACs.

3. Application of SACN Catalysts for Light-Driven Processes

The application of CN-based SACs in organic synthesis represents a new frontier in light-driven processes. Within this section, the importance of these heterogeneous dual catalytic systems will be emphasized through the discussion of some representative examples. Song and co-workers reported the preparation of a novel nickel-based single atom photocatalyst (*Ni-SACN-1*), using a *g*-CN obtained by calcination of urea and $\text{NiCl}_2 \cdot 6(\text{H}_2\text{O})$ as Ni source (Figure 3a).^[24] The nickel content in the final materials ranged from 0.04 wt% to 0.36 wt%. The presence of isolated Ni(II) atoms was confirmed by aberration corrected high-angle annular dark-field scanning transmission electron microscopy (AC-HAADF-STEM). The authors use this material to perform cross-coupling reactions between different alcohols **2** and various electron-deficient aryl halides **1** under visible-light irradiation using quinuclidine and imidazole as additives (Figure 3b). In all cases, the desired products **3** were obtained in good to excellent yields. Interestingly, water could be used as starting material to afford the corresponding phenol derivative **3c**.

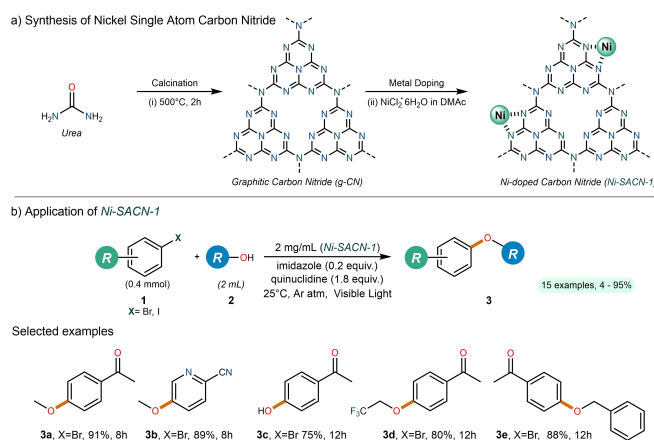


Figure 3. a) Synthesis of *Ni-SACN-1* from urea. b) Application of *Ni-SACN-1* in cross-coupling reaction of aryl halides with alcohols.^[24]

Disappointingly, a large excess of methanol was needed to obtain the model product **3a** in a satisfactory isolated yield (91%).

It is worth noticing that the coordination of Ni on the photoactive support could also be achieved directly by adding *g*-CN and the nickel source separately to the reaction mixture. The resulting heterogeneous material contained up to the 75% of the amount nickel used for its preparation. Nonetheless, the so-obtained material showed lower performances in the model cross-coupling reactions, both in terms of yield and selectivity when compared with *Ni-SACN-1*. However, it remains still unclear if the process involves the nickel metal in a fully heterogeneous mechanism or if a homogeneous contribution must be considered. This aspect represents one of the possible controversy of the semiconductor-metal dual catalysis, and it requires a combination of experiments to define the true mechanism. It is worth noticing that imidazole was needed as an auxiliary ligand to efficiently obtain the desired product. Inductively coupled plasma mass spectrometry (ICP-MS) analysis has also highlighted a lower stability of nickel on the photocatalyst when imidazole is present in the reaction mixture, suggesting a possible homogeneous step in the mechanism.

Following a similar synthetic approach, Reisner and co-workers prepared a nickel-deposited mesoporous carbon nitride (*Ni-mpgCN*), that was used as photocatalysts to drive the cross-coupling reactions between aryl halides **1** and alcohols **2** to give the corresponding aromatic ethers **3** (Figure 4b).^[25] The pre-photocatalyst was prepared from cyanamide using SiO_2 as a hard-templating agent to afford the mesoporous graphitic carbon nitride (*mpg*-CN, Figure 4a).^[45] Then, the nickel-deposited CN material was obtained through a microwave-assisted protocol using NiCl_2 in acetonitrile. Moreover, with the same Ni-photocatalyst, the authors conducted the amination of aryl halides **1** with sodium azide.^[46] The photoactive material could drive the amination of aryl halides **1** bearing electron-withdrawing groups providing the corresponding anilines **4** in good yields.

