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Graphitic Carbon Nitride (g-C₃N₄) Based Heterogeneous Single Atom Catalysts: Synthesis, Characterisation and Catalytic Applications

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Abstract

Graphitic carbon nitride (g-C₃N₄), the well-known visible light active, two-dimensional organic semiconductor is gaining further prominence as a potential matrix for developing heterogeneous single atom catalysts. g-C₃N₄ by virtue of its abundant and periodically separated nitrogen atoms effectively stabilises single atoms of metal through the electron lone pairs of nitrogen acting as anchoring sites. Herein, the synthetic strategies adopted for the development of g-C₃N₄ based single atom catalysts (SACs) are summarised in detail for an understanding of the state-of-the-art designing of g-C₃N₄ SACs. Advanced characterisation techniques like Extended X-ray absorption fine structure (EXAFS), X-ray absorption near-edge structure (XANES), Electron energy-loss spectroscopy (EELS), X-ray photoelectron spectroscopy, and Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) offer valuable inputs to determine the electronic and geometric structure of g-C₃N₄ based SACs are discussed. Furthermore, the experimental and computational efforts carried out in demonstrating the potential applications of g-C₃N₄ SACs in the field of photocatalysis, organic reaction catalysis and electrocatalysis are reviewed. The challenges associated with the practical utility of g-C₃N₄ based SACs and their future perspectives in heterogeneous catalysis are outlined.

Key words: Single atom catalysts, Graphitic carbon nitride ($g\text{-C}_3\text{N}_4$), Extended X-ray absorption fine structure (EXAFS), X-ray absorption near-edge structure (XANES), Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), Photocatalysis, Electrocatalysis, Thermal catalysis

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1 Introduction

Heterogeneous catalysts comprising metal nanoparticles on supports are widely employed for accelerating the kinetics of industrially important reactions. Nevertheless, the full potential of such systems is hitherto unexploited as the atoms exposed only on the metal nanoparticle surface are active and the atomic utilisation of metal is low. Moreover, the predominant use of precious metals like Pt, Rh imparts exorbitant costs for heterogeneous catalysts. Single Atom Catalysts (SACs) or Atomically Dispersed Metal Catalysts (ADMCs) refer to an incipient class of materials where active centers of metals are individually dispersed on appropriate support through coordination with atoms like Nitrogen, Oxygen, Sulphur, etc. The partial positive charges on metal sites due to decreased electron density offer modified interactions thereby enhancing the rate of conversion of substrate into product. Furthermore, metal atoms in SACs/ADMCs are spatially isolated to influence the adsorption characteristics of reactive intermediates, thereby preventing the unwanted side reactions that proceed through adjacent metal sites. The development of SACs and ADMCs provides the most ideal strategy for creating catalysts that are cost-effective for a multitude of applications including photocatalysis, electrocatalysis and organic transformations.

One of the essential requirements for realisation of SACs is the effectiveness of coordination of metal centers with matrix/support atoms. The free energy of metal increases as it tends to manifest itself in the finest form and a strong coordination with support atoms is imperative to counter aggregation tendencies. In this context, 2D materials owing to their surface area and weak van der Waals forces possess significant advantages, to be employed as the matrices for SACs and ADMCs. Consequently, a host of supports like N-doped Carbon, graphene, and high surface area metal oxides are explored. More recently, 2D layered $g\text{-C}_3\text{N}_4$, an organic semiconductor was established as an effective candidate for visible-light induced photocatalysis by virtue of its band gap of 2.7 eV. $g\text{-C}_3\text{N}_4$ is constructed of layered

hexagonal building blocks of tri-s-triazine units and forms sheet-like pi conjugated structures composed of sp^2 C and sp^2 N.¹

The abundant nitrogen atoms in g-C₃N₄ facilitate the anchoring of single metal atoms through the effective coordination between empty (or partially empty) orbitals of metal atoms with the electron lone pairs of nitrogen. g-C₃N₄ has thus been demonstrated to be an excellent host for the development of SACs, despite its below average surface area. Atomic level dispersion of metal species over g-C₃N₄ results in the development of 6 major varieties of catalyst systems (Figure 1) depending upon the metal distribution and loading. The conventional terminology of g-C₃N₄ based single atom catalysts (SACs) refers to the ideal condition of uniformly dispersed, individual, isolated metal atoms coordinated to g-C₃N₄ matrix. In g-C₃N₄ based atomically dispersed metal catalysts (ADMCS), metal atoms are dispersed in the form of clusters containing dimers, trimers, etc along with isolated single metal atoms. More recently g-C₃N₄ based dual metal single atom catalysts emerged where two different metals are coordinated to the matrix as single atoms (DM-SACs). Ultra-high density single atom catalysts (UHD-SACs) refer to the atomic level dispersion of metal atoms at very high metal loading (>20 wt%) and with ultrahigh atom density (5–15 atoms nm⁻² at a spacing of 0.2–0.5 nm).² Depending upon the positioning of single atoms on g-C₃N₄ matrix two more classifications are reported. In edge confined single atom catalysts (EC-SACs) the metal atoms are preferentially located at the edges of g-C₃N₄ sheets through unsaturated vacancies along the edges. On the other hand, in interlayer coordinated SACs (ILC-SACs), confinement of the single atoms occurs in between the layers of g-C₃N₄ through coordination with appropriate functional groups.

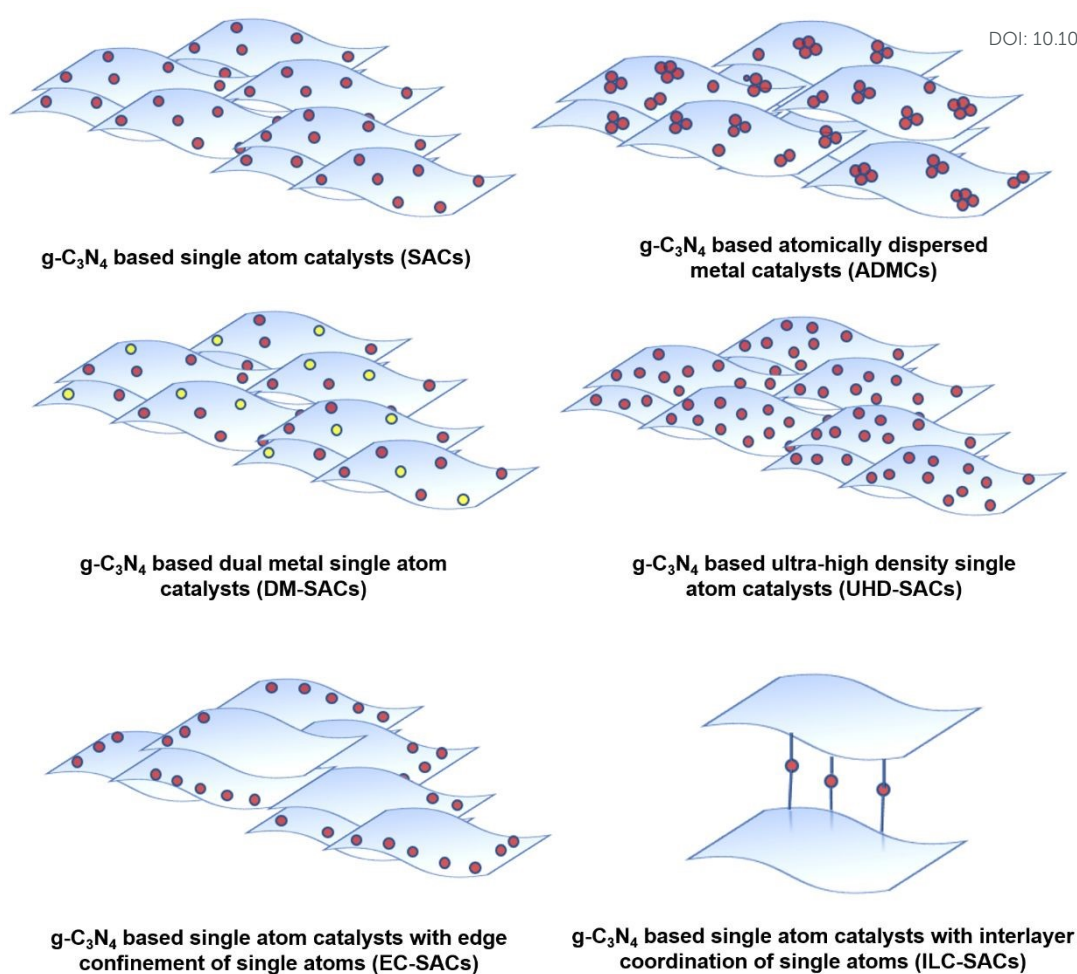


Figure 1. Various configurations of metal atom dispersions over g-C₃N₄ matrix

The chronology of developments leading to the establishment of SACs based on g-C₃N₄ is provided in the timeline below (Figure 2)

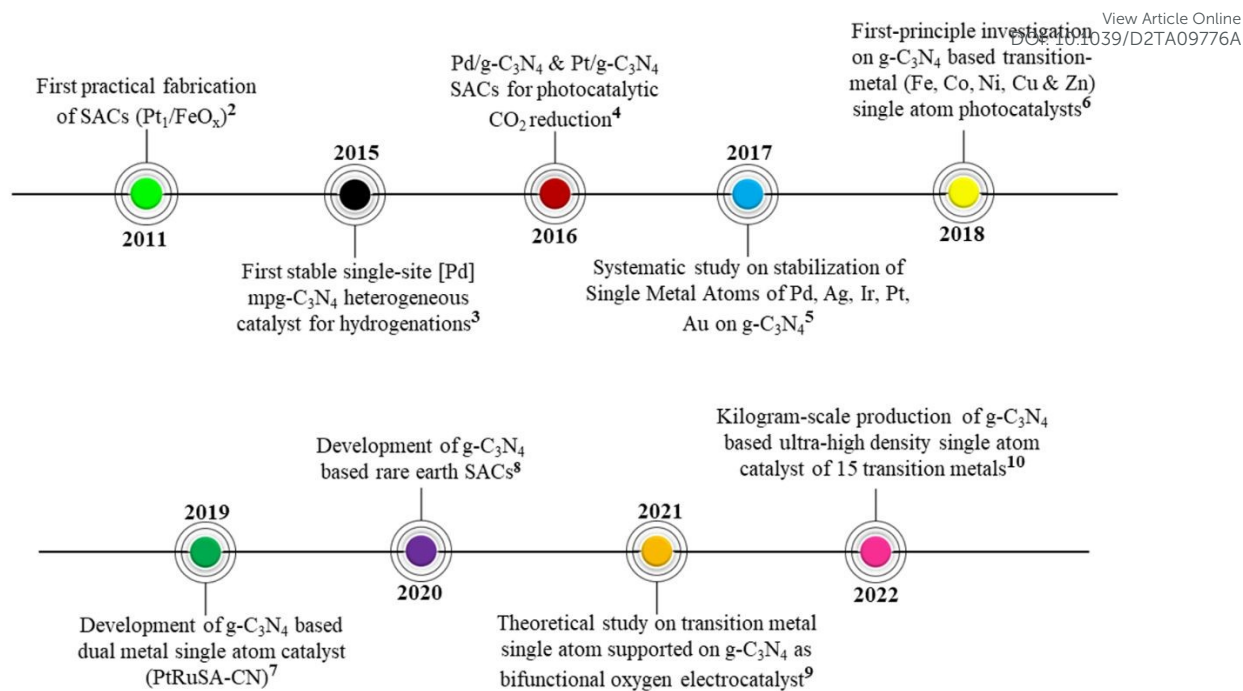


Figure 2. Timeline representing the chronology of advancements in SACs based on g-C₃N₄³⁻¹¹.

In this review, we attempt to comprehensively analyse the developments based on g-C₃N₄ supported single atom catalysts (SACs) and cover its applications in the areas of photo, electro and thermal catalysis. A tutorial like description of the fundamental aspects related to the synthesis and characterisation of g-C₃N₄ SACs is included. DFT studies in the reported works are also incorporated primarily to throw light on the prospective experimental works that can be pursued. To the best of our knowledge, this review is the first attempt to cover all the applications thus far explored on g-C₃N₄ SACs.

2 Graphitic carbon nitride as support for SACs

g-C₃N₄ consists of s-triazine or tri-s-triazine rings as the basic constituent units that offer uniformly placed, abundant nitrogen atoms to confine single metal atoms effectively and with high loading. The terminal tri-s-triazine unit of g-C₃N₄ comprises different types of nitrogen as presented schematically in Figure 3.¹² The various N-species in g-C₃N₄ are demonstrated to be very effective for catalytic reactions as they impart H-bonding, tunable basicity, Lewis acidity. Strong metal-support interaction is essential to stabilise the well-dispersed metal species as isolated single metal atoms for imparting selectivity

and catalytic activity. This will also prevent the diffusion and aggregation of single atoms at the time of synthesis as well as during the utilisation of SACs at various reaction conditions. This is primarily facilitated by the substantially greater surface energy of metal single atoms compared to their nanoclusters and nanoparticles.¹³

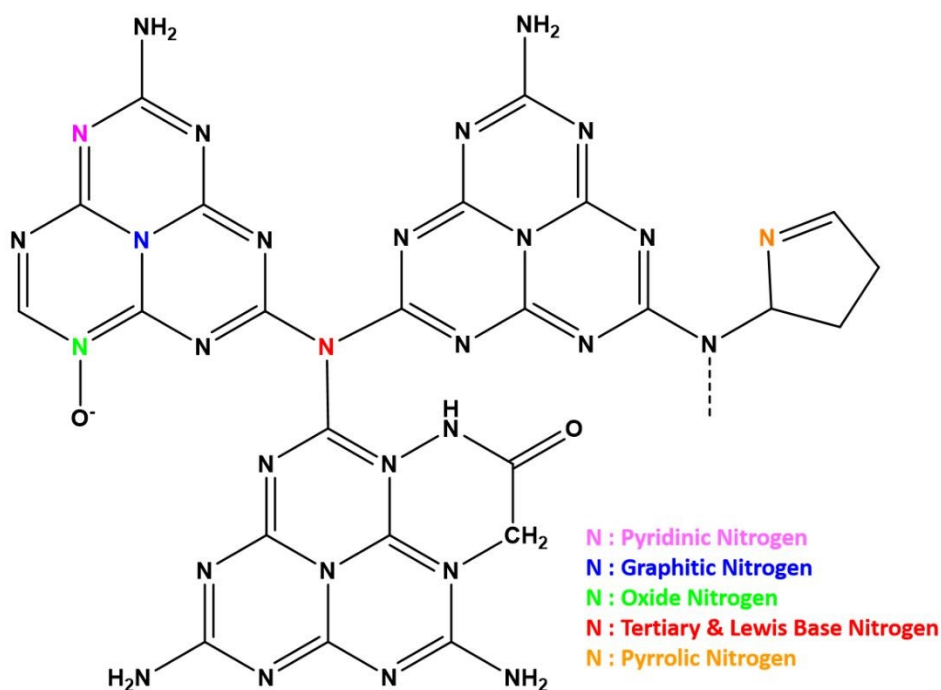


Figure 3. Types of nitrogen functionalities in g-C₃N₄

Synthesis of g-C₃N₄ is carried out by thermal decomposition and polymerisation of N-rich precursors like melamine, cyanamide, dicyandiamide, urea, thiourea and their mixtures at 550 °C in air,¹⁴ as shown schematically in Figure 4. The bulk material formed at 550 °C is similar irrespective of the atmosphere of firing but may differ in the degree of condensation and product yield. Generally, all the precursors first condense to melamine at 235 °C followed by a self-condensation leading to the formation of a dimer called melam (N₂-(4,6-Diamino-1,3,5-triazin-2-yl)-1,3,5-triazine-2,4,6-triamine). Essentially melamine (triazine) based structures are formed up to a temperature of 350 °C. At 390 °C melam units are converted into tri-s-triazine units called melem by the rearrangement of melamine. Finally, the networked polymeric g-C₃N₄ is formed by the successive condensation of melem units at 520 °C. The material is unstable above 600 °C and complete decomposition to volatile components occurs at temperatures >700 °C in

air.¹⁵ Template assisted thermal polymerisation of $g\text{-C}_3\text{N}_4$ precursors results in the formation of mesoporous polymeric $g\text{-C}_3\text{N}_4$ (mpg- C_3N_4) with enhanced surface area. Thermal exfoliation of bulk $g\text{-C}_3\text{N}_4$ (BCN) leads to the formation of $g\text{-C}_3\text{N}_4$ nanosheets/ Exfoliated $g\text{-C}_3\text{N}_4$ (ECN) with improved surface area. All the 3 forms of $g\text{-C}_3\text{N}_4$ i.e., BCN, mpg- C_3N_4 , ECN can perform as a support for SACs.

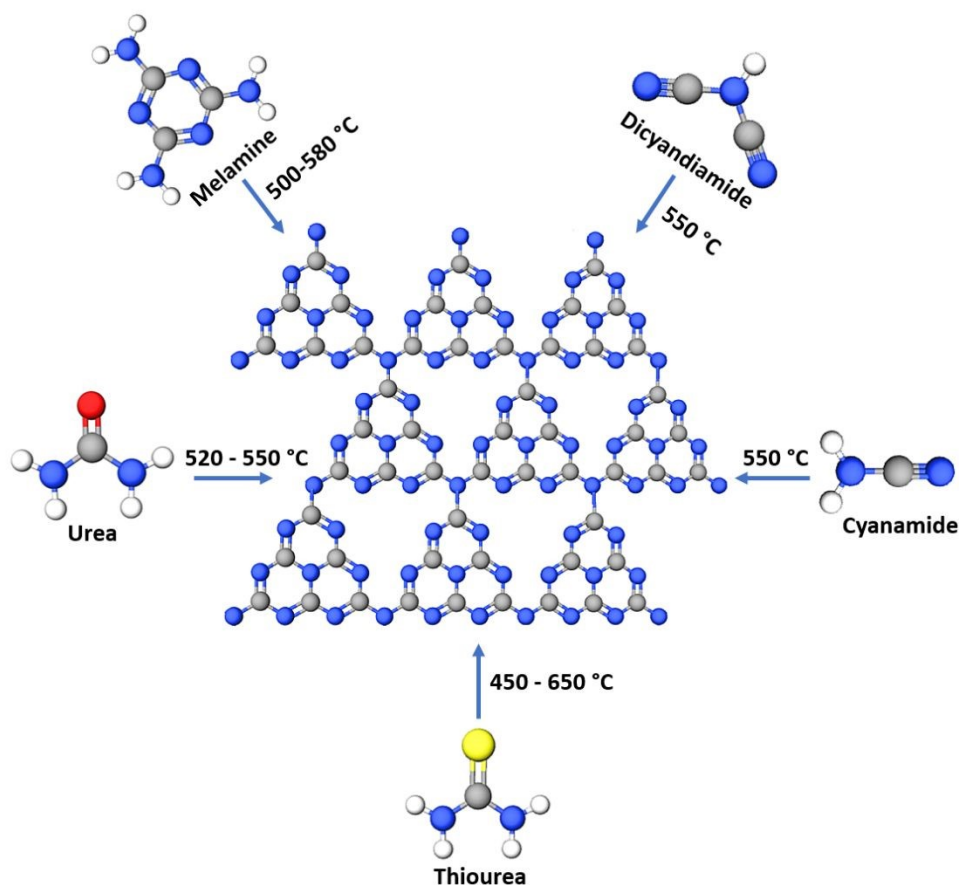


Figure 4. Synthesis of $g\text{-C}_3\text{N}_4$ from various nitrogen abundant precursors

3 Synthesis of $g\text{-C}_3\text{N}_4$ based single atom catalysts

Pérez-Ramírez et al proposed direct and post-synthesis approaches for $g\text{-C}_3\text{N}_4$ based SACs. Direct synthesis involving the pyrolysis of the $g\text{-C}_3\text{N}_4$ precursors with metal salts is a bottom-up approach. During the polymerisation of $g\text{-C}_3\text{N}_4$ from precursors, single metal atoms are anchored on to the $g\text{-C}_3\text{N}_4$ support. Post synthesis is a strategy employed to disperse single atoms on synthesised $g\text{-C}_3\text{N}_4$ types like bulk $g\text{-C}_3\text{N}_4$, mpg- C_3N_4 , ECN, etc which are prepared either through template free or template assisted synthesis strategy.⁶ Figure 5 depicts the multiple approaches involved in both the above categories for the preparation of $g\text{-C}_3\text{N}_4$ SACs.

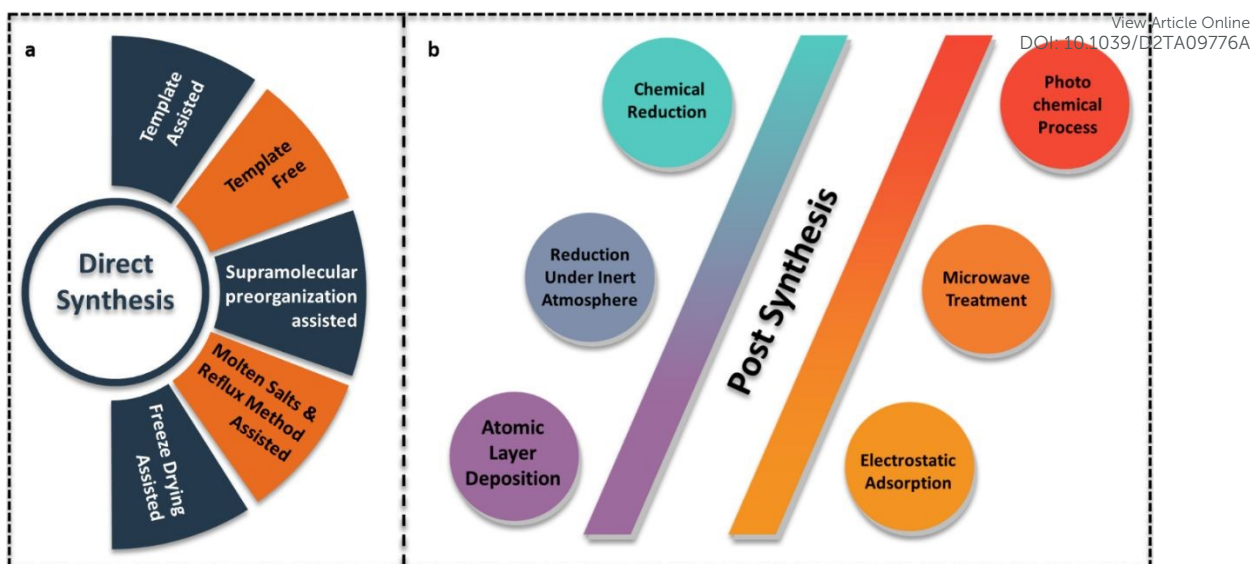


Figure 5. Various strategies employed during (a) direct and (b) post synthesis of $g\text{-C}_3\text{N}_4$ SACs

3.1 Direct synthesis

3.1.1 Template free direct synthesis

Template free direct synthesis involves the pyrolysis of the mixture containing $g\text{-C}_3\text{N}_4$ precursor and a corresponding metal salt. Dong et al demonstrated the synthesis of rare-earth La single-atoms dispersed carbon nitride (O/La-CN) by the one-step calcination of $\text{La}_2(\text{CO}_3)_3$ and urea at $550\text{ }^\circ\text{C}$ resulting in amorphous $g\text{-C}_3\text{N}_4$ with homogeneously dispersed La single atoms (Figure 6(a)).¹⁶

3.1.2 Template assisted direct synthesis

Template assisted direct synthesis involves the pyrolysis of $g\text{-C}_3\text{N}_4$ precursor with metal salt in the presence of templates like silica, SBA-15, etc. to arrive at mpg- C_3N_4 as the support for single atoms. Dontsova et al demonstrated the synthesis of single atom silver dispersed mpg- C_3N_4 (AgTCM-mpg-CN) through the pyrolysis of the precursor mix containing cyanamide and silver Tricyanomethanide (AgTCM) in the presence of SiO_2 nanoparticles as the template leading to AgTCM-mpg-CN with enhanced surface area. The use of AgTCM as a reactive co-monomer facilitated silver doping as negative charges are introduced into the C_3N_4 framework which provided strong binding sites for Ag single atoms. The template assisted direct synthesis required the removal of the SiO_2 template using NH_4HF_2 .¹⁷

3.1.3 Molten salts and reflux method assisted direct synthesis

Xiang et al demonstrated the preparation of single Cu atoms dispersed over crystalline g-C₃N₄ through molten salt and reflux method assisted direct synthesis (Figure 6(b)). Cu atoms are incorporated into the framework of melamine by mixing melamine and CuCl₂ in the presence of HCl forming [H₂mela]₂[CuCl₅]Cl (where 'mela' is depicted as melamine) comprising of negatively charged layers of [CuCl₅]_n³ⁿ⁻Cl⁻ ions are then removed from [H₂mela]₂[CuCl₅]Cl during the second step of the synthetic procedure. Subsequent polymerisation of melamine formed g-C₃N₄ with heptazine basic units which on molten salt treatment with KCl and LiCl followed by sulphuric acid leaching led to the formation of crystalline g-C₃N₄ with atomically dispersed Cu atoms.¹⁸

3.1.4 Supramolecular preorganisation assisted direct synthesis

Chen et al synthesised g-C₃N₄ with atomically dispersed cobalt through supramolecular preorganisation followed by calcination. The reaction of dicyandiamide with nitric acid led to the formation of dicyandiamidine nitrate precursor which self-assembled intermolecularly with dicyandiamide resulting in the formation of a crimped supramolecular precursor. The thermal treatment of supramolecular precursor together with cobalt chloride led to the formation of g-C₃N₄ matrix embedded with atomically dispersed Co species (Figure 6(c)).¹⁹

3.1.5 Freeze drying assisted direct synthesis

Freeze drying assisted direct synthesis facilitates atom confinement and coordination (ACC) (Figure 6(d)). Wang et al employed this ACC strategy to synthesise high density rare-earth single-atom Er catalyst using g-C₃N₄ support. Melamine sponge soaked in an aqueous solution containing erbium salt (Er(NO₃)₃·5H₂O) and urea is frozen by liquid N₂ for an evenly distributed concentration of the precursors. The complete moisture removal from the frozen sponge is ensured by freeze drying, and the sample is annealed under N₂ to form erbium single atoms decorated g-C₃N₄ with tubular morphology (Er₁/CN-NT). The nitrogen atoms present in melamine sponge and urea enable the coordination of erbium atoms and the employment of ultralow temperatures of liquid N₂ and freeze drying facilitates the atomic confinement of Er forming the formation of low- and high-density Er₁/CN-NT.⁹

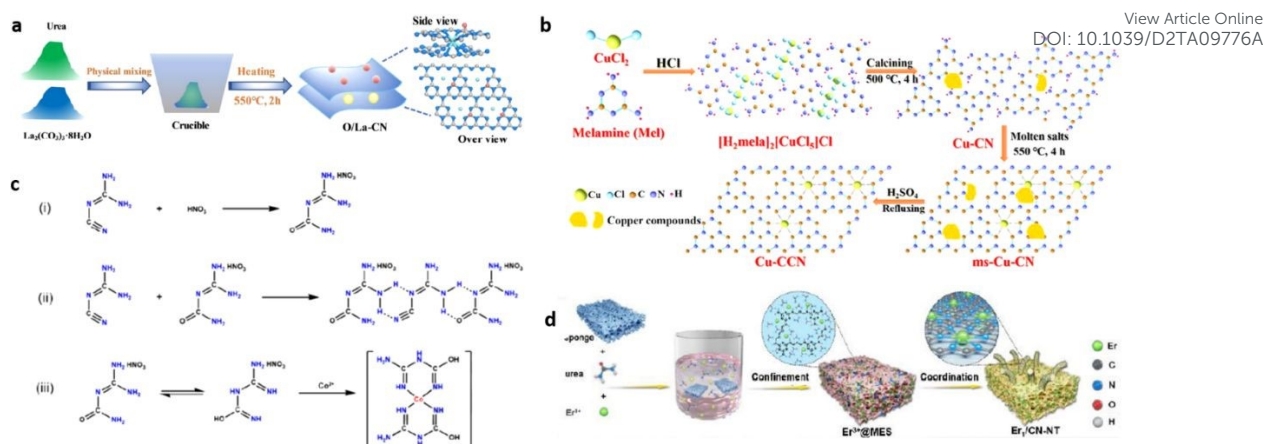


Figure 6. (a) Template free direct synthesis of La single-atoms dispersed carbon nitride (O/La-CN). Reproduced with permission from ref. 16. Copyright 2020 American Chemical Society. (b) Direct synthesis of single Cu atoms supported crystalline $\text{g-C}_3\text{N}_4$ (Cu-CCN) through molten salts-reflux method. Reproduced with permission from ref. 18. Copyright 2020 American Chemical Society. (c) Mechanism of supramolecular preorganization of $\text{g-C}_3\text{N}_4$ based cobalt SAC. Reproduced with permission from ref. 19. Copyright 2020 Elsevier. (d) Freeze drying assisted direct synthesis of erbium single atoms decorated $\text{g-C}_3\text{N}_4$ ($\text{Er}_1/\text{CN-NT}$). Reproduced with permission from ref. 9. Copyright 2020 John Wiley and Sons.

3.2 Post synthesis

Use of template like silica, SBA-15, etc during the pyrolysis of $\text{g-C}_3\text{N}_4$ precursors, forms mpg- C_3N_4 with enhanced surface area. Exfoliated $\text{g-C}_3\text{N}_4$ is obtained through thermal or chemical exfoliation. Post synthesis strategy involves the mixing of metal salts in $\text{g-C}_3\text{N}_4$ dispersion and its conversion to single metal atoms using techniques like chemical reduction, reduction under an inert atmosphere, photochemical reduction, microwave treatment, electrostatic adsorption, and atomic layer deposition (ALD).

3.2.1 Chemical reduction

Chemical reduction involves the usage of chemical reducing agents such as NaBH_4 for the deposition of metal as single atom. Pérez-Ramírez et al demonstrated this post synthetic strategy for the incorporation of single metal atoms of Pt, Ir, and Pd on $\text{g-C}_3\text{N}_4$ of varying morphologies (Bulk $\text{g-C}_3\text{N}_4$, mpg- C_3N_4 , ECN). A sequential wet deposition/wet impregnation–chemical reduction approach (NaBH_4) employing metal

salts of Pd/Pt/Ir (PdCl_2 , $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$, $\text{K}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$) yielded g- C_3N_4 SACs with a metal loading of 0.5 wt%.⁶

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3.2.2 Microwave treatment

Li et al showed the formation of single Co single atoms on mpg- C_3N_4 by microwave assisted thermal treatment of a precursor mix containing CoCl_2 , g- C_3N_4 , triethylamine (TEA). TEA enhanced the deposition of Co^{2+} with the increase of CoCl_2 content and cobalt loading upto 0.430 $\mu\text{mol}/\text{mg}$ of mpg- C_3N_4 was achieved. However, a cobalt content of 0.016 $\mu\text{mol}/\text{mg}$ was only achieved without TEA despite the use of large excess of CoCl_2 .²⁰

Similarly, Radek Zbořil and co-workers successfully employed microwave heating assisted post synthesis strategy for the development of ruthenium single atom dispersed mesoporous g- C_3N_4 catalyst (Figure 7(a)).²¹

3.2.3 Electrostatic adsorption

Liu et al developed $\text{Au}_1\text{N}_x/\text{C}_3\text{N}_4$ SACs through the post synthesis strategy involving electrostatic adsorption (Figure 7 (b)). g- C_3N_4 derived from urea precursor is treated with ammonia solution to develop surface positive charges, which on subsequent reaction with HAuCl_4 forms Au_1N_x single-sites over g- C_3N_4 .²² In a similar approach, single atom $\text{Pt}^{\text{II}}-\text{C}_3\text{N}_4$ catalyst was also developed by the same group.²³

3.2.4 Atomic layer deposition (ALD)

ALD is also employed as a post synthetic strategy to develop g- C_3N_4 SACs. Yao et al deposited Co single atoms over surface functionalised g- C_3N_4 . Prior to Co ALD, phosphorous doping (phosphidation) using sodium hypophosphite as the non-metal, alters the surface functionalities as well as porous structure of the g- C_3N_4 matrix via CoP_4 center formation. ALD using Cobalt bis(Cyclopentadienyl) followed by O_3 treatment led to the formation of a single Co_1-N_4 site over the matrix with a cobalt loading of 1 wt%.²⁴

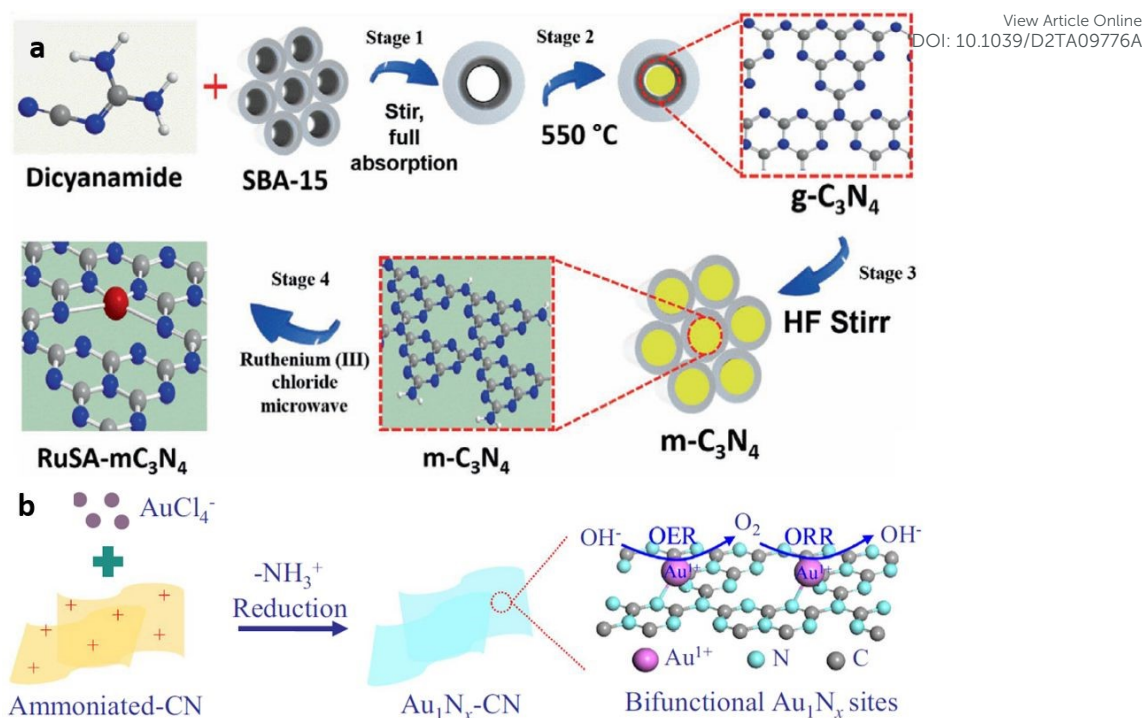


Figure 7. (a) Schematic of microwave assisted post synthetic strategy for the development of ruthenium single atoms decorated mesoporous C_3N_4 (RuSA- mC_3N_4) catalyst. Reproduced with permission from ref. 21. Copyright 2021 John Wiley and Sons. (b) Schematic of electrostatic adsorption mediated post synthetic strategy for Au_1N_x single-site/ C_3N_4 catalyst synthesis. Reproduced with permission from ref. 22. Copyright 2018 Elsevier.

3.2.5 Photochemical reduction

Guo et al synthesised Pt single atoms on N-deficient g- C_3N_4 employing a photochemical process involving the mixing of H_2PtCl_6 with an aqueous dispersion of g- C_3N_4 . Freezing under liquid N_2 temperature followed by photochemical reduction with UV light resulted in the formation of single atom Pt decorated nitrogen deficient g- C_3N_4 . On the contrary, g- C_3N_4 loaded with Pt nanoparticles was formed when the reduction was conducted without liquid N_2 assisted freezing.²⁵

3.2.6 Reduction under an inert atmosphere

Chen et al successfully demonstrated the development of single atom Au supported on mpg- C_3N_4 with a metal loading of 0.0519 wt %. $HAuCl_4$ is added to an aqueous dispersion of mpg- C_3N_4 and the resulting product is annealed at the low temperature of 100°C under an inert atmosphere of H_2/Ar . The Au ions are thus reduced to single Au

atoms and the Au loading in the catalyst is regulated by changing the annealing temperature.²⁶

Ultra-high density single atom catalysts (UHD-SACs) by atomic level dispersion of 15 transition metals on suitable supports having different structural and chemical characteristics were illustrated recently by Lu and co-workers. Consequently, UHD-SACs on supports like N doped carbon (NC), polymeric C₃N₄ (PCN) and metal oxide (CeO₂) were developed through a post synthetic strategy involving the impregnation of aqueous solutions of metal salts on supports followed by two-step annealing under inert atmosphere to realise a metal loading up to 23 wt%. The two-step annealing process facilitated the removal of ligands from metal precursors in a controlled manner and selectively coordinated metal ions to all the available anchoring sites present on the support surface to realise ultra-high metal loading. The first annealing step was done at temperatures (T₁) lower than the decomposition temperatures of the metal salts under an inert atmosphere. The unbound metal species were removed by washing to prevent the aggregation and sintering of the metal species in the subsequent annealing step. Further, the second stage of annealing at a higher temperature (T₂) completely removed the remaining ligands and transformed the chemisorbed metal species into highly stable UHD-SAC systems. The above two-step annealing strategy enabled the kilogram-scale production through robot assisted-automatic synthesis taking Ni UHD-SAC on PCN as a case study.¹¹

Table 1 summarises the synthesis strategies with their attributes. In comparison, the direct synthesis route is more beneficial than post synthesis route to achieve g-C₃N₄ SACs with high metal content. Post synthetic methods suffer from the drawback of promoting aggregation leading to nanoparticle formation at high concentrations of the localised metal species. On the other hand, direct synthesis methodologies enable uniform distribution of single atoms but are susceptible to reduced atom efficiency owing to the entrapment of metal in the support matrices.

Table 1 Common synthetic approaches for g-C₃N₄ based SACsView Article Online
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Synthesis	Techniques	Remarks
Direct Synthesis	<ul style="list-style-type: none"> • Template free synthesis • Template assisted synthesis • Molten salts & reflux method assisted synthesis • Supramolecular preorganisation assisted synthesis • Freeze drying assisted synthesis 	<ul style="list-style-type: none"> • Effective stabilisation of single atoms as coordination occurs along with polymerisation of g-C₃N₄ precursors • High & ultra-high metal loading can be realised • Easily scalable & low cost • Necessarily involves high temperature pyrolysis (550 – 600 °C) • Possibility for entrapment of metal in the matrix
Post synthesis	<ul style="list-style-type: none"> • Chemical reduction • Reduction under an inert atmosphere • Photochemical reduction • Electrostatic adsorption • Microwave treatment (MW) • Atomic layer deposition (ALD) 	<ul style="list-style-type: none"> • Better control of the textural properties like surface area • Low metal loading in general • Metal-support interaction is weak compared to direct synthesis • MW & ALD are hardware intense

4 Analytical tools for understanding g-C₃N₄ based single atom catalysts

The atomically dispersed metal species over g-C₃N₄ matrix, act as a catalytically active centre for facilitating various catalytic reactions. It is imperative to cognise the atomic and electronic structure of the single atom sites of SACs to elucidate the mechanism governing its catalytic activity. Various analytical tools have thus been employed to substantiate the occurrence of metal species in single atom configuration, to determine its distribution over g-C₃N₄ matrix and its coordination environment. In this section, we examine the various characterisation techniques used for analysing g-C₃N₄ SACs and the elucidation of data from those techniques (Figure 8).

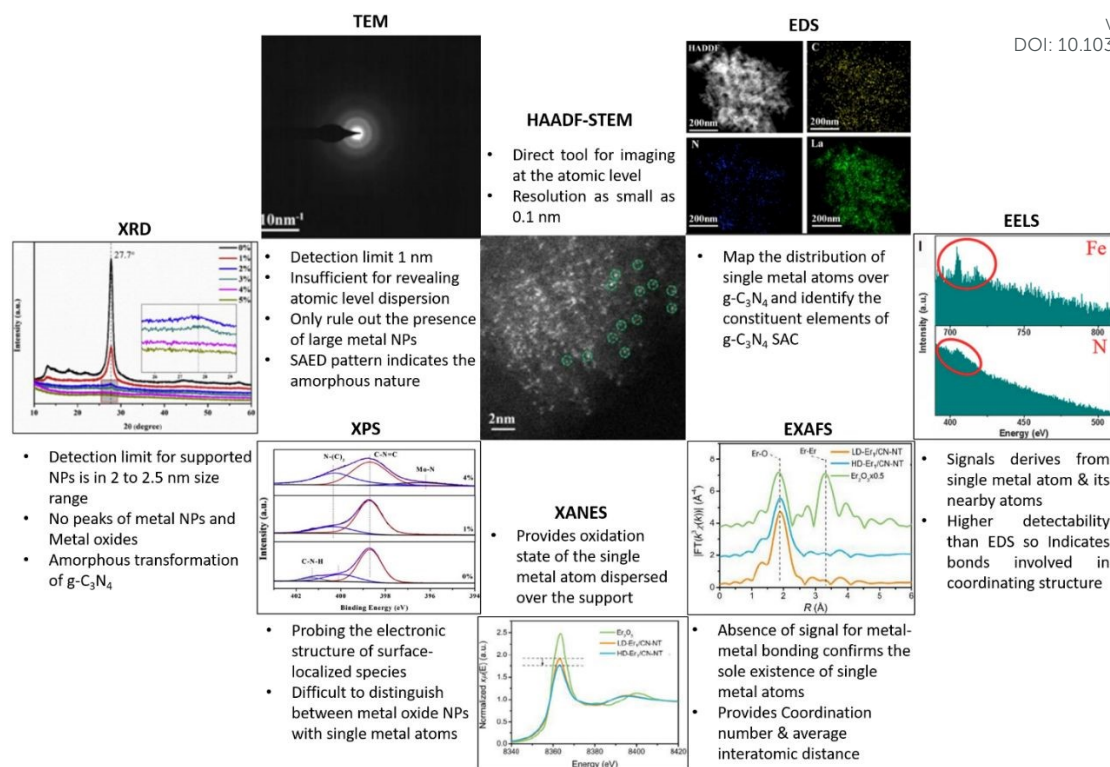


Figure 8. Various analytical tools for the characterisation $g\text{-C}_3\text{N}_4$ based SACs. Reproduced with permission from ref. 9. Copyright 2020 John Wiley and Sons. Reproduced with permission from ref. 16. Copyright 2020 American Chemical Society. Reproduced with permission from ref. 27. Copyright 2019 Elsevier. Reproduced from ref. 28.²⁸

4.1 XRD analysis

The detection limit of conventional X-ray powder diffraction for supported nanoparticles is often set at 2–2.5 nm size range, below which low signal to noise ratios make size detection challenging.²⁹ Absence of peaks in the XRD pattern of $g\text{-C}_3\text{N}_4$ based SACs merely rules out the existence of metal NPs and metal oxides, but not confirming the formation of metal single atoms. $g\text{-C}_3\text{N}_4$ exhibit two characteristic XRD diffraction peaks at 2θ values of 13.3° and 27.8° are attributed respectively to the in-planar structural packing of (100) crystallographic plane and the (002) lattice plane corresponding to the interplanar stacking of aromatic systems.³⁰ Due to the atomic level dispersion of single atoms over $g\text{-C}_3\text{N}_4$ matrix, the above characteristic XRD peaks diminish. For e.g., Zhou and co-workers reported the complete disappearance of peaks when the Mo loading is

increased to 4% (Figure 9 (a)). The long-range order of g-C₃N₄ is thus disturbed inducing the amorphous transformation of g-C₃N₄.²⁷

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4.2 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) is extensively employed for the morphological and structural identification of material. However, the conventional TEM of nanoscale resolution is insufficient for imaging single-atoms as its normal detection limit is ≈ 1 nm. A combination of high-resolution TEM imaging and SAED imaging is commonly used to rule out the presence of large metal NPs in a given area of the SAC sample.^{13, 31} Nevertheless, the mentioned tools cannot be used to confirm the absence of NPs in the bulk sample. Additionally, the absence of lattice fringes and diffractions in HRTEM image and the selected area electron diffraction (SAED) pattern confirm the amorphous nature, as has been demonstrated by Dong et al in g-C₃N₄ system with atomic level dispersion of La (O/La-CN) (Figure 9b (i-ii) & Figure 9b (iv)).¹⁶

4.3 Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM)

Recent developments in the field of electron microscopy have led to the emergence of aberration-corrected high-angle annular dark-field imaging scanning TEM (HAADF-STEM), with a resolution as small as 0.1 nm providing atomic scale information.³² Single metal atoms are identified on supports with the aid of HAADF-STEM with aberration correctors, provided the atomic number of the metal atom of interest is much higher than the constituent element of the supports. The single-atoms dispersed on the g-C₃N₄ matrix and its spatial distribution can be directly imaged using aberration corrected HAADF-STEM analysis.³³ For example, HAADF-STEM imaging and the associated analysis of rare-earth La single atoms on carbon nitride (O/La-CN) (Figure 9 b (iii) and Figure 9 b (vi-viii)) revealed the existence of single La atoms over g-C₃N₄ matrix.¹⁶

4.4 Energy-dispersive X-ray spectroscopy (EDS) and Electron energy-loss spectroscopy (EELS)

Energy-dispersive X-ray spectroscopy (EDS) and/or electron energy-loss spectroscopy (EELS) are always used in conjunction with STEM for validating the composition of the synthesised g-C₃N₄ SACs.^{34, 35} Energy-dispersive X-ray spectroscopy (EDS/EDX)

together with HAADF-STEM is used to map the distribution of single metal atoms over $g\text{-C}_3\text{N}_4$ matrix and to identify the constituent elements. The energy-dispersive spectroscopy (EDS) mapping of O/La-CN confirmed the uniform distribution of La, N and C elements in the $g\text{-C}_3\text{N}_4$ framework (Figure 9 b(v)). EELS spectra derived from the positioning of an electron probe directly over a single atom can deliver information about the coordination environment by nearest neighbouring atoms. EELS spectra of O/La-CN from two selected locations are compared in (Figure 9 c). The presence of N and La atoms in this location, with no evident O, suggests La-N coordination structure.¹⁶

HAADF-STEM in combination with EDS/EELS allows the direct visualisation of single atoms only in a limited area and cannot provide conclusive evidence for the absence of metal nanoparticles in the bulk of the material. So, it's critical to analyse microscopic observations in conjunction with spectroscopic tools that could provide overall information about SACs such as chemical and electronic structure, coordination environment of $g\text{-C}_3\text{N}_4$ based SACs. X-rays, owing to their short wavelength (0.01–1 nm), are the most suitable source for atomic scale structural information, X-ray Absorption Spectroscopy (XAS) is thus used to detect the detailed coordination environment of single atoms. Spectroscopic techniques, in comparison with microscopic tools, can better resolve elements of similar atomic weights (e.g., N and C, Co and Mo) and can thus be utilised to derive qualitative and quantitative information about the valence state of single atoms.³⁶ In situ and operando characterisations are enabled in XAS as it can operate without ultrahigh vacuum requirements. Similarly, X-ray photoelectron spectroscopy (XPS) measurements can identify the variations in surface composition and valence state.³⁷