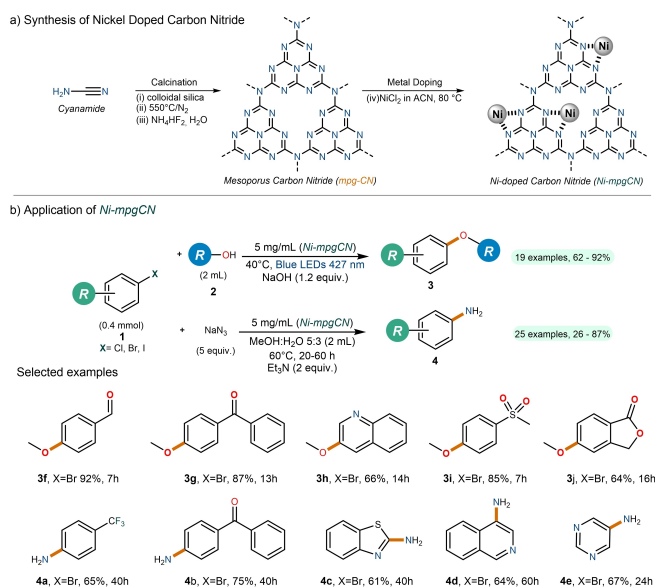


Figure 4. a) Synthesis of Ni-mpgCN from cyanamide. b) Application of Ni-mpgCN for the cross-coupling reaction of aryl halides with alcohols and amination reaction aryl halides with sodium azide.^[25,46]

Furthermore, electron-neutral or electron-donating groups were also tolerated, although a slower kinetic paired with incomplete conversion was observed (Figure 4b). Lastly, it should be noted that the authors have not conclusively demonstrated that the nickel is mainly present in the form of single atoms on the Ni-mpgCN surface. To this end, a combination of HAADF-STEM and EXAFS could have been employed to confirm the presence or absence of single metal atoms on the catalyst.

In 2022, Yoo and collaborators employed a wet impregnation synthetic protocol, which was followed by low-temperature calcination in a reductive atmosphere, to obtain a new Ni-single atom CN, labelled Ni-SACN-2 (Figure 5a).^[26] Ni-SACN-2 was used to catalyze the cross-coupling reaction between

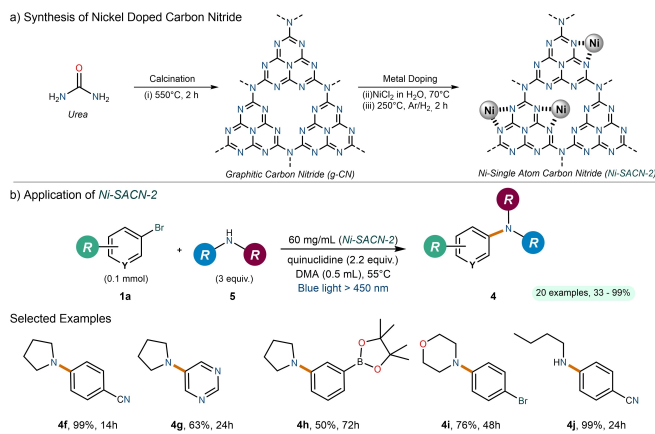


Figure 5. a) Synthetic scheme for Ni-SACN-2 preparation. b) Application of Ni-SACN-2 for the cross-coupling reaction of aryl bromides and secondary amines.^[26]

aryl bromides **1 a** and cyclic secondary amines **5** affording the corresponding aniline derivatives (**4**, Figure 5b).