4.5 X-ray photoelectron spectroscopy (XPS)

XPS is an essential characterisation tool for probing the electronic structure of surface-localised species and for determining the valence states of surface elements. Single metal atoms supported on 2D matrices normally possess partial (or full at times) positive charge due to the strong covalent coordination or ionic interaction with neighbouring surface atoms or ligands. The heterogeneity/homogeneity of single atom species is mostly identified through a singlet peak in the XPS analysis which indicates a unified positive charge for the metal elements.^{38, 39}

XPS analysis of a single Mo atom dispersed on g-C₃N₄ matrix (a-Mo/C₃N₄, where a (0–4%)) revealed the amorphous transformation of g-C₃N₄ due to atomic level dispersion of Mo atoms over the matrix. The C1s spectra of pure g-C₃N₄ exhibit peaks at 284.8 eV and 288.2 eV which are attributed to the adventitious C contamination and C-N bonds respectively. For a-Mo/C₃N₄, the peak at 284.8 eV related to the C-C bond has grown significantly, and the peak of the C-N bond has shifted to 287.8 eV. The “outward twisting of melon units” and the hydrogen bond cleavage of polymeric strands of melon units are responsible for these changes in the XPS spectra, confirming that g-C₃N₄ has undergone an amorphous transformation. The high-resolution N1s XPS spectra of g-C₃N₄ displayed peaks corresponding to C-N-C bond and N-(C)₃ bond, and C-N-H bond at 398.7 eV, 400.1 eV, and 401.3 eV respectively. The dispersion of Mo single atoms induces the disappearance of C-N-H bond peak due to the above-mentioned H-bond cleavage. A new peak for a-Mo/C₃N₄ can be seen at 396.2 eV, which is derived from the Mo-N bond, demonstrating the creation of the Mo-N bond after the insertion of Mo atoms. The O1s spectra of pure g-C₃N₄ have a peak at 532.0 eV due to the C-O bond, and a second peak at 531.1 eV appears due to the -OH bond during the formation of Mo single atoms from ammonium molybdate precursor. Furthermore, Mo(VI) and Mo(V) 3d_{3/2} orbitals are evidenced by peaks at 235.4 and 234.3 eV respectively, while Mo(VI), Mo(V), and Mo(IV) 3d_{5/2} orbitals are confirmed from peaks at 232.4, 231.1, and 229.7 eV, revealing the abundant valence state of Mo in a-Mo/C₃N₄ (Figure 9 d(i-iv)).²⁷

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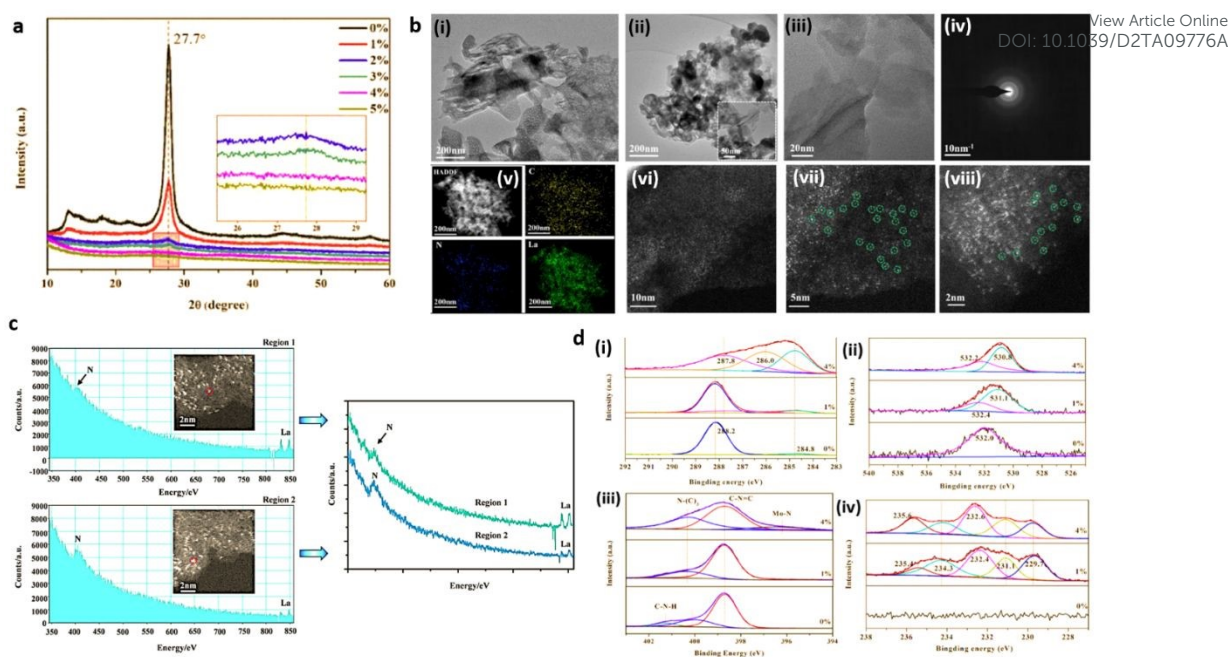


Figure 9. (a) XRD patterns of $g\text{-C}_3\text{N}_4$ (0%) and $\text{Mo}/\text{C}_3\text{N}_4$ (1–5%). Reproduced with permission from ref. 27. Copyright 2019 Elsevier. (b) Morphological analysis of O/La-CN catalyst; (i-ii) TEM images, (iii) HAADF-STEM image of the thinner region, (iv) SAED pattern, (v) HAADF-STEM EDS mapping (yellow, blue, and green color represents carbon, nitrogen and lanthanum), (vi-viii) Spherical aberration-corrected HAADF-STEM images, (c) EELS spectra of two separate labelled regions. Reproduced with permission from ref. 16. Copyright 2020 American Chemical Society. (d) XPS spectra; i) C 1s, ii) O 1s; iii) N 1s, iv) Mo 3d. Reproduced with permission from ref. 27. Copyright 2019 Elsevier.

4.6 X-ray Absorption Spectroscopy

X-ray Absorption Spectroscopy (XAS) is an element-specific technique for probing the local coordination environment by detecting fluctuations in the absorption of an ejected photoelectron due to multiple scattering pathways.^{37, 40} XAS analysis mainly consists of extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) analyses. The atoms surrounding the single atom produce outgoing and backscattered waves and their interference yields EXAFS spectra. EXAFS analysis of SAC provides essential information regarding the coordination number of single atom site(s) and its interatomic distance with backscatter atoms within its vicinity, in

comparison with standard metal foil and metal oxides. The structural disorder and the type of neighbouring atoms present at a specific bond length are also deduced from EXAFS. The absence of signal corresponding to metal-metal interaction in EXAFS spectra rules out the formation of metal NPs and metal oxides.³⁸

XANES analysis further helps in determining the oxidation state of the single metal atom dispersed over the support. XAS analysis techniques establish the identity of single metal atoms through EXAFS and derive quantitative data related to coordination. Further, XAS analysis proposes suitable geometric arrangements for single metal atoms through the curve-fitting of XANES data based on predictable coordination environments. Figure 10 (a-e) shows the XAS analysis details of low-density (2.5 wt% Er loading) and high-density (20.1 wt% Er loading) Er single atom anchored on g-C₃N₄ nanotubes (Er₁/CN-NT). Fourier transform-extended X-ray absorption fine structure (FT-EXAFS) reveals radial distance resolution (R-space) while wavelet transform-extended X-ray absorption fine structure (WT-EXAFS) can discriminate the backscattering atoms to provide resolution in both R-space and k-space. FT-EXAFS spectra, of LD-Er₁/CN-NT and HD-Er₁/CNNT samples, exhibited only one main peak at around 1.8 Å. The absence of a peak at about 3.5 Å, corresponding to Er-Er interaction for LD-Er₁/CN-NT and HD-Er₁/CNNT samples confirmed the formation of a single Er atom over CNNT without the formation of metallic crystalline Er species. WT-EXAFS plots also supplemented the above observation due to the presence of only one intensity maximum at around 4.0 Å⁻¹ corresponding to Er-N bond for the LD-Er₁/CN-NT and HD-Er₁/CN-NT samples.

The white line intensity reduction of Er L₃-edge XANES spectra with the increase in Er loading from 2.5wt% to 20.1wt%, indicate a decrease in the oxidation state of Er in the order Er₂O₃> LD-Er₁/CN-NT> HD-Er₁/CN-NT. In comparison to LD-Er₁/CN-NT, HD-Er₁/CN-NT has a flattened white-line peak at 8360 eV, implying an interaction between central and surrounding Er atoms resulting in the charge redistribution due to the shortening of spatial distance between neighbouring Er atoms. Quantitative least-squares EXAFS analysis demonstrated that both LD-Er₁/CN-NT, and HD-Er₁/CN-NT exhibited one main peak at around 1.8 Å arising from the first shell of Er-N scattering. EXAFS results also indicated that the single Er atoms have a first shell coordination number of six in both LD-Er₁/CN-NT and the HD-Er₁/CN-NT samples.⁹

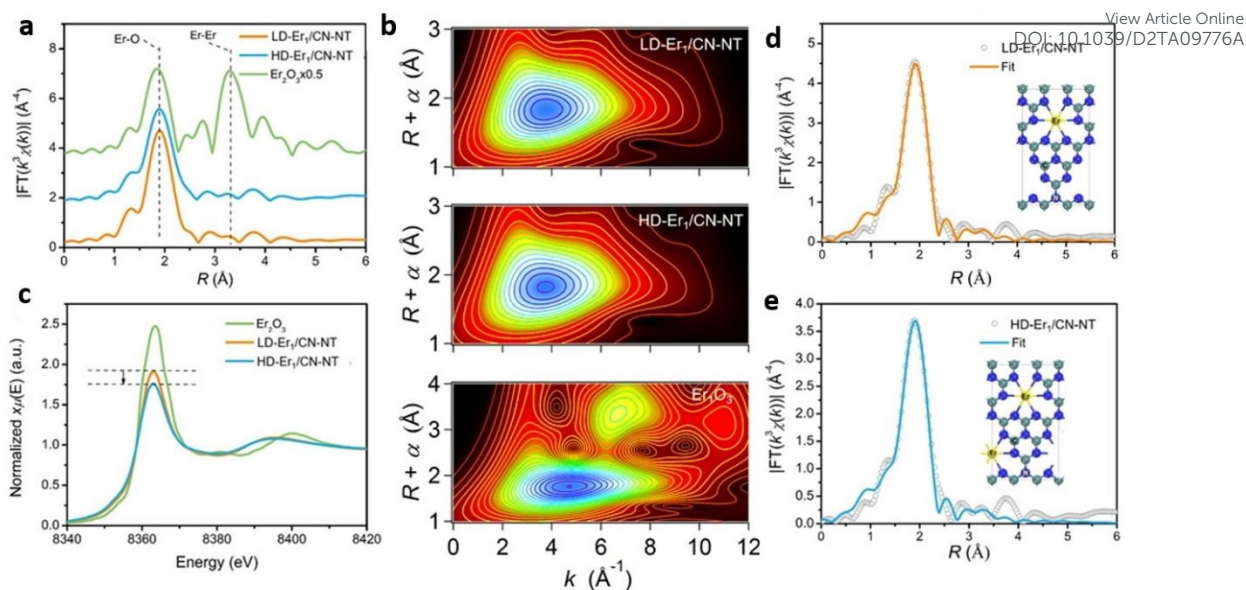


Figure 10. (a) The k_3 -weighted Fourier transform spectra from EXAFS for Er₂O₃, LD-Er₁/CN-NT, HD-Er₁/CN-NT in R space (b) Wavelet transform (WT) contour plots of Er₂O₃, LD-Er₁/CN-NT, HD-Er₁/CN-NT (c), the normalised XANES spectra at the Er L₃ edge of Er₂O₃, LD-Er₁/CN-NT, HD-Er₁/CN-NT, The EXAFS R space fitting curves and corresponding model for (d) LD-Er₁/CN-NT and (e) HD-Er₁/CN-NT respectively Er, N, C atoms are represented by yellow, blue, green spheres respectively. Reproduced with permission from ref. 9. Copyright 2020 John Wiley and Sons.

5 Catalytic applications of single atom confining on g-C₃N₄ matrix

5.1 Photocatalysis

Visible light-driven semiconductor photocatalysis is widely pursued as an environmentally benign and sustainable solution for pollution control and energy production. Photocatalyst alters the kinetics of a chemical reaction upon light irradiation through the creation of highly effective reactive oxygen species (ROS) and has been demonstrated for applications like the degradation of organic pollutants in wastewater, creating self-cleaning surfaces, splitting water for hydrogen evolution, etc.⁴¹ The photocatalyst possesses a favourable combination of electronic structure, excited-state life time, light absorption properties and charge transport characteristics.⁴²

g-C₃N₄, because of its flexible indirect band edge positions, excellent thermal stability, resistance to acids and bases, and insolubility in common solvents like water, ethanol, acetone, etc., is found suitable for a wide range of photocatalytic applications. These

properties originate from the van der Waals force that holds together the stacked graphitic layers.^{43,44} Nevertheless, the application of g-C₃N₄ is limited as it utilises only a small region of the visible spectra. A low specific surface area in the range of 10-30 m²g⁻¹ for bulk g-C₃N₄ is also an impediment to widespread applications owing to the reduction in reactive sites. The high rate of recombination of excitons, poor light harvesting, and limited generation of radical species are the factors primarily responsible for its low catalytic efficiency during the redox reactions.⁴⁵

The recombination process in g-C₃N₄ is perceived to be controlled by facilitating separation between photogenerated electron-hole pairs and various strategies such as heterostructure formation, incorporation of metal co-catalyst, impurity doping, etc are demonstrated thus far. Among them, the incorporation of a metal co-catalyst is a viable strategy to reduce exciton recombination as the metal fermi level is positioned in between the band edge positions of C₃N₄. The transfer of photogenerated electrons from the conduction band (CB) to the metal enables the separation of the exciton pairs leading to improved photocatalytic efficiency.⁴³

The usage of noble metals such as Au, Pt, Pd as co-catalyst is effective but is limited due to their high cost. Replacement of noble metals with cost-effective transition metals is an affordable solution for the applications of g-C₃N₄ based photocatalysts. However, very low atom utilisation efficiency, availability of minimal catalytically active species and poor selectivity of the metal nanoparticles are the bottlenecks for its practical application. Metal particles of appropriate sizes can only act as catalytically active species while those with non-optimal sizes may facilitate various undesired secondary reactions which further reduce the catalytic efficiency of the catalyst. To overcome these limitations, g-C₃N₄ based catalysts with atomic level dispersion of metal are recently developed.⁴⁶

SACs comprising of spatially isolated, individual metal atoms stabilised on C₃N₄ matrix, show unusual potential due to unsaturated coordination sites for realising maximum atom-utilisation efficiency. Consequently, C₃N₄ based on SACs and ADMCs with unique electronic structures serve as potential candidates for catalysing various reactions by virtue of their advantages such as remarkably high catalytic activity, reduced catalyst amount, and abundance of single active sites.¹³

The past few years have seen significant research efforts leading to the development of a research domain of g-C₃N₄ based single atom photocatalysts for various applications (Figure 11).

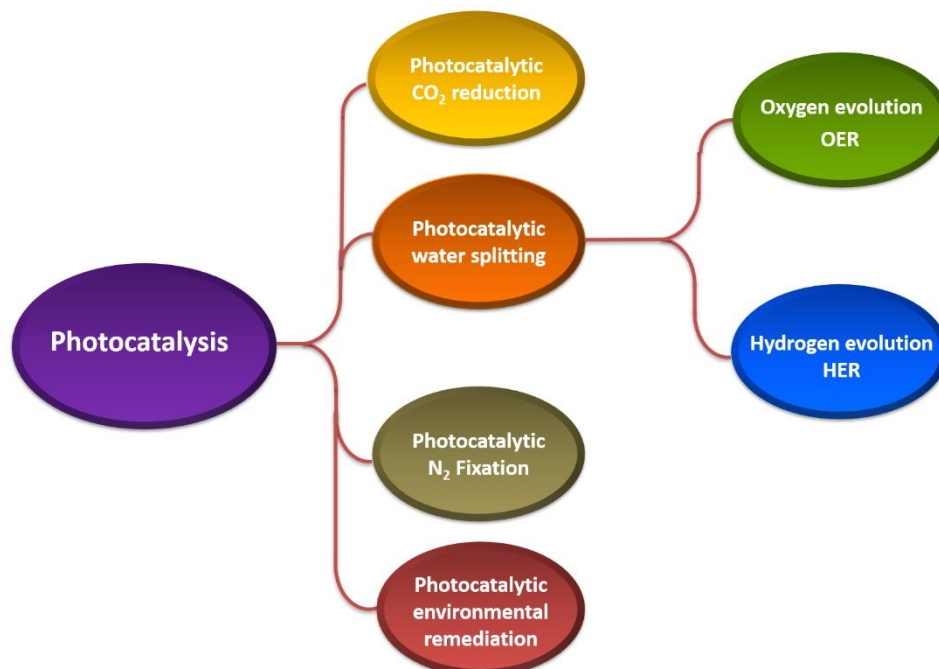
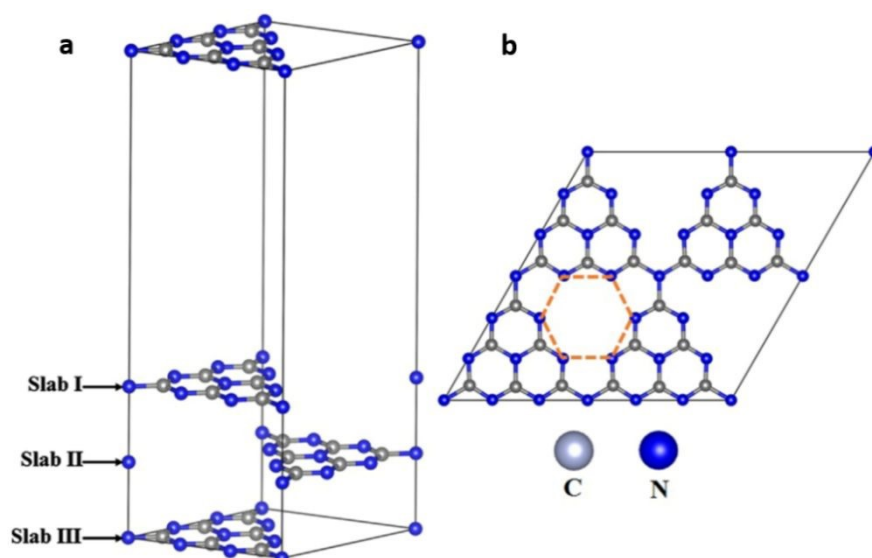


Figure 11. Various reactions catalysed by g-C₃N₄ based SACs in the area of photocatalysis

Zhang et al employed density functional theory (DFT) to study the improved photocatalytic activity of g-C₃N₄ based transition-metal (Fe, Co, Ni, Cu and Zn) single atom catalysts. To identify the adsorption sites of single atoms of various transition metals on multi-layered g-C₃N₄ sheets, a three-layer g-C₃N₄ structure was constructed by cleaving the (001) g-C₃N₄ surface. The structure comprising 24 N atoms and 18 C atoms and with the optimised lattice parameter values of a=b=7.13 Å, c=21.54 Å contained numerous six-fold cavities capable of trapping metal single atoms (Figure 12).⁷



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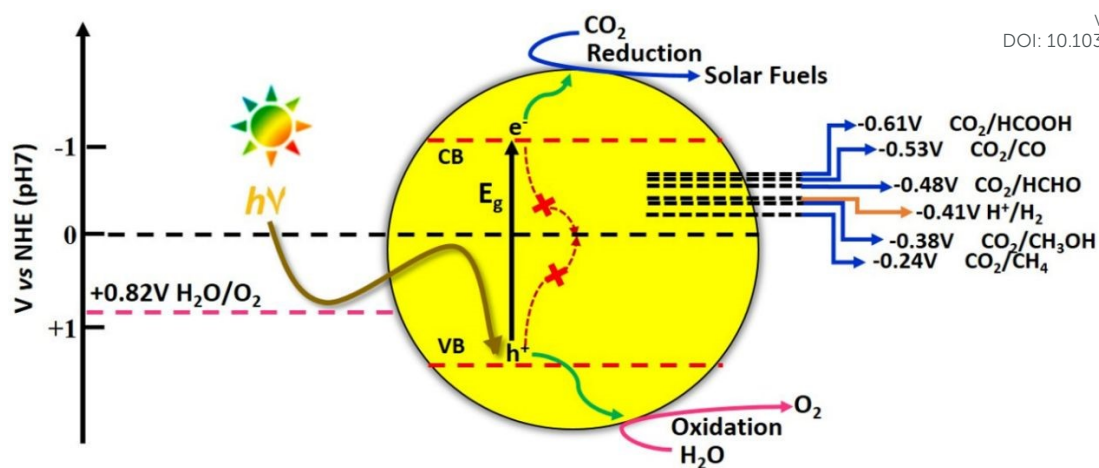
Figure 12. (a) Schematic representation of three-layer $g\text{-C}_3\text{N}_4$ model, (b) $2\times 2\times 1$ supercell monolayer $g\text{-C}_3\text{N}_4$. The highlighted ring composed of six numbers of bi-coordinated nitrogen atoms is referred to as six-fold cavity. Reproduced with permission from ref. 7. Copyright 2018 Elsevier.

Due to the presence of empty d orbitals in transition metals, single atoms of Fe, Co, and Ni were inserted into the layers of $g\text{-C}_3\text{N}_4$ sheets through strong coordination with their neighbouring C, N atoms. On the other hand, Cu and Zn atoms with completely filled d orbitals stay at the six-fold cavities present in the $g\text{-C}_3\text{N}_4$ surface through coordination with N atoms present at the edge of the cavities. The charge carrier transfer between the interlayers of $g\text{-C}_3\text{N}_4$ is reduced due to the high interlayer distance of 3.27 \AA resulting in a high rate of exciton recombination. Incorporating single atoms of metal altered the interlayer spacing of $g\text{-C}_3\text{N}_4$. The loading of Fe, Co, and Ni single atoms significantly shortens the interlayer distance between slabs I and II. The value decreased from 3.27 to 2.25 , 2.41 and 2.39 \AA for Fe, Co and Ni respectively. The interlayer charge transfer was thus accelerated for aforementioned SACs. However, the incorporation of Cu and Zn atoms hardly affected the interlayer spacing with minimal reduction in values to 2.90 \AA and 2.75 \AA respectively. Similar reductions in the interlayer spacing between slab II and slab III were also observed in Fe/ $g\text{-C}_3\text{N}_4$, Co/ $g\text{-C}_3\text{N}_4$ and Ni/ $g\text{-C}_3\text{N}_4$ with interlayer distances of 2.47 \AA , 2.48 \AA and 2.45 \AA respectively. For Cu/ $g\text{-C}_3\text{N}_4$ and Zn/ $g\text{-C}_3\text{N}_4$, the interlayer spacing between slab II and III remains almost unchanged at 3.28 \AA .⁷

The bond population is an effective measure of the nature of a chemical bond and a low value indicates that the ionic nature of the bond increases and the covalent nature decreases. The covalent nature of C-N bond in g-C₃N₄ is justified by its bond population value of >0.7. The bond population values for all the bonds between metal atoms and adjacent non-metal atoms (C or N) present in the catalysts are significantly lower than 0.7, which indicates greater electron delocalisation leading to accelerated charge transfer between g-C₃N₄ layers. The formations of Cu-N and Zn-N (Metal-Nitrogen bonds) in Cu/g-C₃N₄ and Zn/g-C₃N₄ are not sufficient to improve the charge transfer between layers while the presence of both metal-carbon and metal-nitrogen bonds in Fe/g-C₃N₄, Co/g-C₃N₄ and Ni/g-C₃N₄ systems exhibited enhanced charge transfer properties.⁷

5.1.1 Photocatalytic carbon dioxide reduction

The rational design of photocatalytic systems that are responsive to visible light holds great potential for the effective conversion of carbon dioxide (CO₂) to value-added feedstock, thereby combating the increased environmental issues created by uncontrolled emissions. The chemical reduction of CO₂ to simple C₁/C₂ chemicals such as CO, HCOOH, CH₄, HCHO, C₂H₅OH, CH₃OH, and other hydrocarbon compounds using renewable and inexhaustible solar energy mediated photocatalytic process has emerged as a possibility.⁴⁷ However, the high C=O dissociation energy of ~750 kJ mol⁻¹ and the optically inert nature of CO₂ molecule in the wavelength range of 200–900 nm, render the reduction process extremely difficult and complex with multiple proton and electron transfer pathways.⁴⁸ It is therefore imperative to develop photocatalytic systems with appropriate band structures that are responsive to solar radiation. The resulting photogenerated electrons facilitate the CO₂ reduction process to various value-added products. The one-electron reduction of CO₂ to CO₂⁻ is thermodynamically unfavourable due to the highly negative reduction potential value of -1.90 V vs NHE, at pH 7.0.⁴⁹ The multiple proton-electron assisted CO₂ reduction reactions occur at lower redox potential values as listed in Figure 13.



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Figure 13. Schematic illustration of photocatalytic carbon dioxide reduction

However, the reaction pathways are all uphill reduction processes ($\Delta G > 0$) and the conversion efficiencies are not yet appreciable for the reduction of CO_2 to hydrocarbon fuels using H_2O as a reductant.⁵⁰ Moreover, due to the very close matching of redox potentials of possible products, the selectivity is very poor, particularly for C_2 products. Furthermore, the stability of the intermediate formed during multiple proton-electron transfer pathways involved in the reduction reaction determines the product selectivity.⁵¹

In the early emerging period of SACs, Du and co-workers explored the potency of Pd and Pt single metal atoms supported on $\text{g-C}_3\text{N}_4$ towards photocatalytic CO_2 reduction by density functional theory (DFT) calculations. Pd and Pt single atoms are stably confined into the six-fold cavity of $\text{g-C}_3\text{N}_4$ through the interaction of electron lone pairs present in the neighbouring pyridinic nitrogen atoms. The calculated binding energies for Pd and Pt were respectively -2.17 eV & -2.95 eV. In Pd/ $\text{g-C}_3\text{N}_4$ & Pt/ $\text{g-C}_3\text{N}_4$ systems, the noble metal atoms act as active sites, while the $\text{g-C}_3\text{N}_4$ matrix serves as a source of hydrogen which is generated through hydrogen evolution reaction. The evaluation of reaction pathways suggests HCOOH, with a reaction barrier of 0.66 eV, as the product expected for Pd/ $\text{g-C}_3\text{N}_4$. On the other hand, Pt/ $\text{g-C}_3\text{N}_4$ system was expected to reduce CO_2 to CH_4 with a reaction barrier of 1.16 eV. This study established the correlation between the metal and the product selectivity during the photoreduction process. The distribution of Pd or Pt metal as single atoms over $\text{g-C}_3\text{N}_4$ framework led to enhanced visible light absorption, thereby making it a potential candidate for visible light driven photocatalytic

CO₂ reduction. This theoretical study paved the way for developing various g-C₃N₄ based SACs for CO₂ photoreduction reaction and its experimental validation.⁵

Li and Co-workers synthesised visible light active non-noble metal Co²⁺@C₃N₄ catalyst for CO₂ reduction by stabilising cobalt single atoms on g-C₃N₄ matrix through Co-N coordination. Photocatalysts containing single Co²⁺ sites on C₃N₄ exhibited excellent CO₂ reduction capacity and product selectivity towards CO formation. The effect of metal loadings on CO production and product selectivity was studied by varying cobalt content between 0.004 and 0.430 μmol Co²⁺ per 1 mg C₃N₄. A significant amount of CO formation was observed with cobalt loading lower than even 0.010 μmol/mg. The CO formation increased linearly until a cobalt loading of 0.128 μmol/mg was reached. Further increase in metal loading led to a slight decline in CO production due to the formation of inactive cobalt oxides. The product selectivity of the reduction reaction was however unaffected by the presence of dormant cobalt oxide formed at relatively high Co content.⁵²

Zhou and co-workers successfully demonstrated the amorphous transformation of g-C₃N₄ by atomically dispersing Mo atoms over g-C₃N₄ matrix. The Mo-C and Mo-N bonds altered the long-range order of g-C₃N₄ and the retention of each melon unit led to a crystalline to an amorphous phase transition. This transformation to amorphous g-C₃N₄ enabled significant enhancement in its light absorption in the visible range with a strong band tail and an absorption edge up to 750 nm. Additionally, the newly formed Mo-C and Mo-N bonds enhanced the charge separation dynamics by acting as pathways for photogenerated excitons. The excellent photocatalytic CO₂ reduction capacity of Mo/C₃N₄ systems was attributed to the enhanced visible light activity of the catalyst along with the reduced recombination rate of photo excitons. Under visible light irradiation, Mo/C₃N₄ systems exhibited the CO and H₂ production rates of 18 and 37 μmol g⁻¹ h⁻¹ respectively which is 10.6- and 4-folds greater than that of crystalline g-C₃N₄.²⁷

Wang et al developed atomically dispersed rare earth erbium (Er) atoms on carbon nitride nanotubes for CO₂ reduction through a strategy involving “atom confinement and coordination (ACC)”. The methodology of confining Er precursor and urea on melamine sponge, achieved at liquid N₂ temperature, facilitated coordination between dispersed Er ions and N atoms of the g-C₃N₄ precursor. The ACC strategy helped to fine tune the metal content from 2.5 wt% to 20.1 wt% and could also be utilised for a variety of rare earth

metals of lanthanide series. Photocatalytic CO₂ reduction by high-density Er single-atom catalyst (HD-Er₁/CN-NT) under simulated solar light produced CH₄ and CO at the rates of 2.5 μmol g⁻¹h⁻¹ and 47.1 μmol g⁻¹h⁻¹ respectively which is higher than that of low-density Er single-atom catalyst (LD-Er₁/CN-NT) and bare g-C₃N₄ nanotube catalyst (CN-NT). The presence of Er active sites in large numbers is presumed to be the cause for improved CO₂ conversion rates. Moreover, the availability of multiple basic sites for CO₂ adsorption, as corroborated by CO₂-TPD measurements, promoted enhanced reduction capacity in HD-Er₁/CN-NT samples. DFT calculations revealed that the gaseous CO formation has a low theoretical limiting potential (0.3 V) than CH₄ (0.39 V). Advantageously, the limiting potential for H₂ evolution reaction, calculated to be 0.82 V, was much greater than that of CO and CH₄. Hence unfavourable H₂ production could be successfully alleviated by Er atom catalysts.⁹

Another prominent school of thought practiced in SACs is on the synthesis of crystalline g-C₃N₄, primarily to overcome the demerits associated with the bulk morphology and excessive defects of amorphous g-C₃N₄. Xiang and co-workers reported the development of copper single atoms incorporated crystalline g-C₃N₄ nanorods (Cu-CCN) by molten salt and reflux method. The prepared Cu-CCN photocatalyst showed 100% CO selectivity with an improved generation rate of 3.086 μmol h⁻¹ g⁻¹ compared to 1.68 μmol h⁻¹ g⁻¹ and 0.895 μmol h⁻¹ g⁻¹ for crystalline and bulk counterparts. The CO₂ adsorption capacity of Cu-CCN samples was enhanced as single Cu atoms served as sorption sites for CO₂. Theoretical calculations revealed that the reduction of CO₂ to CH₄ is an entropy increasing process on Cu-CCN samples, while the reduction of CO₂ to CO is a process of decreasing entropy, thereby facilitating 100% product selectivity towards CO (Figure 14 (a)).¹⁸

In a noteworthy contribution, Cao et al developed a g-C₃N₄ based photocatalyst with atomically fused-Cu atoms through C-Cu-N₂ four-center bond formation. An artificial enzyme like configuration, similar to hemocyanin, is created where the single atom copper exhibited a mixed valence state of Cu⁺/Cu⁰ at the oxidation potential of +1.5 V. Composition with 0.25 wt% copper produced CO, CH₃OH and CH₄ at the rates of 11.21, 1.75 and 0.61 μmol g⁻¹ h⁻¹ respectively. Further increase in copper content led to the decline of photocatalytic activity owing to the surplus metal sites acting as charge recombination centres. CO was the major product of CO₂ reduction, as the desorption of

CO molecules was made easier at single Cu atom active centres. The DFT studies revealed that the terminal C-Cu-N₂ four-centre active sites present in g-C₃N₄ nanosheets served as a sink for photogenerated electrons while providing reactive binding sites for CO₂ activation. The proposed reaction pathway (Figure 14(b)) followed the sequences of CO₂ adsorption followed by its hydrogenation to form *COOH. Subsequently, OH group dissociates from *COOH forming adsorbed *CO followed by the desorption of CO molecule from the catalyst surface. The enhanced CO₂ reduction performance of Cu/CN system over CN is attributed to the low free energy change (ΔG) of 0.95 eV associated with the rate limiting step (desorption of CO) on Cu/CN compared to a large ΔG of 2.71 eV associated with rate limiting step (hydrogenation of adsorbed *CO₂) on bare CN (Figure 14(c)).⁵³

In a recent contribution, Dong et al converted CO₂ to CO efficiently by employing single-atoms of La on C₃N₄ by creating La-N charge bridges for efficient electron transport. The photocatalyst (O/La-CN), synthesised by one-step calcination involving the precursors of urea and lanthanum carbonate, exhibited complete amorphisation characterised by the absence of XRD peaks of g-C₃N₄. O/La-CN exhibited 80.3% selectivity at the high yielding rate of 92 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ for CO. The La-N bridge, formed by the combination of various electronic states originating from 4f and 5d orbitals of La and the p-d orbital hybridisation, facilitated the CO₂ activation, COOH* formation and CO desorption steps.¹⁶

The Ni-anchored g-C₃N₄ photocatalyst was designed by anchoring single atoms of Ni on a few-layer g-C₃N₄ synthesised through a self-limiting process. Such a few-layer g-C₃N₄ structure with high porosity offers ligands for trapping Ni atoms, thereby realising a high density of single atoms. The single Ni atoms were distributed on the edges of the g-C₃N₄ sheets through an “active unsaturated edge confinement strategy” providing maximum atom-utilisation efficiency for high CO₂ adsorption capacity. The highly unsaturated Ni-N coordination offered pathways for the electron transfer from g-C₃N₄ to single Ni atoms realising improved photocatalytic activity for CO₂ conversion to CO. The prepared photocatalysts contained 2.54, 7.95, and 12.18 wt% of Ni content respectively for Ni₁-CN, Ni₅-CN, and Ni₁₀-CN compositions. The Ni₅-CN composition produced 8.6 $\mu\text{mol g}^{-1}$ of CO and 0.5 $\mu\text{mol g}^{-1}$ of CH₄ generation in the first 1 h, and was much higher than those of bare CN (CO: 1.1 $\mu\text{mol g}^{-1} \text{h}^{-1}$, CH₄: 0.1 $\mu\text{mol g}^{-1} \text{h}^{-1}$), and Ni_p+CN (CO: 2.7

$\mu\text{mol g}^{-1} \text{h}^{-1}$, CH_4 : none), and NiCl_2+CN (CO : $3.3 \mu\text{mol g}^{-1} \text{h}^{-1}$, CH_4 : none) compositions (Figure 14 (d-i)).⁵⁴

Combining experimental and computational studies, Hao et al evaluated photocatalytic reduction of CO_2 to CO using water as a reductant and $\text{g-C}_3\text{N}_4$ containing single-atom Fe as a catalyst. The photo-physical and photo-chemical processes associated with CO_2 reduction mechanisms were analysed in detail. The reduction mechanism involved the activation of CO_2 molecules, formation of COOH radicals through water oxidation (proton transfer from H_2O to CO_2) and cleavage of C-O bond in COOH radicals. It is proposed that the activation process initiates through hydrogen-bonded complexes between CO_2 , H_2O , and photocatalysts i.e., $\text{g-C}_3\text{N}_4$ or $\text{Fe-g-C}_3\text{N}_4$. As represented in Figure 14 (j), there are two hydrogen bonds, namely HB-1 (H-bond between O atom of CO_2 and the H atom of H_2O) and HB-2 (H-bond between H atom of H_2O and the N atom of $\text{g-C}_3\text{N}_4$) formed when $\text{g-C}_3\text{N}_4$ is used as a catalyst. In the photocatalyst with single atom Fe, in addition to the formation of HB-1, CO_2 and H_2O molecules, are coordinated with Fe atom through Fe-C and Fe-O coordination bonds, resulting in a four-coordination structure for Fe (Figure 14 (k)).⁵⁵ Fe single atoms dispersed in $\text{g-C}_3\text{N}_4$ matrix serve as catalytically active centres and facilitate the activation of CO_2 . The reaction barrier for the cleavage of the C-O bond in the COOH radical was reduced from $32.3 \text{ kcal mol}^{-1}$ to $15.3 \text{ kcal mol}^{-1}$. The change of catalytically active sites from N atom to single atom Fe accelerates the photochemical processes, thereby enhancing the CO evolution rate from $2.7 \mu\text{mol g-cat.}^{-1}$ and $5.1 \mu\text{mol g-cat.}^{-1}$.⁵⁵

Zbořil and coworkers reported ruthenium-based SACs on $\text{mpg-C}_3\text{N}_4$ support for the efficient photocatalytic conversion of CO_2 using water as a reductant. Mesoporous C_3N_4 , obtained through a silica template assisted pyrolysis of dicyanamide, is used as a matrix for the microwave assisted precipitation and dispersion of Ru single atoms. Catalyst with Ru loading as low as 0.4 wt% yielded methanol as the conversion product, at a yield of $1500 \mu\text{mol g}^{-1}$ within 6 h. Single atoms of Ru bonded to N/C sites facilitated enhanced electron transfer by virtue of increased charge density around it.⁵⁶

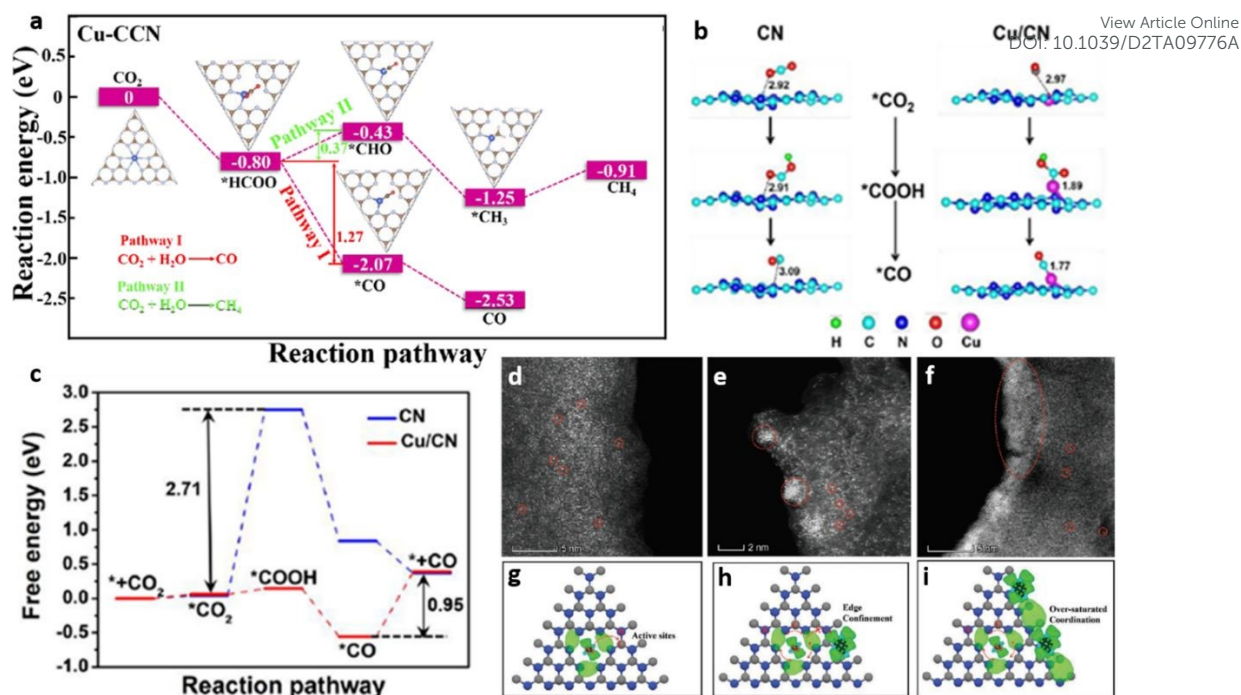


Figure 14. (a) Schematic of the photocatalytic CO₂ reduction pathway on Cu-CCN derived from DFT calculation. Reproduced with permission from ref. 18. Copyright 2020 American Chemical Society. (b) Proposed structures and CO₂ reduction pathway corresponding to CN & Cu/CN photocatalyst (c) Free energy diagram for the conversion of CO₂ to CO on CN and Cu/CN photocatalysts. Reproduced with permission from ref. 53. Copyright 2020 American Chemical Society. Aberration-corrected HAADF-STEM images of d) Ni₁-CN, e) Ni₅-CN, f) and Ni₁₀-CN, Models showing a difference in the charge distribution of (g) Ni₁-CN, (h) Ni₅-CN, and (i) Ni₁₀-CN. Reproduced with permission from ref. 54. Copyright 2020 John Wiley and Sons.

SACs based on g-C₃N₄ support exhibited superior photocatalytic carbon dioxide reduction efficacy compared to conventional metal-semiconductor heterostructures and the developments are summarised below in Table 2.

Table 2 Summary of g-C₃N₄ SACs for photocatalytic carbon dioxide reduction

System	Single atom & loading	Synthesis method	Products & Rate	Coordination site or structure & oxidation state	Reference
Pd/g-C ₃ N ₄ & Pt/g-C ₃ N ₄	Pd, Pt	DFT Study	HCOOH for Pd/g-C ₃ N ₄ & CH ₄ for Pt/g-C ₃ N ₄	Nitrogen	5
Co ²⁺ @C ₃ N ₄	Co-0.128 μmol/mg	Microwave assisted post synthesis	CO 1.056 μmol/mg for 2h	Nitrogen, +1	52
a-Mo/C ₃ N ₄	Mo 3.3 %	Template free direct synthesis	CO & H ₂ , 18 & 37 μmol g ⁻¹ h ⁻¹	Mo-C & Mo-N	27
Er ₁ /CN-NT	Er 18.4 wt%	Freeze drying assisted direct synthesis	CH ₄ & CO 2.5 & 47.1 μmol g ⁻¹ h ⁻¹	Er-N ₃ , +1	9
Cu-CCN	Cu Atomic fraction 10.95 %	Molten salts & reflux method (direct synthesis)	CO 3.086 μmol g ⁻¹ h ⁻¹	Nitrogen	18
Cu/CN	Cu 0.25%	Supramolecular pre-organisation (direct synthesis)	CO, CH ₃ OH, CH ₄ 11.21, 1.75 & 0.61 μmol g ⁻¹ h ⁻¹	C-Cu-N ₂	53
O/La-CN	La	Template free direct synthesis	CO 92 μmol g ⁻¹ h ⁻¹	La-N	16
Ni/C ₃ N ₄	Ni 2.54 wt%	Template free direct synthesis	CO & CH ₄ 1.1 μmol g ⁻¹ h ⁻¹ & 0.1 μmol g ⁻¹ h ⁻¹	Ni-N	54
Fe/C ₃ N ₄	Fe 1.4 wt%	Post synthesis	CO 5.1 μmol g-cat ⁻¹ in 10 h	Fe-N	55
Ru/mpg-C ₃ N ₄	Ru 0.4%	Microwave assisted post synthesis	CH ₃ OH 1500 μmol g ⁻¹ within 6 hours	Ru-N/C	56

5.1.2 Photocatalytic water splitting reaction

The energy demand of modern society is fulfilled by the consumption of non-renewable fossil fuels. However, its fast depletion has necessitated the search for alternative sources of clean and sustainable energy. Hydrogen has thus become the focus of attention and among the myriad ways of generating it, the production and storage of hydrogen fuel

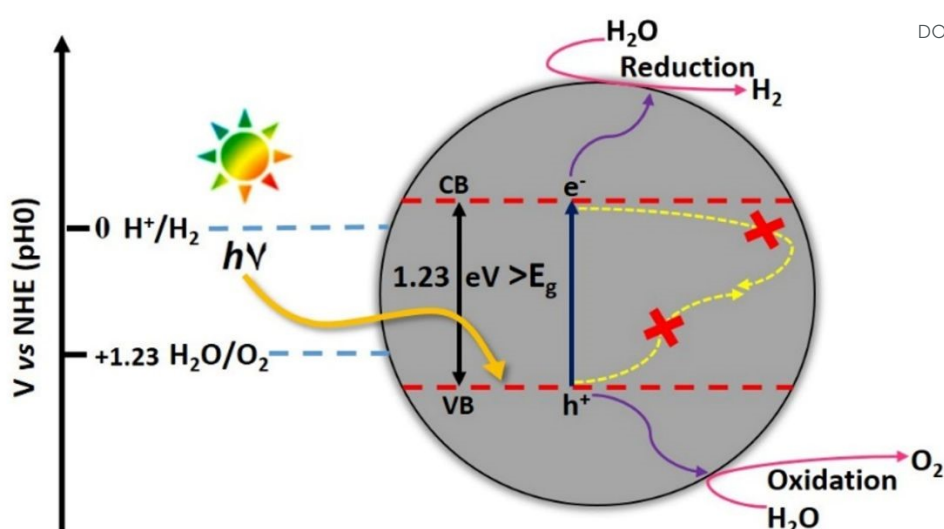
through solar light driven water splitting has drawn considerable attention.⁵⁷ Water covers nearly 72 percent of the earth's surface and splitting it into H₂ and O₂ in a cost-effective, sustainable, and inexhaustible manner is an attractive proposition to realise the ever increasing energy demands.⁵⁸ Water splitting reaction proceeds as two half-reactions namely, photogenerated electrons mediated hydrogen evolution reaction (HER) and photogenerated holes mediated oxygen evolution reaction (OER).⁵⁹

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Fujishima and Honda introduced photocatalytic water splitting using TiO₂ photoelectrode under UV light irradiation⁶⁰ and since then, numerous studies on H₂ generation from photocatalytic water splitting using a variety of semiconductor photocatalysts have been conducted. The positive Gibbs free energy change (ΔG) of 237 kJ/mol, associated with the energetics of splitting water into H₂ and O₂, indicates it to be an uphill reaction pathway thermodynamically.⁶¹

The photocatalytic water splitting proceeds through the three steps (i) Exciton generation on the absorbance of energy equivalent to the band gap energy of the semiconductor (ii) Separation and migration of photogenerated excitons (e⁻ and h⁺ pairs) to the semiconductor surface and (iii) Electrons mediated reduction of H⁺ ions to H₂ and holes mediated oxidation of H₂O to O₂ (Figure 15). Among oxygen evolution and hydrogen evolution reactions (OER and HER), OER is the more complicated half-reaction as it involves the release of 4e⁻ from two H₂O molecules to form the double bond between two oxygen atoms.⁶²

The pre-requisite condition that a semiconductor must satisfy for facilitating the photocatalytic water splitting reaction, is that the valence band (VB) maxima should be more positive than the oxidation potential of water (+1.23 V vs NHE) for OER, while the conduction band (CB) minima should be more negative with respect to the H⁺ reduction potential (0 V vs NHE). The formation of water by the recombination of H₂ and O₂ is a detrimental step to catalytic efficiency and should be prevented.⁶³



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Figure 15. Schematic diagram of photocatalytic water splitting