It was demonstrated that the preassembled photocatalyst (Ni-SACN-2) provided the desired coupling products **5** with higher yield when compared to the reactions run with the nickel salt (NiCl₂) and g-CN added separately in the reaction mixtures. In this case, the higher performances of the Ni-SACN-2 can be attributed to different factors, including: (i) a faster photo-induced electron transfer process from the carbon nitride to nickel atom. In fact, this photochemical initiation process is drastically slowed down in the case of homogeneous complexes that have to diffuse toward the CN surface; (ii) the homogeneous nickel atoms not coordinated to the CN-based support can more easily aggregate leading to the catalyst deactivation in inactive nickel black.^[47]

In 2022, Teixeira and collaborators took advantage of ion-exchange strategy employing an ionic carbon nitride as a scaffold for the preparation of a single-atom catalyst based on iron (III), which is an inexpensive and abundant first-row transition metal.^[32] In this approach, sodium-poly(heptazine imides) (Na-PHI) was prepared from melamine precursor with sodium chloride (Figure 6a), and subsequently Fe-PHI materials were obtained by cation exchange using different concentration of FeCl₃·6(H₂O) to prepare catalysts with various Fe loadings (from 0.002 to 5 wt%). This material was then tested in the photo-oxidation of ethylbenzene **6a** to give acetophenone **7a**, using H₂SO₄ and pure molecular oxygen as green oxidants under blue light irradiation. Although the reaction scope is limited to a handful of substrates, the Fe-SACs with a Fe (III) of 0.1 wt% was able to effectively drive in a dual catalytic mode the oxidation of hydrocarbons **6** to the corresponding ketones in appreciable yields (Figure 6b).

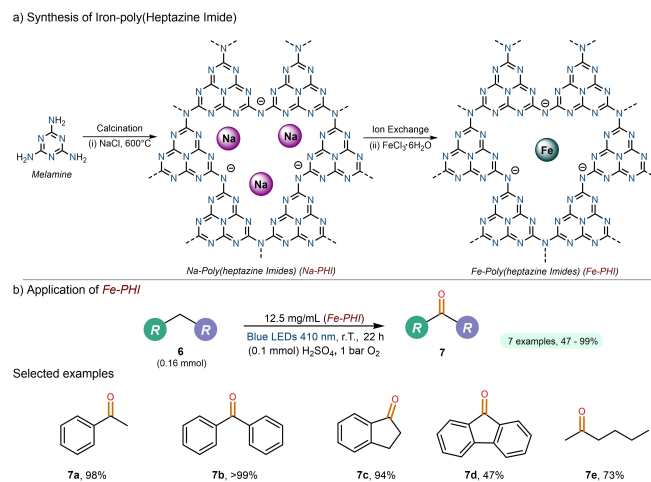


Figure 6. a) Work-flow for the preparation of Fe-PHI. b) Fe-PHI catalyzed oxidation of hydrocarbons.^[32]

4. Conclusions and Future Perspectives

This Concept mainly focused on the recent progresses toward the preparation and application of CN-based SACs to promote light-driven dual catalytic transformations of synthetic relevance. However, several unexplored opportunities and challenges remain unaddressed in this field. First, we foresee that a deep understanding of the nature of CN surface functionalities and defects has to be achieved. A thorough assessment of the binding sites on CNs, as well as determining their ability in complexing the metals, is crucial in the development of new and more active SACs. In fact, depending on the reaction conditions (substrates, solvents, temperature, source of photons, etc.) the leaching of the metal ions from the material surface could take place. This results in the deactivation of the SAC, thus hampering its reuse. Novel insights on the chemical structures of the CNs may be achieved through the combination of conventional (e.g., X-ray photoelectron spectroscopy) and advanced characterization techniques, including nanoIR, solid-state NMR spectroscopy (^{13}C and ^{15}N) and EPR.^[48] In this context, these advanced characterizations can help to evaluate the surface structural features arising from simple post-synthetic modifications of g-CN (for instance: thermal, reductive and oxidative treatments) giving new insights into metal coordination on host surface. This strategy, relatively unexplored to date, can lead to the manufacturing of novel photoactive materials with improved efficiency and industrially viable. The next coming years could usher in the era of industrial applications as manufacturing of durable single atom catalysts is perfected. Indeed, we believe that these heterogeneous photocatalytic systems, in combination with solar light, could be used for the large-scale productions of a number chemicals and materials of wide-spread use. This would fit most of the aspects of "green chemistry", where integrating sustainability criteria into chemical production is the core mission.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Carbon nitrides · Dual catalysis · Nanostructures · Photoredox catalysis · Synthetic methods

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