Copolymerising silver tricyanomethanide (AgTCM) along with mesoporous $g\text{-C}_3\text{N}_4$ precursors was demonstrated to be advantageous for the synthesis of Ag/mpg- C_3N_4 SACs. The uniform dispersion of Ag species in the semiconductor matrix was realised by inducing negative charges to C and N of C_3N_4 matrix. This approach was demonstrated to be superior to the conventional impregnation-chemical reduction method that often results in the formation of metal nanoparticles. The AgTCM-mpg-CN catalysts with up to 10 wt% of well dispersed Ag species displayed much better performance for Pt assisted photocatalytic water reduction ($39.5 \mu\text{mol H}_2/\text{h}$ generation for 2 wt % AgTCM compared to a value of $9.8 \mu\text{mol H}_2/\text{h}$ for mpg-CN).¹⁷

Wu et al synthesised highly dispersed, isolated single Pt atoms anchored on $g\text{-C}_3\text{N}_4$ (Pt-CN) as a stable photocatalyst for HER. Achieving atomic level dispersions of Pt cocatalyst over $g\text{-C}_3\text{N}_4$ enhances the overall photocatalytic HER activity by facilitating the charge transfer as well as by providing an increased number of proton reduction sites. HAADF-STEM analysis revealed that >99% of Pt species are less than 0.2 nm in size corroborating the presence of isolated single atoms of Pt over $g\text{-C}_3\text{N}_4$ matrix. The cluster formation was avoided up to a Pt loading of 0.16 wt%. As the Pt loading was increased to 0.38 wt% Pt nanoparticle formation was observed. The Pt-CN with Pt loading of 0.16 wt% exhibited the highest HER activity with a turnover frequency (TOF) of 775 h^{-1} , compared to a TOF of 83 h^{-1} obtained for Pt-NPs-CN (Figure 16 (a-b)). Ultrafast transient

absorption (TA) spectroscopy was employed to elucidate the unique role of Pt single atom in enhancing the HER activity. Average recovery lifetime values, a measure of the extent of separation of photogenerated excitons, of g-C₃N₄, Pt-CN, and Pt-NPs-CN were found to be ≈ 237 ps, ≈ 433 ps, and ≈ 117 ps respectively (Figure 16 (c-d)). The two-fold and four-fold enhancement in average recovery lifetime for Pt-CN compared to bare g-C₃N₄ and Pt-NPs-CN was attributed to the incorporation of Pt single atoms in g-C₃N₄ framework. The incorporation of isolated single Pt atoms modifies the near band-edge electron trap states of g-C₃N₄ favouring the H⁺ reduction process by photogenerated electrons (Figure 16 (e-f)).⁶⁴

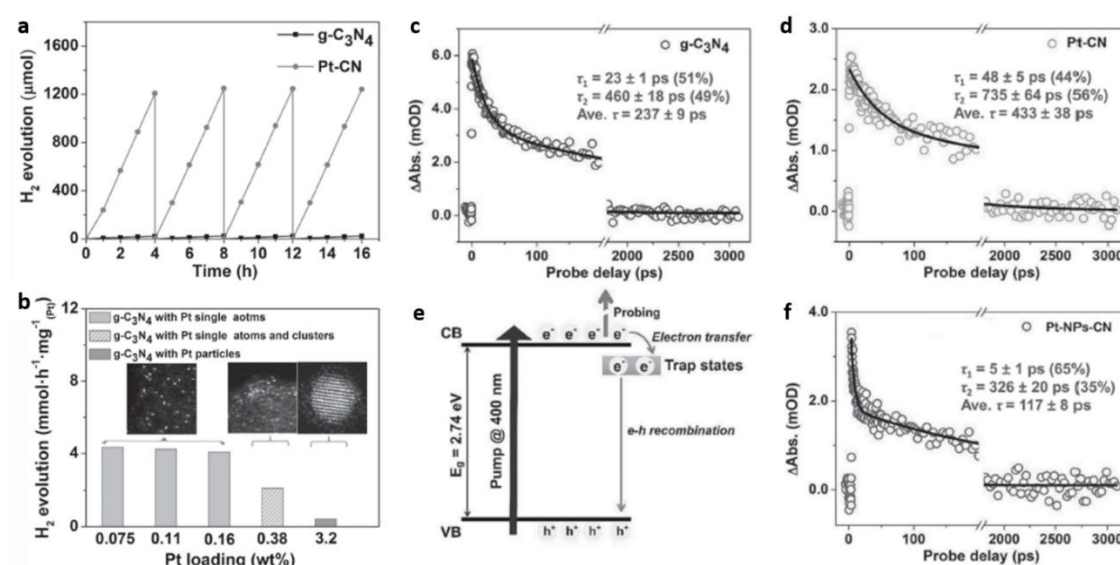


Figure 16. (a) Photocatalytic H₂ evolution with time for g-C₃N₄ and Pt-CN, (b) Photocatalytic H₂ evolution with varying Pt content (normalised per Pt atom), Average recovery lifetime values in mOD (optical density) of (c) g-C₃N₄, (d) Pt-CN, (e) An illustration of the various mechanisms involved, (f) Data on TA kinetics for Pt-NPs-CN. Reproduced with permission from ref. 64. Copyright 2016 John Wiley and Sons.

Yao et al employed phosphidation followed by atomic-layer-deposition (ALD) to atomically disperse single-site Co atoms on g-C₃N₄ nanosheets (Co₁/PCN) for the photocatalytic HER reaction using triethanolamine (TEOA) as the sacrificial electron donor. The grafting of Co atoms over C₃N₄ nanosheet is achieved through the formation of a covalently bonded Co₁-N₄ structure. Co-N coordination is confirmed with the aid of XANES, EXAFS and XPS. Co₁/PCN exhibited XANES spectrum which is different in

shape from that of cobalt oxides (CoO and Co₃O₄) presumably due to Co-C/N coordination. Similarly, a single peak observed at 1.58 Å in Fourier-transformed (FT) k³-weighted $\chi(k)$ function of Co₁/PCN is close to Co-N bond present in the reference material (CoPc) ruling out the formation of Co-Co, Co-P and Co-O bonds. XPS spectrum of Co₁/PCN further confirmed the existence of Co-N bond with a Co 2p_{3/2} peak located at a significantly higher binding energy value of 781.1 eV compared to that of Co-O bond at 780 eV. Additionally, the presence of N vacancies in Co₁/PCN sample is substantiated by XPS analysis as the pyridinic N content observed in the high-resolution N 1s spectra is decreased. To understand the structural configuration of the Co single site in Co₁/PCN, various possible atomic configurations are proposed with specific deposition sites/coordination sites. Accordingly, Co single atoms may be at the corner and center of the six-N cavity (Co-N₂ and Co-N₆ respectively), top of the five-membered ring (Co N₃C₂), and unsaturated coordination site containing four in-plane N atoms (Co N₄). The Co-N bond length value of 2.02 Å obtained from EXAFS spectra ruled out the existence of Co-N₆ structure where the Co-N bond length value should be 2.40 Å. The experimental Co K-edge XANES spectra of Co₁/PCN exactly matched with calculated XANES spectra for Co-N₄ configuration which confirmed the formation of Co₁-N₄ structure (Figure 17 (a-d)). Co₁/PCN with a metal mass loading of 1.0 % exhibited an improved H₂ production rate of 10.8 μmol h⁻¹ which is approximately an order of magnitude higher than the PCN with a H₂ production rate of 1.0 μmol h⁻¹ confirming the unique role of Co₁-N₄ site in improved activity (Figure 17 (e)). The coordinated nitrogen atom present in Co₁-N₄ structure enhanced the electron density around the Co atom. The energy barrier was lowered for the formation of Co hydride intermediate with 3H atom co-adsorbed configuration promoting H-H coupling for accelerated H₂ evolution (Figure 17 (f)).²⁴

Wei et al designed HER and OER phosphorus-doped g-C₃N₄ (PCN) photocatalysts with active Co₁-phosphide species. Co₁-phosphide/PCN composite photocatalyst was synthesised by the phosphidation of Co₁ Oxo/C₃N₄ composite obtained through the pyrolysis of cobalt precursor and g-C₃N₄. The phosphidation of Co₁-Oxo/C₃N₄ using sodium hypophosphite altered the coordination environment around Co metal atoms from oxygen to phosphorus to form Co₁-P₄ structure. Co₁-phosphide/PCN photocatalyst with a Co mass loading of 0.4% exhibited superior photocatalytic activity than most of the g-C₃N₄ and oxynitride based materials. H₂ production rate of 410.3 μmol h⁻¹g⁻¹ and O₂ production rate of 204.6 μmol h⁻¹g⁻¹ were achieved without using noble metal co-

catalysts, sacrificial reagents, or other additives and by employing pure water under simulated sunlight. The superior photocatalytic water splitting capacity of Co₁-phosphide/PCN can be attributed to the enhanced light absorption in UV to visible wavelength range and to the introduction of a new mid-gap state within the band structure of Co₁-phosphide/PCN. The band-gap energy (E_g) and transition energy (E_t) from VB to the mid-gap states for Co₁-phosphide/PCN system were estimated to be 2.97 and 2.15 eV, respectively (Figure 17 (g)). Enhanced light harvesting capacity of Co₁-phosphide/PCN was ascribed to the small energy gap between the mid-gap state and VB, favouring the excitation of an electron from VB to the mid-gap states (Figure 17 (h)).⁶⁵

Zhong et al prepared Pt single atoms dispersed on g-C₃N₄ nanosheets (Pt-SA-CN) by a copolymerisation strategy involving melamine, cyanuric acid and 2,4-diamino-6-methyl-1,3,5-triazine. Pt loading less than 0.3 wt% has been realised by the wet impregnation method using H₂PtCl₆. The immobilisation and atomic level dispersion of Pt atoms over g-C₃N₄ was established through Pt-N coordination bonds. Pt-SA-CN catalyst with a Pt loading of 0.20 wt% displayed enhanced H₂ production of 4875.0 μmol/g in 4 h. A correlation is established with the Pt single atom size on the metal loading and its corresponding photocatalytic activity. The size of Pt atoms in Pt -SA-CN with 0.2 and 0.3 wt % Pt loading was found to be 0.21 and 0.5 nm respectively and a subsequent reduction in the H₂ evolution was observed with increasing Pt size.⁶⁶

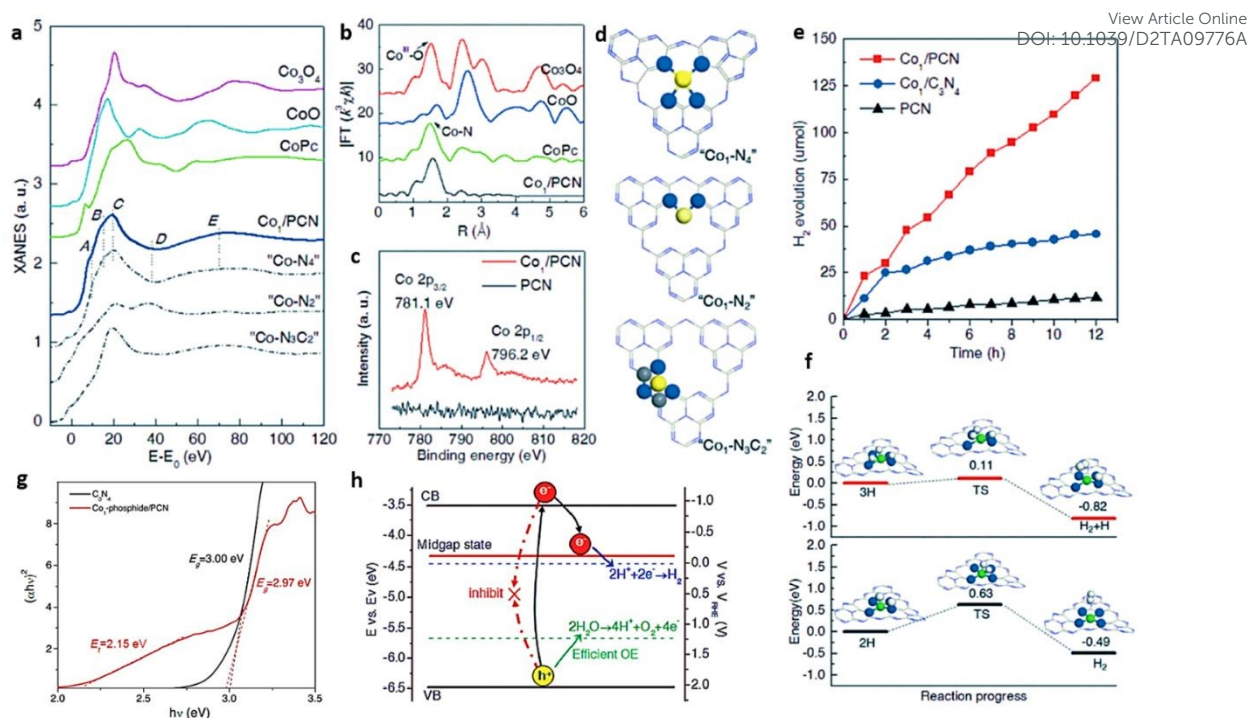


Figure 17. (a) XANES (Co K-edge) spectra of Co₁/PCN in comparison with standards and possible atomic configurations (b) Fourier spectra of Co₁/PCN in comparison with standards (c) XPS Co 2p spectra of Co₁/PCN and C₃N₄, (d) Model structures of “Co₁-N₄”, “Co₁-N₂”, “Co₁-N₃C₂” with blue, yellow and grey spheres representing N, Co and C atoms, respectively, (e) H₂ evolution with time under simulated solar irradiation, (f) Energy diagram of Co₁-N₄ for H₂ evolution on single-sites with the transition state of the reaction TS-(H+H→H₂). N (blue), Co (green) and H (white) spheres. Reproduced with permission from ref. 24. Copyright 2017 John Wiley and Sons. (g) The Tauc plot of the g-C₃N₄ and Co₁ phosphide/PCN catalysts (h) Electronic band structure of Co₁-phosphide/PCN catalyst. Reproduced with permission from ref. 65. Copyright 2017 John Wiley and Sons.

Liu et al successfully developed Pt^{II}-C₃N₄ single atom catalyst for efficient photocatalytic water splitting by employing high-valence metal single-atom confinement strategy. Pt^{II}-C₃N₄ exhibited H₂ evolution at the rate of 140 μmol g⁻¹ h⁻¹, which is ~10 times higher compared to that of Pt NP-C₃N₄ (15 μmol g⁻¹ h⁻¹). Upon visible light irradiation, the Pt^{II}-C₃N₄ system shows a quantum efficiency of 1.5% at 420 nm. Anchoring Pt^{II} single atoms on g-C₃N₄ matrix via Pt^{II}-N bond formation facilitated higher absorption of visible light and effectively suppressed exciton recombination. The E_g values for g-C₃N₄, Pt^{II}-C₃N₄,

Pt nanoparticle- C_3N_4 , derived from Tauc plot were found to be 2.77, 2.72, and 2.6 eV respectively. The flat band potential of $Pt^{II}-C_3N_4$ (-1.01 V vs RHE) is appreciably shifted to a more positive value compared to Pt NP- C_3N_4 (-1.25 V) and g- C_3N_4 (-1.44 V) (Figure 18(a)). Ultraviolet photoelectron spectra (UPS) revealed that the VB maxima for $Pt^{II}-C_3N_4$ were shifted downward by ~ 0.27 V compared to g- C_3N_4 , which may be due to the hybridisation of 5d orbital of Pt^{II} & 2p orbital of N atom present in the g- C_3N_4 framework (Figure 18(b)). The modified electronic band structure of $Pt^{II}-C_3N_4$ effectively promoted the overall photocatalytic water splitting reaction (Figure 18(c)). Band structure calculations based on the first principles were performed to understand the correlation between the electronic structure of $Pt^{II}-C_3N_4$ photocatalyst and its improved charge carrier transfer kinetics. Electron density of state (DOS) analysis on g- C_3N_4 (Figure 18(d)) revealed that the fermi level (middle of the band gap) is devoid of mobile electrons but an intersection of the valence band and fermi level is evident in the DOS of $Pt^{II}-C_3N_4$ photocatalyst (Figure 18(e)). In addition, the strong electrophilic nature of the valence band of $Pt^{II}-C_3N_4$ formed through the hybridisation of Pt^{II} 5d and N 2p orbitals promotes the electron transfer to CB catalysing HER and leaving behind the holes at the VB to facilitate OER (Figure 18(f)).²³

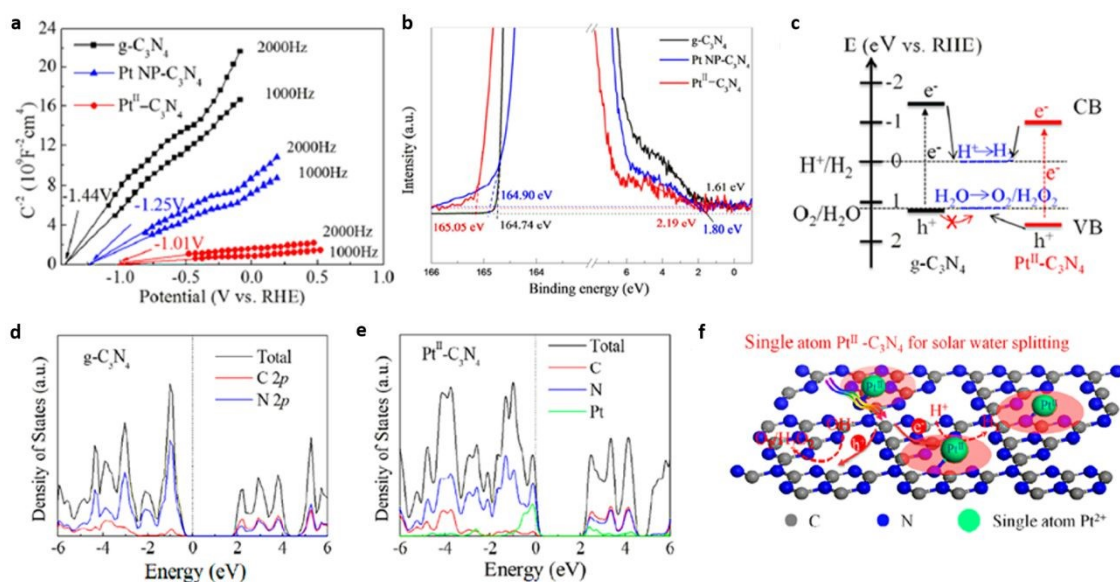


Figure 18. (a) Mott-Schottky plot of $Pt^{II}-C_3N_4$ in comparison with g- C_3N_4 and Pt NP- C_3N_4 , (b) UPS spectra of g- C_3N_4 , $Pt^{II}-C_3N_4$ & Pt NP- C_3N_4 , (c) Schematic band structure alignment, DOS of (d) g- C_3N_4 and (e) $Pt^{II}-C_3N_4$, (f) Mechanistic pathways

(schematic) of the photocatalytic water splitting by Pt^{II}-C₃N₄. Reproduced with permission from ref. 23. Copyright 2018 American Chemical Society. View Article Online
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g-C₃N₄ functionalised with amino groups at the edges were utilised to develop atomically dispersed Fe SACs for solar driven photocatalytic hydrogen generation. The spontaneous coordination of dicyandiamidine nitrate with Fe ions led to the formation of porous crimped g-C₃N₄. The incorporation of Fe single atoms altered the band and electron structures enabling faster charge transfer kinetics realising hydrogen evolution rate of 3390 μmol h⁻¹ g⁻¹ at a quantum efficiency of 6.89% at 420 nm.⁶⁷

A promising approach to optimise catalytically active sites is by tuning the reactive metal support interaction (RMSI) which is conventionally realised by the high-temperature reactions (T>550 °C) of reducible oxides. Guo et al reported strong RMSI in Pt single atom containing g-C₃N₄ obtained by the in situ photocatalytic reduction of (H₂PtCl₆) at liquid nitrogen temperatures. The strong RMSI, induced by rich N vacancies in C₃N₄ provided a record single atom coverage density of 0.35 mg m⁻² leading to 174.5 mmol g⁻¹ h⁻¹ of hydrogen evolution. Simulation studies indicated that RMSI stabilises single atoms of Pt through chemical bonds with two coordinated C (C₂C) formed by the N vacancies.²⁵

A photoactive, single atom cobalt loaded g-C₃N₄ catalyst obtained through a supramolecular polycondensation process based on dicyandiamide is demonstrated for photocatalytic hydrogen evolution using TEOA as a sacrificial agent and 3wt% Pt as cocatalyst. The synthesised Co@g-C₃N₄ composite exhibited improved photocatalytic hydrogen evolution at a rate of 2481 μmol h⁻¹ g⁻¹. The incorporation of Co single atoms strengthened the reducing capability of the conduction band (CB) electrons due to a shift in the CB edge minima to a more negative value compared to that of g-C₃N₄ (0.83 V and -0.95 V vs SCE respectively).¹⁹

Employing 2D confinement strategy, Quan et al developed Pt single atoms confined on carbon nitride photocatalyst with ultrahigh Pt loading of 8.7 wt% for the H₂ evolution reaction. The photocatalytic performance of the synthesised samples was dependent on the location of the Pt atoms at either the surface or within the inner layers of g-C₃N₄ (Figure 19(a-d)). The interlayer interactions altered the electronic structure by

delocalising the charge density of the Pt atom which in turn facilitated the adsorption of protons and caused the reduction of the energy barrier for HER (Figure 19 (e-f)). The developed photocatalyst exhibited H₂ evolution rate of 22.65 mmol·g⁻¹·h⁻¹ with an apparent quantum yield (AQY) of 22.5 % at 420 nm.⁶⁸

C₃N₄ hollow spheres dispersed with single atoms of Cu were developed by a molecular assembly involving melamine (ME) and cyanuric acid (CA) with copper nitrate. Single atoms of Cu were either embedded within g-C₃N₄ sheets (Cu1@HCNS) or dispersed on its surface (Cu1/HCNS) as Cu₁N₃ species through Cu-N coordination. The copper single atoms embedded within the sheets were more effective in promoting interfacial charge transfer as well as tuning the electronic band structure. The Cu1@/HCNS exhibited improved HER activity (using 3wt% Pt cocatalyst) with AQY of 7.1% which is 1.6, 2.7 35.4 times higher compared to Cu1/HCNS, HCNS, and bulk PCN respectively.⁶⁹

Pd single atoms dispersed on ultrathin nanosheets of cyano group rich C₃N₄ (Pd/D_N-UCN), obtained by the copolymerisation of urea and NH₄Cl followed by wet impregnation was demonstrated to possess improved photoinduced hydrogen evolution rate. Pd atom coordinated with one N of the cyano group and two sp² hybridised N atoms of the adjacent g-C₃N₄ layers was firmly stabilised in g-C₃N₄ interlayers inducing a mid-gap state in the band structure (Figure 19 (g-h)). SACs with 0.16 wt% of Pd (0.16%Pd/D_NUCN_{0.50}) produced noticeably higher hydrogen evolution rate, compared to Pd nanoparticle coordinated C₃N₄ based catalysts, at an apparent quantum yield of 15.8 % at 400 nm light irradiation.⁷⁰

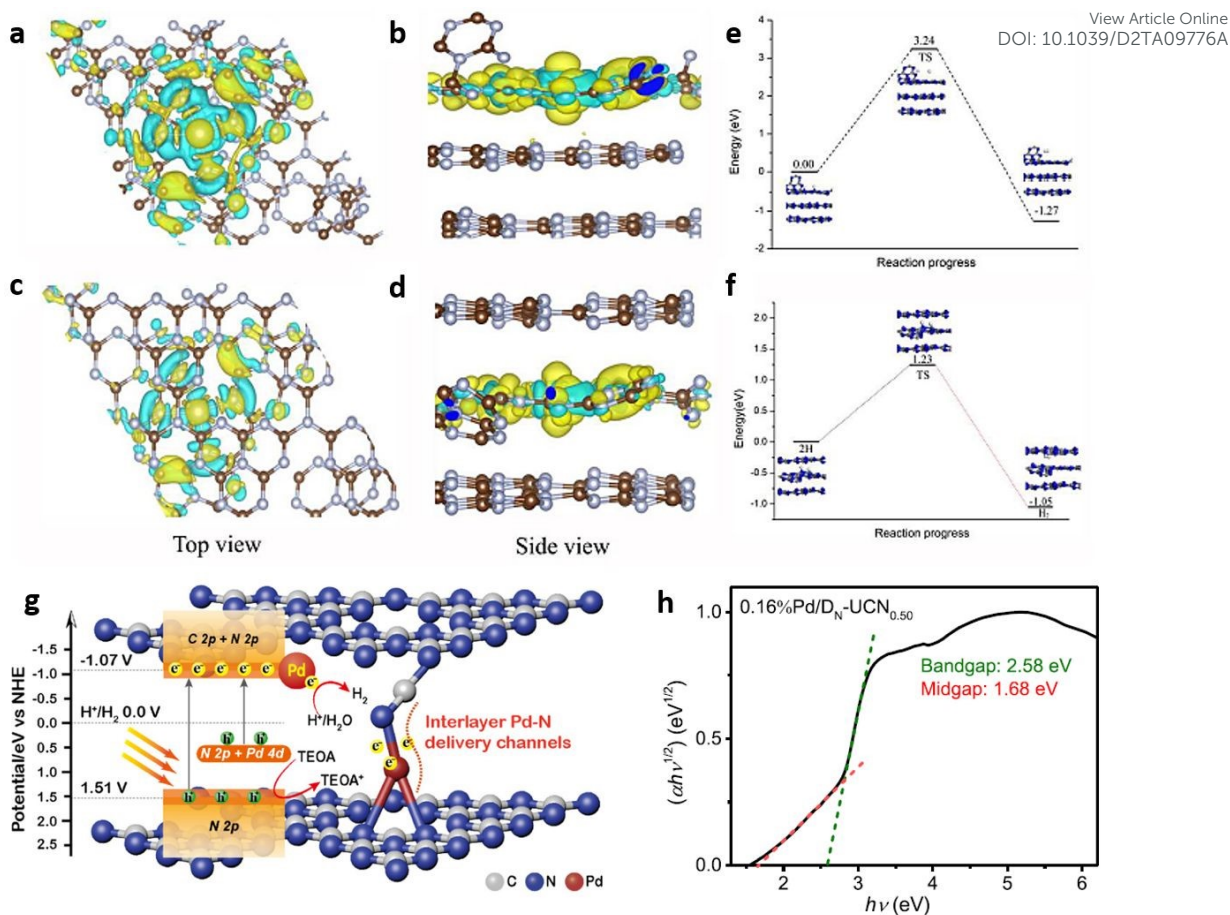


Figure 19. Charge distributions (top and side view) on Pt single atoms (a-b) on C₃N₄ surface (SA-Pt/g-C₃N₄-Sur), (c-d) within the inner layer of C₃N₄ (SA-Pt/g-C₃N₄-In), Energy profiles of HER over Pt atom (e) on C₃N₄ surface and (f) within the inner layer of C₃N₄. Reproduced with permission from ref. 68. Copyright 2020 Elsevier.⁶⁸, (g) Mechanism of Charge Separation, Transfer and H₂ Evolution in the photocatalyst 0.16%Pd/D_N-UCN_{0.50}, (h) Kubelka–Munk plot of 0.16%Pd/D_N-UCN_{0.50}. Reproduced with permission from ref. 70. Copyright 2022 American Chemical Society.

A two-component synergistic photocatalyst with atomic dispersions of Co and nanoparticles of Pt-Co alloy on C₃N₄ nanosheets exhibited hydrogen production at the rate of 300.9 mmol/h-g during overall water splitting (OWS). The single Co atoms efficiently activated HER while the alloy particles of PtCo were active sites for OER. The synergistic combination enabled high atom utilisation and the presence of different reaction centres permitted the transport of reaction intermediates with efficient exciton separation.⁷¹ The salient features of the reported works are summarised in Table 3.

Table 3 Summary of g-C₃N₄ SACs for photocatalytic water splitting

System	Single atom & loading	Synthesis method	HER Rate	Coordination site or structure & Oxidation state	Reference
AgTCM-mpg-CN	Ag 2 wt%	Template assisted direct synthesis	39.5 $\mu\text{mol H}_2/\text{h}$	C/N, +1	17
Pt-CN	Pt 0.16 wt%	Post synthesis - photo chemical reduction	318 $\mu\text{mol h}^{-1}$	N/C	64
Co ₁ /PCN	Co 1 wt%	Post synthesis-atomic layer deposition (ALD)	10.8 $\mu\text{mol h}^{-1}$	Co ₁ -N ₄	24
Co-phosphide/PCN	Co 0.4wt%	Post synthesis	H ₂ 410.3 $\mu\text{mol h}^{-1}\text{g}^{-1}$, O ₂ 204.6 $\mu\text{mol h}^{-1}\text{g}^{-1}$	Co ₁ -P ₄	65
Pt-SA-CN	Pt 0.11 wt%	Post synthesis	4875.0 $\mu\text{mol/g}$ in 4 h	Nitrogen	66
Pt/C ₃ N ₄	Pt	Post synthesis-Electrostatic deposition	140 $\mu\text{mol g}^{-1}\text{h}^{-1}$	Nitrogen, +2	23
Fe@g-C ₃ N ₄	Fe 0.5 at%	Supramolecular preorganisation assisted direct synthesis	3390 $\mu\text{mol h}^{-1}\text{g}^{-1}$	Nitrogen, +2	67
Pt-SA-CN	Pt 1.72 wt%	Post synthesis - photo chemical reduction	3.02 $\text{mmol g}^{-1}\text{h}^{-1}$	Nitrogen, Carbon	25
Co@g-C ₃ N ₄	Co 0.305 wt%	Supramolecular preorganisation assisted direct synthesis	2481 $\mu\text{mol h}^{-1}\text{g}^{-1}$	Nitrogen Oxidation state between +3 & +2	19
SA-Pt/g-C ₃ N ₄	Pt 8.7 wt%	Post synthesis - photo chemical reduction	22650 $\mu\text{mol g}^{-1}\text{h}^{-1}$	Pt-N ₄ Oxidation state < +2	68
Cu ₁ /HCNS	Cu	Post synthesis	3261 $\mu\text{mol g}^{-1}\text{h}^{-1}$	Cu ₁ N ₃ , +1	69
Pd/D _N -UCN	Pd 0.16 %	Post synthesis-Photochemical reduction	441.6 μmol in 4 h	Pd-N ₃ , +2	70
Co _{SAs} /PtCo@CNN	Co	Post synthesis - photo chemical reduction	300.9 $\mu\text{mol/h}\cdot\text{g}$	Co(II)N _x , +2	71

5.1.3 Photocatalytic Nitrogen Fixation

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Despite constituting more than 78% of the atmosphere, the dinitrogen molecule (N_2) is not directly utilised by most organisms owing to its attributes like strong $N \equiv N$ bond with a bond energy of -941 kJmol^{-1} , high ionisation potential, and non-polarity. Since nitrogen is indispensable for the sustenance of life, living organisms take N_2 in the form of ammonia or nitrates. This is mostly realised through 3 important pathways of biological nitrogen fixation by azobacteria, high energy nitrogen fixation by geochemical processes such as lightning and industrial nitrogen fixation through the well-known Haber-Bosch process. However, the contributions from biological and geochemical processes are extremely low and most of the demand is met from the energy intensive Haber-Bosch process that operates at both high temperatures ($400\text{--}500^\circ\text{C}$) and pressures ($150\text{--}250 \text{ atm}$). Moreover, in the industrial synthesis of ammonia, 1.87 tons of CO_2 is released for every ton of NH_3 produced. Photocatalytic nitrogen fixation thus assumes larger significance and is hence pursued widely as a sustainable process for ammonia production in an environmentally benign manner.⁷²

Photocatalytic nitrogen fixation proceeds by the rate determining step of $N \equiv N$ bond cleavage through electron mediated activation at the reducing sites of semiconductor photocatalysts. However, till date no reported photocatalyst possesses the appropriate electronic band structure to facilitate the one-electron transfer reduction of N_2 . The defect type activation centers utilised by most semiconductors are not adequate to make the process efficient and commercially viable. In this context single atom photocatalysts by virtue of their abundant, defect-free surface-active sites for effective N_2 adsorption and activation, offer promise for efficient photocatalytic N_2 fixation.¹³

In one of the earlier works on 'single atom like' copper-doped $g\text{-}C_3N_4$ containing $Cu(I)\text{-}N$ active sites, the charge density differences were used to simulate the electron transfer process between Cu^+ and N_2 molecules leading to electron depletion and accumulation on Cu^+ and N_2 respectively. Further successive electron transfer processes lead to NH_4^+ through high-energy intermediates like $-N_2^-$, $-N_2H$, or $HN=NH$, etc. DOS results confirmed the delocalisation of $\sigma g 2p$ orbital (highest occupied molecular orbital (HOMO) of N_2) upon adsorption on Cu centres as well as the shifting of $\pi g^* 2p$ orbital (lowest unoccupied molecular orbital (LUMO) of N_2) near to fermi level. This led to a decrease in the electron states of the LUMO orbital from 6.9 eV for free N_2 to 1.0 eV for

M_S-Cu-CN facilitating the activation of N₂ molecule and subsequent H⁺ attack leading to the formation of NH₄⁺.⁷³

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Wang and co-workers demonstrated, by first-principles calculations, the potential use of a metal-free photocatalyst with boron (B) single atoms decorated on g-C₃N₄ (B/g-C₃N₄) for efficient N₂ reduction. The sp³ hybridised B with three half-filled and one empty orbital form two B-N bonds with g-C₃N₄ matrix (utilising two of the half-filled sp³ orbitals), facilitating the atomic level distribution of B atoms. During the N₂ fixation process, one half-filled and the empty sp³ orbitals remaining in the B atom interact with N₂ through the “acceptance-donation” process facilitating active sites for N₂ adsorption and subsequent reduction Figure 20(a-f).⁷⁴ The high binding energies of -1.04 and -1.28 eV can thus be realised in B/g-C₃N₄ SACs through side-on and end-on bonding with N₂ respectively. Photoreduction of N₂ to NH₃ over B/g-C₃N₄ catalyst may follow any of the three typical mechanisms of distal, alternating, and enzymatic mechanisms (Figure 20g). The low onset potential of 0.20 V obtained by B/g-C₃N₄ SACs supported the enzymatic pathway for N₂ reduction Figure 20(h-j). This theoretical study also predicted low formation energy for B/g-C₃N₄ SACs, enhanced light absorption in the visible and infrared region, and high thermal stability upto 1000K enabling sustainable NH₃ production through photocatalytic N₂ fixation. The B/g-C₃N₄ SACs showed enhanced visible light and infrared light absorbance, high thermal stability and ease of preparation enabling them to be effective for photocatalytic nitrogen reduction.⁷⁴

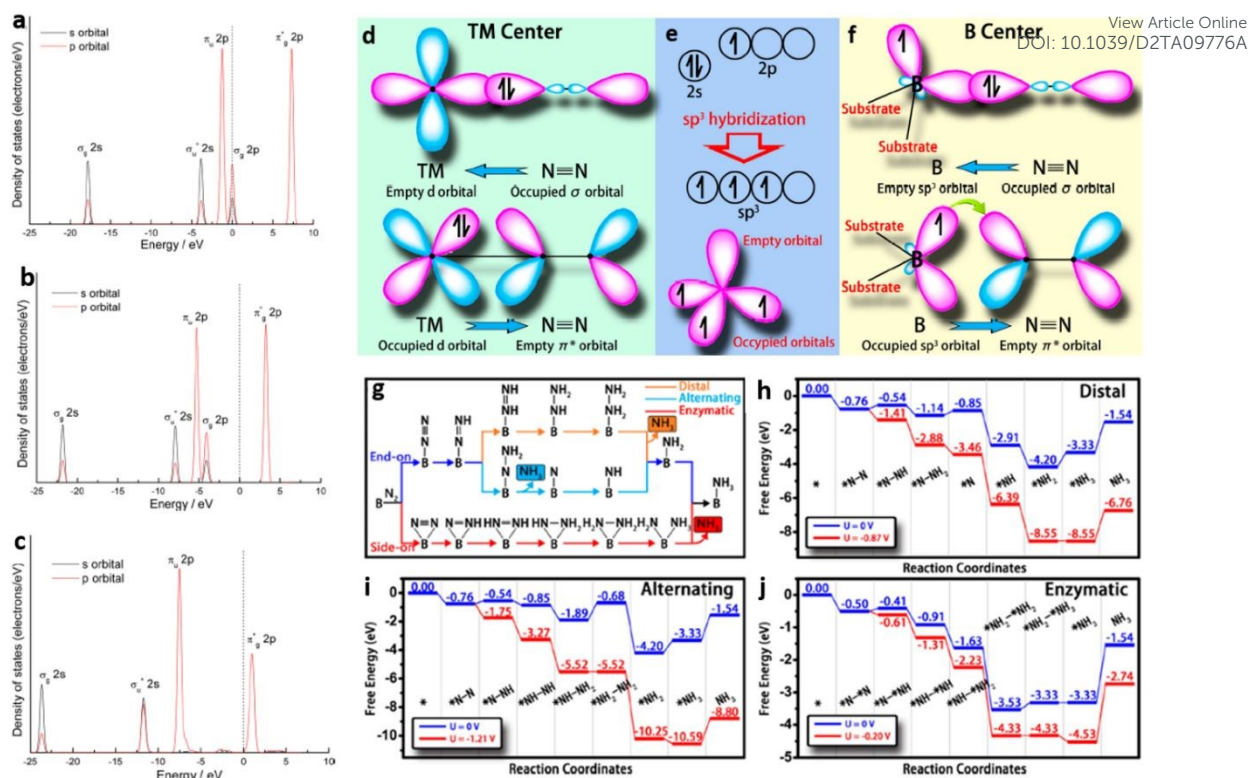


Figure 20. (a) DOS of free N_2 molecule, (b) N_2 molecule adsorbed on pure GCN and (c) N_2 molecule adsorbed on $\text{M}_5\text{-Cu-CN}$. Reproduced with permission from ref. 73. Copyright 2017 American Chemical Society. (d) Illustration of N_2 bonding to transition metals, (e) formation of sp^3 orbitals in B atom, (f) N_2 binding to the B atom stabilised on $\text{g-C}_3\text{N}_4$, (g) distal, alternating, and enzymatic mechanisms for N_2 reduction, Free energy diagrams for (h) distal, (i) alternating, (j) enzymatic pathways for N_2 reduction on B/ $\text{g-C}_3\text{N}_4$. Reproduced with permission from ref. 74. Copyright 2018 American Chemical Society.

Mo single-atoms on in-situ formed $\text{g-C}_3\text{N}_4$ were prepared by the calcination of urea and $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ by establishing coordination with two N donors of $\text{g-C}_3\text{N}_4$ to form MoN_2 structures. The active sites for N_2 chemisorption provided by low-coordinated Mo centers in 3-Mo-PCN catalyst, with a metal loading of 0.346 wt%, facilitated high photocatalytic activity towards NH_3 evolution in pure water at a rate of $50.9 \mu\text{mol gcat}^{-1} \text{h}^{-1}$. The use of ethanol as an electron scavenger increased the rate to $830 \mu\text{mol gcat}^{-1} \text{h}^{-1}$ at a quantum efficiency of 0.70% at 400 nm. DFT calculations supplemented experimental observations and predicted that coordinatively unsaturated Mo single atom centres strongly adsorb N_2 through an end-on configuration resulting in the elongation of the

N≡N bond from 1.11 Å to 1.15 Å. The photogenerated electrons are thus transferred to the weakened N≡N bond providing efficient N₂ reduction at ambient conditions.⁷⁵

Chen and co-workers successfully synthesised multifunctional single atom cobalt loaded g-C₃N₄ (Co@g-C₃N₄) photocatalyst for N₂ fixation reaction in a methanol/H₂O medium. Co@g-C₃N₄-1 with a metal loading of 0.305 wt% selectively reduced N₂ to NH₃ at the rate of 50.2 μmol h⁻¹ and without any by-products like hydrazine hydrate and nitrates. In comparison bulk g-C₃N₄ and g-C₃N₄ obtained through the supramolecular route exhibited a production rate of 8.2 μmol h⁻¹ and 19.5 μmol h⁻¹ respectively.¹⁹

Single atoms of ruthenium (Ru) dispersed on the g-C₃N₄ surface were obtained by the pyrolysis of a precursor mix containing dicyandiamide and RuCl₃.xH₂O in an argon atmosphere. SAC containing 0.05 atomic % of Ru exhibited photocatalytic nitrogen fixation at the rate of 2.26 mg L⁻¹ g_{cat}⁻¹ h⁻¹ in pure water and without hole-scavengers. The rate was 1.5 times greater than that of pure g-C₃N₄ (Ru-CCN-0). The improved catalytic activity was ascribed to the high N₂ adsorption capacity combined with increased light absorbance in the spectral region of 200 to 800 nm owing to a redshift in the absorption edge of Ru-CCN-0.05 compared to that of Ru-CCN-0.⁷⁶ The SAC systems demonstrated for photocatalytic nitrogen fixation are listed in Table 4.

Table 4 Summary of g-C₃N₄ SACs for photocatalytic nitrogen fixation

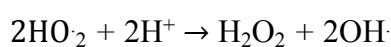
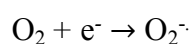
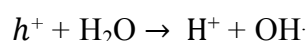
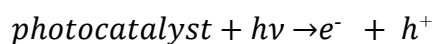
System	Single atom & loading	Synthesis method	NH ₃ evolution rate	Coordination site or structure & oxidation state	Reference
M _S -Cu-CN	Cu 0.25 wt %.	Direct synthesis	8.8 mg·L ⁻¹ ·h ⁻¹ ·g _{cat} ⁻¹	Cu(I)-N, +1	⁷³
B/g-C ₃ N ₄	B	DFT Study	-	Nitrogen	⁷⁴
Mo-PCN	Mo 0.346wt%	Template free direct synthesis	50.9 μmol g _{cat} ⁻¹ h ⁻¹ in pure water & without using electron scavenger, 830 μmol g _{cat} ⁻¹ h ⁻¹ using ethanol as electron scavenger	Mo-N ₂ , Oxidation state in between 0 & +4	⁷⁵

Co@g-C ₃ N ₄	Co 0.305wt%	Chemical reduction assisted Post synthesis	50.2 μmol h ⁻¹	Nitrogen, +2	19 View Article Online DOI: 10.1039/D2TA09776A
Ru-CCN	Ru 0.34 wt%	Direct synthesis	2.26 mg L ⁻¹ gcat ⁻¹ h ⁻¹ in pure water	Nitrogen,	76

5.1.4 Photocatalytic environmental remediation

One of the potential methods that is perceived for wastewater and pollutant treatment is photocatalysis.⁷⁷ Irradiation of a photocatalyst with energy more than or equal to its band gap energy excites valence band (VB) electrons to the conduction band (CB) creating electron-hole pairs. The excitons then migrate to the catalyst surface without recombination, engaging in various redox reactions with H₂O, O₂, and organic contaminants leading to pollutant degradation.⁷⁸ During the process, electrons from CB react with molecular oxygen forming superoxide radical (O₂^{•-}) which is an extremely powerful oxidising agent. On the other hand, holes from VB react with hydroxide ions (OH⁻) or water (H₂O) forming hydroxyl radical (OH[•]) which is also an important non-selective oxidising agent.⁷⁹ The superoxide and hydroxide radicals degrade a variety of organic pollutants like dyes, antibiotics, etc. into CO₂, H₂O and inorganic ions. The feasibility of these redox reactions depends on the CB and VB positions of the photocatalyst. The necessary condition for oxidation warrants the VB potential to be more positive than the oxidation potential of the surface reaction to be accomplished.⁸⁰ Similarly reduction reaction proceeds when the CB potential is more negative with respect to the reduction potential of the surface reaction. These redox reactions form basic pathways for every photocatalytic environmental remediation.⁸¹

Reactions:



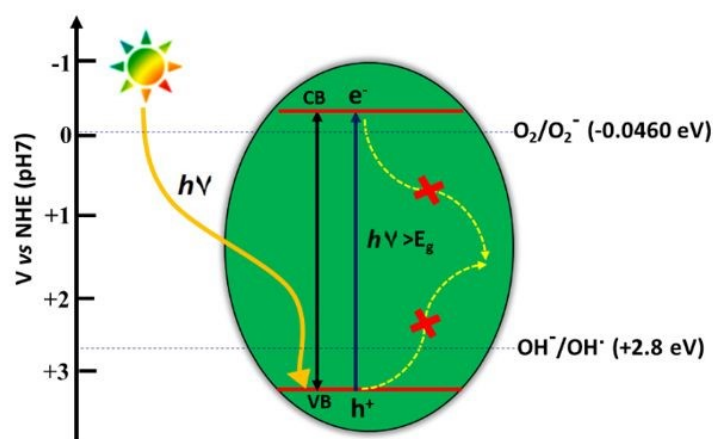


Figure 21. Schematic of the photocatalytic process

Zhao and co-workers developed single-atom Ag supported mpg-C₃N₄ (Ag/mpg-C₃N₄) by a method involving the co-condensation of dicyandiamide and silver tricyanomethanide (AgTCM) through a silica templating approach. The photocatalytic activity was demonstrated by peroxydisulfate (PMS) mediated bisphenol A (BPA) degradation by 10% Ag/mpg-C₃N₄ catalyst, where in 100% activity was achieved within 1 h of visible light illumination. The improved catalytic activity was realised due to the synergistic effect of atomically dispersing Ag atoms on high surface area g-C₃N₄ leading to a reduction in band gap from 2.5 eV (mpg-C₃N₄) to 2.09 eV (10% Ag/mpg-C₃N₄).⁸²

Single Pt atom catalyst on g-C₃N₄ described earlier⁶⁶ for photocatalytic HER has been successfully employed for the selective photocatalytic NO oxidation to NO₃⁻. The oxidation proceeded progressively over 150 min with a removal ratio of 96.2% for Pt 0.2-SA-CN. In comparison, pure g-C₃N₄ and g-C₃N₄ with 0.1 and 0.3 wt% of single atom Pt (Pt 0.1-SA-CN, Pt 0.3-SA-CN) exhibited 78.9%, 84.7%, and 92.0% of NO removal respectively. Additionally, g-C₃N₄ with photo-deposited Pt nanoclusters of 4 nm size (Pt 0.2-VL-CN) samples exhibited 90.9% NO removal. The negative shift of CB and the increased generation of ROS (h⁺, •OH or •O₂⁻) expedited the photo-induced catalytic activity.⁶⁶

Liu et al synthesised Ag loaded SAC on ultrathin g-C₃N₄ sheets (AgTCM/UCN) via copolymerisation of dicyandiamide and silver tricyanomethanide (AgTCM) in presence of NH₄Cl. AgTCM/UCN with 1 wt% Ag loading photocatalytically degraded 86.4% of

sulfamethazine (SMT) in the presence of PMS during the 21 min of visible light irradiation. Aberration corrected HAADF-STEM analysis revealed that Ag single atoms of ~ 0.25 nm diameter were dispersed over the g-C₃N₄ matrix. The photodegradation of SMT was shown to proceed via any of the three pathways involving sulfonamide bond cleavage, SO₂ extrusion, and aniline oxidation.⁸³

g-C₃N₄ based catalyst containing Fe single atoms and ultra-small clusters with Fe(II)-N_x active sites was prepared by pyrolysing a precursor mix containing melamine (MA) and iron imidazole complex (Fe-ICC). High Fe content up to 18.2 wt% was realised in a composition (I-FeN_x/g-C₃N₄-5) with an optimum ratio of MA/Fe-ICC to be 5. DFT calculations revealed that Fe single atoms preferably occupy the interlayers of g-C₃N₄ via bonding with nitrogen located above and below it and with a binding energy (BE) of -3.92 eV compared to a low BE of -2.77 eV in Fe atom at the center of the 6-fold cavity. Additionally, ultra-small Fe clusters (Fe₂ dimer as a model) are stable only at the interlayers with a BE of -2.50 to -2.83 eV. A high binding energy value (-3.92 eV) further revealed that Fe atoms remain isolated preferably over its cluster formation (Figure 22(a-d)). The developed I-FeN_x/g-C₃N₄-5 catalyst are shown to exhibit rapid photo-fenton degradation (100% within 15 min at pH 7) of organic contaminants like methylene blue (MB), methyl orange (MO), rhodamine B (RhB), and phenol. The degradation process proceeds via the rapid generation of HO· radicals from H₂O₂ at the Fe(II)-N_x active sites.⁸⁴

Silver single-atom catalyst based on amorphous g-C₃N₄ was developed by Tong et al through a supramolecular gel formation involving precursors of melamine and silver nitrate. The thermal polymerisation yielded a high density of silver atoms that selectively broke H-bonds of layered g-C₃N₄ inducing amorphisation. An optimised MA composition with Ag atomic ratio of 11.6 % exhibited a narrow E_g value of 2.54 eV, improved visible light absorption, and accelerated charge transfer leading to the effective degradation of naproxen (NPX).⁸⁵

Ammonia-assisted selective catalytic reduction (SCR-NH₃) is the conventional methodology to reduce NO emissions but suffers from the disadvantages of particulate formation, hardware corrosion and direct release of unreacted NH₃. Direct reduction of NO with CO, without NH₃ injection, is an environmentally benign approach to circumvent the disadvantages of the SCR-NH₃ process. Ni Single atoms on monolayer g-

C_3N_4 (Ni-g- C_3N_4) were demonstrated to be an efficient and stable catalyst for the photocatalytic reduction of NO to N_2 at about 350 °C and space velocity of 15,000 h⁻¹. Ni-g- C_3N_4 adsorbed multiple numbers of NO molecules simultaneously and the N_2O intermediate was rapidly reduced to N_2 with an energy barrier of 0.50 eV. The oxidised catalyst was regenerated rapidly by CO through OR2 mechanism with an energy barrier of 0.16 eV.⁸⁶

Zeng et al employed an in-situ growth process to develop single-atom cobalt based polymeric C_3N_4 (pCN) catalyst and demonstrated its catalytic efficacy for the degradation of oxytetracycline (OTC). The anchoring of single-atom Co on pCN was realised through Co-O and Co-N covalent bond formation. The catalyst with the cobalt loading of 1.28% (Co(1.28%)-pCN) displayed an excellent rate constant of 0.038 min⁻¹ for OTC degradation which was nearly 4 times more than that of pCN.⁸⁷

Zhao et al evaluated the photodegradation of pharmaceutical pollutants utilising single-atom Ni dispersed on C_3N_4 nanosheets (saNi-n C_3N_4). The pyrrolic N mediated Ni-N coordination confirmed by spectrometric analyses, is responsible for the improved interfacial charge transfer via N–Ni–N bridges. Gemfibrozil, a model pollutant was degraded up to 75.9% in 30 minutes of visible light irradiation. The degradation efficiency of saNi-n C_3N_4 was better than the widely used TiO_2 photocatalyst.⁸⁸

Chen et al prepared single atoms of various transition metals (SA-TM, TM = Cr, Mn, Fe, Co, Cu) on g- C_3N_4 containing abundant pyrrolic N (PN-g- C_3N_4) through an aqueous self-assembly process involving the precursor mix of xanthine, cyanuric acid, melamine. Transition metal ions were adsorbed on the self-assembled MCAXT through binding sites provided by imidazole groups and subsequent calcination in N_2 atmosphere formed SA-TM/PN-g- C_3N_4 catalysts that exhibited excellent performances for Heterogeneous Fenton-Like Reaction (HFLR). Cr dispersed SACs were found effective for visible light induced photocatalytic degradation of bisphenol A, in the pH range of 3.0–11.0 with outstanding cyclic stability. The enhanced charge carrier production as well as their separation along with the cycling of the Cr^{3+}/Cr^{2+} couple boosted the HFLR performance. Theoretical studies predicted that Cr(II)- N_4 active sites with its structure analogous to metalloporphyrin mimicked peroxidase nanozymes for the effective homolysis of peroxide O-O in H_2O_2 .⁸⁹

Wang et al designed Pd SACs (Pd-Cv-CN) for photocatalytic NO conversion, by anchoring Pd atoms on carbon vacancies present in modified g-C₃N₄ (Cv-CN) via a photo-reduction process. The theoretical simulation predicted the possibility of isolated Pd-N₃ active site formation. The DOS plot of Pd-Cv-CN revealed a negative shift in the peak positions on the negative energy side due to the modification of 4d orbital of Pd. (Figure 22 (g-f)). This has led to an increase in band levels and a decrease in the band gap for Pd-Cv-CN compared to that of g-C₃N₄. The developed Pd-Cv-CN effected 56.3 % of NO conversion in 30 min illumination time, while pristine CN and Pd nano-Cv-CN converted only 12.7 % and 46.0 % of NO respectively.⁹⁰

Polymeric g-C₃N₄ containing Pt dispersions in the form of single atoms SA-Pt (0.2 nm), nanoclusters CL-Pt (1 nm), and nanoparticles NP1-Pt and NP2-Pt (4 and 7 nm diameter respectively) was demonstrated for the simultaneous benzaldehyde oxidation to benzoic acid and photocatalytic hydrogen production. The catalytic efficiency was highest for Pt single atoms compared to nanoclusters and nanoparticles of Pt. For SA-Pt catalyst, the benzaldehyde conversion and H₂ evolution reached a value of 70.8 mmol/g_{Pt} and 34 mmol/g_{Pt} respectively in 3 h. Upon visible light excitation, SA-Pt catalyst promoted the transfer of photo-generated holes for benzaldehyde oxidation while CB electrons promoted the proton reduction leading to H₂ evolution (Figure 22 (h)).⁹¹ The SACs explored for photocatalytic environmental remediation with the applications demonstrated are presented in Table 5.

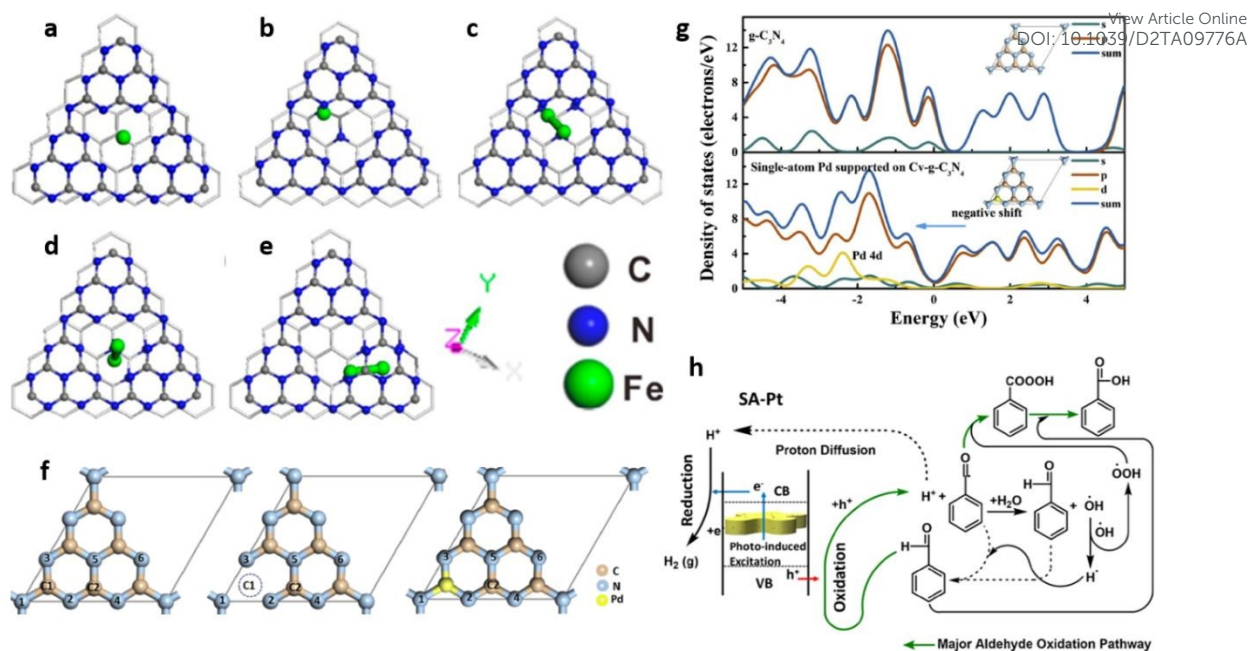


Figure 22. Structures depicting possible locations for Fe single atom and cluster over g-C₃N₄; Fe Single atom in (a) 6-fold cavity centre, (b) interlayer. Fe cluster sites in the interlayer (c), Site 1, (d) Site 2 (e) Site 3. Reproduced with permission from ref. 84. Copyright 2018 American Chemical Society. (f) The carbon vacancies and single atom site of Pd in g-C₃N₄ and (g) corresponding DOS. Reproduced with permission from ref. 90. Copyright 2021 Elsevier. (h) Schematic diagram representing the mechanism of benzaldehyde oxidation and associated H₂ evolution with photoinduced electron and hole transfer. Reproduced with permission from ref. 91. Copyright 2021 Elsevier.

Table 5 Summary of g-C₃N₄ SACs for photocatalytic environmental remediation

System	Single atom & loading	Synthesis method	Catalytic application, Degradation % or rate & Time	Coordination Site or Structure & Oxidation state	Reference
Ag/mpg-C ₃ N ₄	Ag	Template assisted direct synthesis	PMS mediated Bisphenol A degradation, 100%, 60 min	Nitrogen, 0	82
Pt-C ₃ N ₄	Pt 0.2 wt%	Post synthesis Reduction under an inert atmosphere	NO oxidation, 96.2%, 150min	Nitrogen, +2	66
AgTCM/UCN	Ag 1wt%	Template assisted direct synthesis	PMS mediated Sulfamethazine degradation, 86.4%, 21 min	Nitrogen	83
I-FeN _x /g-C ₃ N ₄	Fe	Template free	Photo-Fenton	Fe-N _x	84

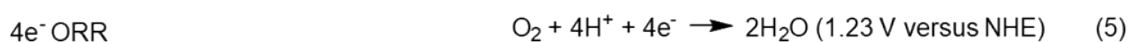
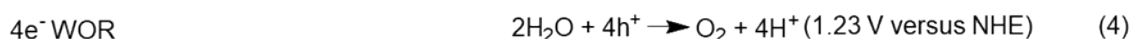
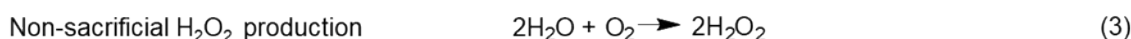
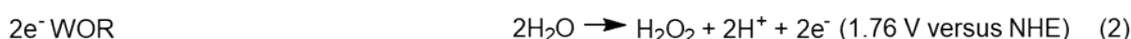
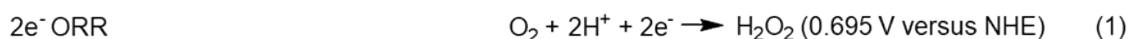
	18.2 wt %	direct synthesis	degradation; Methylene blue, Methyl orange, Rhodamine B, & Phenol, 100%, 15 min	+2 (64.3%), +3 (35.7%)	View Article Online DOI: 10.1039/D2TA09776A
MA (Ag/g-C ₃ N ₄)	Ag 12.0%, (atomic ratio)	Direct synthesis	Degradation of naproxen, 1.92×10 ⁻¹ min ⁻¹	Carbon	85
Ni/g-C ₃ N ₄	Ni	Post synthesis	Photocatalytic degradation of NO with 100% yield Rate-15000h ⁻¹	Nitrogen	86
Co-pCN	Co 1.28%	Template free direct synthesis	Degradation of oxytetracycline, 75.7%, 40 min	Nitrogen, Oxygen	87
saNi-nC ₃ N ₄	Ni 8 wt%	Post synthesis- Microwave treatment	Degradation of gemfibrozil, 75.9%, 30 min	Ni-N _x , +2	88
SA-TM/PN- g-C ₃ N ₄	TM = Cr, Mn, Fe, Co, Cu	Direct synthesis	Degradation of bisphenol A, SA-Cr/PN-g- C ₃ N ₄ exhibited highest activity: 98.8%, 70 min	Cr(II)-N ₄ , +2	89
Pd-Cv-CN	Pd	Post synthesis- Photochemical reduction	NO oxidation, 56.3%, 30 min	Pd-N ₃ , +2	90
Pt/g-C ₃ N ₄ (SA-Pt)	Pt 0.35 wt%	Post synthesis- Photochemical reduction	Benzaldehyde oxidation: 70.8 mmol/g _{pt} & H ₂ production: 34 mmol/g _{pt} in 3h	Nitrogen	91

5.1.1 Photocatalytic H₂O₂ synthesis via oxygen reduction reaction (ORR)

Semiconductor mediated photocatalytic H₂O₂ synthesis from oxygen and water is an attractive and environmentally benign process.⁹² To realise appreciable efficiencies, both the 2e⁻ oxygen reduction reaction (ORR, equation 1) and 2e⁻ water oxidation reaction (WOR, equation 2) need to be catalysed.⁹³ However, the 2e⁻ WOR process occurs at high oxidation potentials (1.76 V versus NHE, normalised hydrogen electrode) owing to thermodynamic considerations and is therefore difficult by photocatalytic approaches.^{94, 95}

H₂O₂, being an excellent hole scavenging material is prone to oxidation at these potential values.⁹⁶ On the other hand, photosynthesis of H₂O₂ by 2e⁻ ORR pathway has been hitherto achieved albeit with a low efficiency of less than 8% for non-sacrificial H₂O₂ production (equation 3).⁹⁷ In order to enhance the efficiency of non-sacrificial H₂O₂ synthesis,

concurrent promotion of both $2e^-$ ORR and $4e^-$ WOR (equation (4)) is necessary.⁹⁸ O_2 , generated in situ as a product of $4e^-$ WOR, is also a reactant for the $2e^-$ ORR and hence the rapid consumption of O_2 by ORR will accelerate the kinetics of WOR.⁹⁶ Therefore, the presence of active sites, in SACs with O_2 selectivity for the $2e^-$ ORR promotes artificial H_2O_2 synthesis via photocatalysis.⁹⁹



The adsorption of O_2 on the metal surface occurs via end on Pauling-type and side on Griffiths and Yeager types (side-on) (Figure 23 (a)).^{99, 100} The Pauling type end-on O_2 adsorption minimises O–O bond fission and the $4e^-$ ORR (equation (5)) can be suppressed.¹⁰¹ End-on and side-on adsorption of O_2 molecules occur on metal particles leading to O–O bond splitting. In SACs O_2 molecules adsorb on atomically dispersed sites through the end-on type, reducing the breaking of O–O bond (Figure 23 (b)).¹⁰²⁻¹⁰⁶

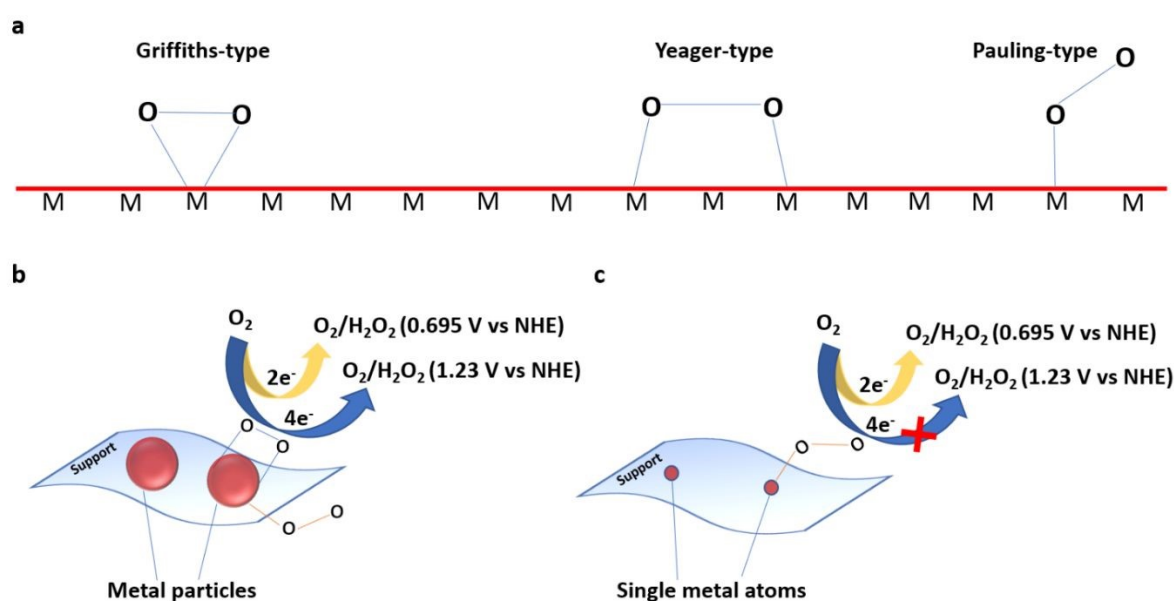


Figure 23. (a) O_2 adsorption modes on a metal surface, ORR pathways on (b) metal nanoparticles and (c) single metal atom sites.

Single atom photocatalysts (SAPCs) with metals of d^{10} electronic configuration favour efficient charge separation through the formation of intermediate bands and form reactive centres with a high density of charge carriers.^{56, 107} Such SACs are considered as potential catalysts for the photocatalytic H_2O_2 synthesis through the $2e^-$ ORR.¹⁰⁸ Ohno et al developed Sb dispersed $g-C_3N_4$ (Sb-SAPC) where single atoms of Sb enabled the photoreduction of O_2 through the 2 electron ORR, generating H_2O_2 at the rate of 12.4 mg l^{-1} in 120 min. The N atoms of C_3N_4 surrounding the Sb single atoms, on the other hand, enhanced the kinetics of water oxidation. The apparent quantum yield (Φ_{AQY} , 17.6% at 420 nm) and conversion efficiency (solar to chemical, 0.61% were better than the best performing photocatalysts reported. The analysis of the products of photocatalysis suggested that the H_2O_2 generation was through the two-electron ORR pathway.^{100, 101}

In another noteworthy contribution, SACs with single atoms of Fe, Ni, Co, In and Sn) were prepared through a wet-chemical synthetic route followed by thermal treatment. Invoking time dependent DFT (TDDFT) calculations, it was demonstrated that the inclusion of metal single atoms on melem units significantly altered the charge separation process. The adsorption energy (E_{abX}) of melem was similar for single atoms of In and Sn suggesting lesser tendencies for charge recombination while Fe (2+ and 3+), Co and Ni (2+) increased the E_{abX} due to dominant recombination. Moreover, iso surfaces created due to the incorporation of In and Sn single atoms favoured the adsorption of oxygen accelerating oxygen reduction at the sites.¹⁰¹ Table 6 lists the reported systems for photocatalytic H_2O_2 synthesis

Table 6 Summary of $g-C_3N_4$ SACs for photocatalytic H_2O_2 synthesis via oxygen reduction reaction (ORR)

System	Single atom & loading	Synthesis method	H_2O_2 Production rate & time	Coordination site or structure & oxidation state	Reference
Sb-SAPC	Sb 10.9 wt%	Template free direct synthesis	12.4 mg l^{-1} , 120 min	Nitrogen, +3	¹⁰⁰
M-SAPC	Fe, Ni, In, Co, Sn, 0.5-0.6 mmol per 1 g catalyst	Template free direct synthesis	In-SAPC & Sn-SAPC exhibited superior H_2O_2 production	Nitrogen, Oxidation state of Fe is between II & III, and for Co, Ni, In & Sn is close to II, II, III & IV respectively	¹⁰¹

5.2 Thermal Catalysis

Catalysts play a vital role in numerous industrial processes for the synthesis of chemicals.¹⁰² The development of efficient catalysts that demonstrate product selectivity in appreciable yields is an essential requirement for the bulk synthesis of chemicals.¹⁰³ Consequently, the majority of industrial catalysts are based on noble metals on appropriate supports as they are capable of activating important molecules like CO, H₂, O₂, H₂O, etc. Nevertheless, the widespread practical application of noble metal-based catalysts in bulk manufacture is significantly hampered by the scarcity and exorbitant cost of precious metals.^{104, 105} Transition metal catalysed organic reactions, which can be classified under thermal catalysis are now actively employed in the fields of pharmaceutical synthesis, materials development, and biological sciences.¹⁰⁶ However, such catalyst systems suffer from shortcomings like poor selectivity, low utilisation efficiency, minimal catalytically active species and unwanted side reactions during their practical application.¹⁰⁷ SACs are currently receiving significant attention by virtue of their high conversion efficiency in thermal catalysis for organic transformations.⁵⁶ The beneficial aspects of both homogeneous and heterogeneous catalysts are integrated in SACs.¹⁰⁸

SACs are shown to catalyse organic reactions efficiently owing to the presence of unsaturated metal centres, unique electronic structure and 100% atom utilisation efficiency. Electron transfer between metal single atoms and the coordinating atoms of the support induces positive charges (partial or full) on the metal atoms of SACs and offers an enhanced rate of conversion of substrate into product. Furthermore, metal atoms are spatially isolated in SACs due to which the reactive intermediates of the catalytic reactions are adsorbed differently to prevent undesirable side reactions for which the presence of adjacent metal sites is mandatory.¹⁰⁹ Development of SACs and ADMCs provides the most ideal strategy for creating cost-effective catalysts for organic transformations (Figure 24).¹¹⁰

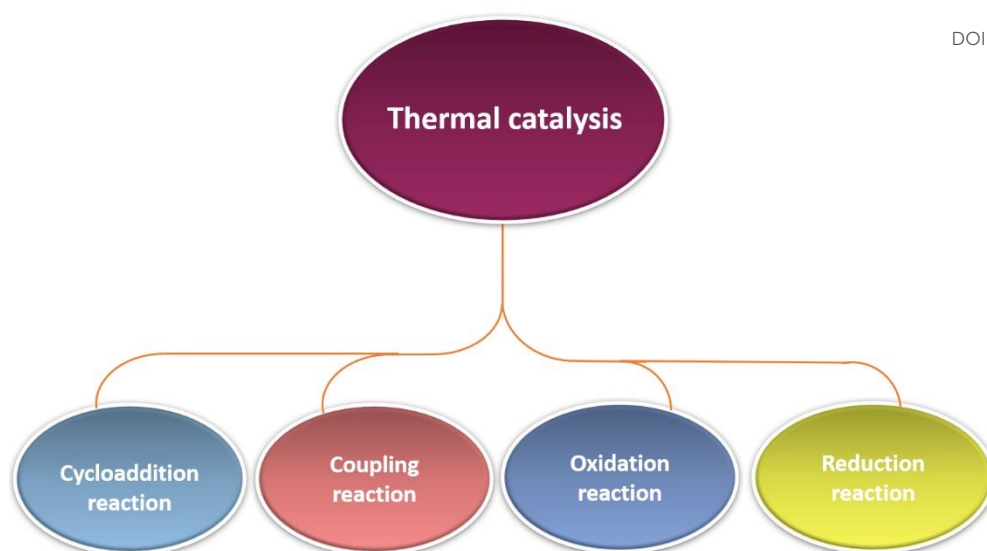


Figure 24. Various reactions catalysed by g-C₃N₄ based SACs in the area of thermal catalysis

Single-site [Pd] mpg-C₃N₄ heterogeneous catalyst obtained by silica templated thermal condensation of cyanamide, was demonstrated as the first stable single-site heterogeneous catalyst for the hydrogenation of alkynes and nitroarenes. Atomically dispersed [Pd] mpg-C₃N₄ with 0.5 wt% of Pd and with an average particle size of 0.3–0.4 nm displayed excellent product selectivity (>90%) and significantly improved catalytic activity over conventional nanoparticle based heterogeneous catalysts. For 1-hexyne hydrogenation, the reaction rate at 30 °C and 1 bar pressure was 3 orders higher in magnitude than the conventional catalysts like Ag, Au, and CeO₂. The performance was further improved at 60 °C and 2 bar pressure where 100% selectivity for 1-hexene was realised. The [Pd] mpg-C₃N₄ single-site catalyst also displayed excellent chemoselectivity and stereoselectivity (cis/trans ratio >20) as has been shown in the hydrogenation reaction of 3-hexyne to cis-3-hexene and 2-methyl-3-butyne-2-ol to 2-methyl-3-buten-2-ol. [Pd] mpg-C₃N₄ catalyst is also capable of catalysing the hydrogenation reaction of nitrobenzene to aniline. The improved catalytic activity of [Pd] mpg-C₃N₄ single-site catalyst was rationalised by DFT calculations which confirmed hydrogen activation and alkyne adsorption on single-site Pd atoms. g-C₃N₄ as a matrix facilitates the homogeneous distribution of Pd atoms, promotes H₂ activation and inhibits CO poisoning of metal active sites.⁴

Dual functional catalyst Ag/mpg-C₃N₄ SAC as mentioned earlier for photocatalytic HER, was also demonstrated to be very effective for alkyne hydrogenation with near 100% selectivity for the conversion of 1-hexyne at a reaction rate exceeding 100 mol_{alkyne} h⁻¹ mol_{Ag}⁻¹ at 303 K and 10 bar compared to the rates of 60 and 40 mol_{alkyne} h⁻¹ mol_{Ag}⁻¹ for catalysts prepared by impregnation–reduction and spray deposition respectively.¹⁷

SAC with extremely low loading (519 ppm) of Au on mpg-C₃N₄ (Au₁/mpg-C₃N₄) demonstrated high turnover frequency (50200 h⁻¹) for the oxidation of silane in presence of water and oxygen. The coordination of Au^I with three N atoms or C atoms in the repeating tri-s-triazine units of g-C₃N₄ provides atomic level dispersion of highly active Au^I. In comparison with Au₁/mpg-C₃N₄, HAuCl₄ and Au nanoparticles showed inferior performance for the oxidation of diphenylmethylsilane with water. Au₁/mpg-C₃N₄ also displayed excellent catalytic activity for the oxidation of various organosilanes with greater than 95% yield. It was proposed that the Au^I single atoms activate the Si-H bond through oxidative insertion forming a Si-Au^{III}-H intermediate which further reacted with H₂O to form silanol and H₂ with the regeneration of the Au^I active sites (Figure 25 (a))²⁶.

Single atom Palladium catalysts (Pd-ECN) on C₃N₄, obtained by the thermal exfoliation, is demonstrated to outperform conventional catalysts (homogeneous and nanoparticle based heterogeneous systems) for the Suzuki coupling between bromobenzene and phenylboronic acid pinacol ester. The ECN matrix not only provides appropriate coordination of Pd atoms in catalyst formation but also participates in the catalytic process through adsorption, stabilisation and activation of substrates and intermediates. The Pd-ECN SACs displayed 63% conversion with 90% selectivity towards biphenyl. The rate of product formation increased linearly from 0.22 to 0.57 mmol product min⁻¹ g_{cat}⁻¹ with the loading of Pd (from 0.25 to 0.66 wt%). However, as the concentration is increased to 1.25 wt%, the reaction rate is decreased to 0.32 mmol product min⁻¹ g_{cat}⁻¹. The turnover frequency (TOF) varied between 558 and 549 h⁻¹, respectively, for 0.25 and 0.66 wt% Pd) but was reduced significantly to 163 h⁻¹ as Pd content increased to 1.25 wt%.¹¹¹ The electron density around the N-sites of ECN matrix activated bromobenzene while the lattice flexibility of ECN facilitated multiple coordination patterns for enhanced stability. This mechanism is further verified by performing the reaction with single atom Pd on mesoporous C₃N₄ (Pd-MCN) which displayed less activity albeit high stability and

selectivity. The mediocre catalytic performance of Pd-MCN is ascribed to the enhanced structural disorder present in MCN relative to ECN.¹¹¹

Guo et al designed SACs with neighbouring Pt and Ru (Pt-Ru) monomers in N deficient g-C₃N₄ (PtRuSA-CN620) by photoreduction at liquid nitrogen temperature. Conventionally the structure of g-C₃N₄ contains a C atom coordinated to three N atoms while a few N atoms (denoted as N_{2C} sites) are coordinated only with two C atoms. The creation of nitrogen vacancy leads to the formation of two neighbouring two-coordinated C atoms (denoted as C_{2C} sites) in the g-C₃N₄ framework. The structure simulation revealed that the creation of N vacancies in g-C₃N₄ increases the largest vertical dimension from 4.20 Å to 5.47 Å which facilitates the incorporation of Pt and Ru atoms of diameter 2.2 Å as two neighbouring monomers. During photoreduction, the photogenerated electrons concentrate on the N vacancies of CN, facilitating the reduction of noble metal ions into monomer atoms.⁸

Due to the electronegativity difference, C_{2C} sites are positively charged while N_{2C} sites are negatively charged. During the photoreduction of Pt and Ru metal ions to Pt-Ru monomers, negatively charged [PtCl₆]²⁻ ions preferentially get adsorbed on C_{2C} sites while the positively charged Ru³⁺ ions are adsorbed on N_{2C} sites to form C-Pt-Ru-N coordination in PtRuSA-CN620 (Figure 25 (b)). Pt-Ru monomers with the above coordination structure contains two Pt-C, one Pt-N and three Ru-N bonds with a more negative adsorption energy (E_{ads}) value of -9.40 eV. They are found to be more stable compared to Pt-Pt/Ru-Ru monomers, Pt-Ru monomers with C-Ru-Pt-N, N-Pt-Ru-N coordination structure, and isolated Pt/Ru atoms.⁸

The PtRuSA-CN620 catalyst with 0.45 wt% Ru and 0.51wt% Pt exhibited 100% CO conversion into CO₂ at the lowest conversion temperature of 150 °C by Eley-Rideal (E-R) mechanism through preferential adsorption of O₂ followed by activation on the catalyst surface (Figure 25 (c)). The feeble IR absorption peaks for CO molecule at 2171 and 2111 cm⁻¹ in the temperature range of 110 to 300 °C, ruled out the possibility of Langmuir-Hinshelwood (L-H) mechanistic pathway for CO oxidation in which both CO and O₂ adsorption take place on catalyst surface (Figure 25 (d)).⁸

Photocatalytic non-oxygenative coupling of amines to imines employing H_2O as an oxidant is a prospective approach, by virtue of its ease of handling, for the bulk synthesis of imines. Single atoms of copper (0.85 wt%) embedded within g- C_3N_4 sheets (Cu1@HCNS) exhibited superior benzylamine oxidation (BOR) to imine at the rate of $10583 \mu\text{mol g}^{-1} \text{h}^{-1}$ and with 96% selectivity. The catalytic activity was found to be 3.8 and 2.5 times better than Cu single atoms on the surface of g- C_3N_4 (Cu1/HCNS) and hollow C_3N_4 spheres comprising of C_3N_4 nanosheets (HCNS) respectively. The BOR activity of Cu1@HCNS was much higher than the most performing precious metal Pt/MOF and was comparable with commonly employed Ni/CdS catalyst which is toxic and photocorrosive.⁶⁹

mpg- C_3N_4 containing single-atom Cu (Cu-CN-x) upto 26.6 wt % was synthesized by a one-pot two step strategy using urea and CuCl_2 . The first heat treatment at 180°C led to the coordination and precondensation between urea derived N-containing species and Cu^{2+} ions through the formation of Cu-N bond. Subsequent calcination at 550°C resulted in the confinement of Cu single atom in CN matrix through the replacement of one C atom and coordination with three N atoms. The synthesized Cu-CN-x (x indicates the Cu wt %) displayed excellent catalytic activity towards carboxylation of terminal alkynes, utilizing atmospheric CO_2 . Cu-CN-8.0 aided the carboxylation of phenylacetylene with 97% yield of phenylpropionic acid and with highest TOF of 9.7 h^{-1} . The mechanism involves the formation of an alkynyl carboxylic intermediate via the addition of deprotonated phenylacetylene to CO_2 . The reaction further proceeds through CO_2 insertion in copper acetylide to result in Cu(I)-propiolate complexes, leading to phenylpropionic acid. DFT calculations supplemented the experimental observations as the above addition reaction on Cu-CN is exothermic in nature with a reaction energy of -0.27 eV and an energy barrier of $+0.85 \text{ eV}$. On the contrary, pure CN was shown to be catalytically inactive due to the high endothermic reaction energy of $+1.39 \text{ eV}$ coupled with a high activation energy barrier of $+2.31 \text{ eV}$ (Figure 25(e)).¹¹²

Atomically dispersed palladium on g- C_3N_4 ($\text{Pd}_1/\text{C}_3\text{N}_4$) was synthesised by confining them into the six-fold cavity via N-coordination employing a spatial confinement-reduction strategy involving urea and Na_2PdCl_4 . The catalytic performance of $\text{Pd}_1/\text{C}_3\text{N}_4$ SACs with Pd loading of 0.18wt% was demonstrated for various selective hydrogenation reactions and the hydrodechlorination reaction of 4-chlorophenol. $\text{Pd}_1/\text{C}_3\text{N}_4$ exhibited a high TOF value of 834 h^{-1} with 98% conversion for hydrogenating styrene to

ethylbenzene. In comparison catalysts with nanoparticles of Pd (Pd NPs/C₃N₄) up to 10 wt % metal loading displayed the TOF values of 476 h⁻¹ only. Alternatively, g-C₃N₄, single atom Pd dispersed in MWCNTs-NH₂ (Pd-MWCNTs-NH₂, 0.32 wt %) and nitrogen doped carbon (Pd₁/N-C, 0.82 wt %) showed negligible activity. The control sample of commercial Pd/C (5 wt %) and Na₂PdCl₄ salt exhibited TOF values of 333 h⁻¹.

Pd₁/C₃N₄ was also utilised for selectively hydrogenating furfural using H₂O as a solvent at 90 °C temperature and 1 atm H₂ pressure. Pd₁/C₃N₄ exhibited 64% conversion of furfural to furfuryl alcohol with a TOF of 146 h⁻¹ and 99% product selectivity. In comparison Pd NPs/C₃N₄ exhibited only 39% of conversion with a TOF of 67 h⁻¹ and 99% product selectivity. Furthermore, Pd₁/C₃N₄ was also utilised for the hydrodechlorination of 4-chlorophenol at 80°C using ammonium formate as the source of hydrogen. 99% conversion and 99% product selectivity towards phenol were achieved within 10 min and with an exceptionally high TOF of 13,333 h⁻¹. In contrast, Pd NPs/C₃N₄, Pd₁/MWCNTs-NH₂, Na₂PdCl₄ salt, and Pd₁/N-C yielded no product while Pd/C exhibited 35% of conversion along with 99% selectivity and a TOF value of 1527 h⁻¹.¹¹³

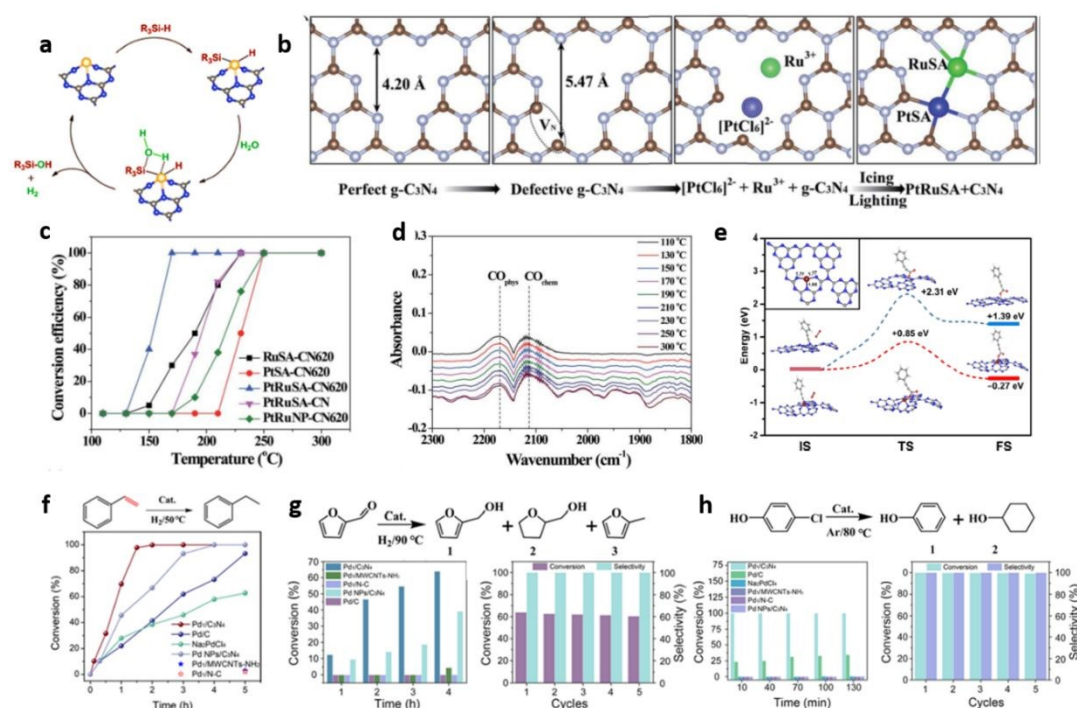


Figure 25. (a) The plausible mechanism of Au₁/mpg-C₃N₄ catalysed water-based silane oxidation. Reproduced with permission from ref. 26. Copyright 2017 John Wiley and Sons. (b) Scheme for the synthesis of PtRuSA-CN620 by the photoreduction method, (c) CO conversion over synthesised catalysts at CO concentration of 1 Vol%, (d) CO oxidation monitored by in situ infrared spectra using PtRuSA-CN620. Reproduced from ref. 8. under the terms of Creative Commons License, published 2019 Royal Society of Chemistry. (e) Reaction profile for CO₂ insertion over Cu-CN-8.0 & CN catalysts (inset: the optimised structure of Cu-CN-8.0). Reproduced with permission from ref. 112. Copyright 2020 American Chemical Society. Reaction scheme and catalytic performance of Pd₁/C₃N₄ for (f) hydrogenation of styrene, (g) hydrogenation of furfural (h) hydrodechlorination of 4-chlorophenol. Reproduced with permission from ref. 113. Copyright 2020 American Chemical Society.

Au SACs (Au₁/g-C₃N₄) synthesised by the calcination of HAuCl₄/g-C₃N₄ in N₂ atmosphere at 300°C, was demonstrated for the acetylene hydrochlorination reaction to produce vinyl chloride which is an important monomer in polyvinyl chloride industry. Au exists in +1 oxidation state and forms Au^I-N₃ active sites through N coordination. DFT study indicated that Au^I-N₃ active sites preferentially coordinate with HCl than acetylene inhibiting Au^I-N₃ to Au⁰ reduction and thereby sustaining the catalytic active sites for hydrochlorination reaction. In contrast, the conventional catalyst, AuCl₃ on carbon preferentially coordinates with acetylene leading to the reduction of Au^{III} ion to Au⁰ thereby losing its catalytic activity. Au atom occupies the Cv2 defect site present in g-C₃N₄. The electron localisation function (ELF) maps revealed that the Au-N₃ sites are having a T-shape structure with lone-pair electrons. (Figure 26 (a-c)). Au₁/g-C₃N₄ single atom catalyst exhibited 70% conversion of acetylene in 600 min without any loss of activity. In comparison, HAuCl₄/g-C₃N₄ catalyst exhibited a maximum conversion of 72.1%, but got significantly decreased to 14.5% in just over 500 min as a result of the reduction of Au^{III} to Au⁰. However, the Au NPs/g-C₃N₄ catalyst showed only very weak activity confirming that Au⁰ is catalytically inactive towards acetylene conversion. Au-N₃ active sites preferentially adsorb HCl by a dissociative mechanism with an adsorption energy (E_{ads}) of -2.25 eV which is higher than the E_{ads} of acetylene (-1.17 eV), preventing the reduction of Au^I to Au⁰ by C₂H₂. But in the case of AuCl₃/C catalyst, C₂H₂ has a higher adsorption energy of -1.04 eV than HCl (-0.74 eV). The interaction of HCl with Au₁/g-C₃N₄ weakens the Au-N bond as evident from the shifting of the d

band center, associated with the Au 5d orbital, farther from the Fermi level in PDOS of HCl adsorbed catalyst. However, in the case of acetylene adsorbed catalyst, there is no shift of band center associated with the 5d and 6s orbital in the PDOS (Figure 26 (d-f)). The competitive HCl adsorption prevents Au^I to Au⁰ reduction rendering enhanced stability for the catalyst. g-C₃N₄ as a support contributes towards the enhanced stability of the catalyst through π - π interaction of its electron-deficient heptazineic center with electron-rich C₂H₂. The HCl adsorbed on the active site interact with the acetylene following Langmuir-Hinshelwood (LH) mechanism. The DFT calculation supplements the improved performance of Au₁/g-C₃N₄ by predicting a small energy barrier for C-H and C-Cl bond formation (0.98 eV) along with small desorption energy of 0.87 eV for the product.¹¹⁴

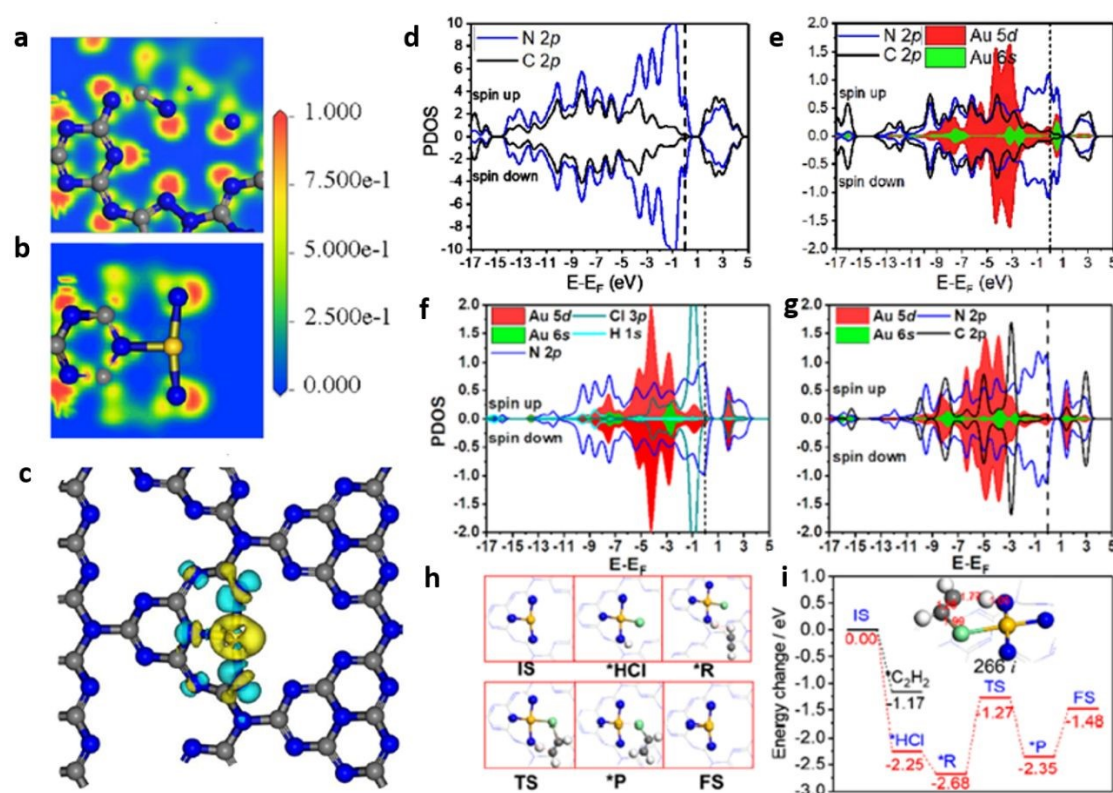


Figure 26. ELF (electron localisation function) map of (a) carbon deficient g-C₃N₄, (b) Au₁/g-C₃N₄, (c) Charge density differences for Au atom on the g-C₃N₄ (yellow for increasing and blue for decreasing charge density), PDOS of (d) one carbon deficient g-C₃N₄, (e) Au₁/g-C₃N₄, Au₁/g-C₃N₄ (f) after HCl adsorption (g) after acetylene adsorption, (h) Reaction species configuration, (i) The reaction profile of hydrochlorination reaction

on Au₁/g-C₃N₄ catalyst. Reproduced with permission from ref. 114. Copyright 2020 American Chemical Society. View Article Online
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The non-oxidative dehydrogenation of propane (denoted as PDH) is an effective synthetic route for the economical production of propylene. The mechanistic pathway for PDH involves C-H bond scission followed by propylene adsorption on the catalysts. Hence low values for C-H bond activation energy (ΔE) and propylene adsorption energies (E_{ad}) on catalysts are essential attributes. Additionally, the desorption energy of propylene should also be low compared to the energy required for breaking the C-H bond to realise higher selectivity towards propylene. Li et al demonstrates that the sum of ΔE and E_{ad} can be used as a theoretical indicator to elucidate the catalyst efficiency. Thus, a positive value suggests that C-H bond dissociation is slower than propylene desorption while a negative value is an indicator of propylene being strongly adsorbed on TM/g-C₃N₄. Employing DFT calculations, the group screened the potential of 12 transition metals supported on g-C₃N₄ (V, Cr, Mn, Zr, Nb, Ru, Rh, Pd, Os, Ir, Pt, Au) as SACs for PDH. The study predicts that a single atom transition metal catalyst can be active and selective for PDH by virtue of its highly exposed d states that enable C-H bond activation and rapid desorption of propylene through weak propylene- π adsorption mode.

g-C₃N₄, being thermally stable up to T ~550°C, can effectively perform the role of stable support for PDH catalysis which conventionally operates at 530 °C. Moreover, the support facilitates firm anchoring of single atoms, preventing agglomeration at high-temperature operating conditions. The adsorption energies of single metal atom should be similar to or higher than their cohesive energies for them to bond on g-C₃N₄. This selection rule is satisfied by five transition metals of V, Cr, Mn, Zr, and Nb. Together with conventionally active metals like Ag, Ru, Rh, Pd, Os, Ir, Pt, and Au, atomically dispersed SACs based on g-C₃N₄ were employed for PDH catalysis. Of the 12 systems studied, Ag₁/g-C₃N₄ displayed poor PDH activity owing to its high reaction energy (ΔE) for the first C-H bond cleavage and high propylene adsorption energy (E_{ad}). On the other hand, the rate-limiting step of PDH was characterised by a low activation barrier of 1.11 eV for V₁/g-C₃N₄ catalyst. Moreover, high selectivity was also displayed by V₁/g-C₃N₄ as the adsorption energy of propylene (-0.59 eV) was much lower compared to the activation barrier for deep dehydrogenation (1.97 eV).

In SACs based on C_3N_4 , the lattice constant of the planar structure (7.14 Å) is slightly higher than the buckled C_3N_4 structure (7.00 Å). The buckled structure is more stable than the planar structure by 2.05 eV. The four possible adsorption sites (A, B, C, D in Figure 27 (a)) of the single metal atoms move from their initial positions on structural relaxations. The adsorption energies of various single metal atoms on the g- C_3N_4 surface are shown in Figure 27 (b). V, Cr, Mn, and Zr are g- anchored firmly on g- C_3N_4 as the cohesive energies are lower than their adsorption energies. Moreover, the Pd single atoms of synthesised $Pd_1/g-C_3N_4$ had adsorption energy smaller than the binding energies of above-mentioned TMs enabling the practical viability of TM based SACs for PDH.¹¹⁵

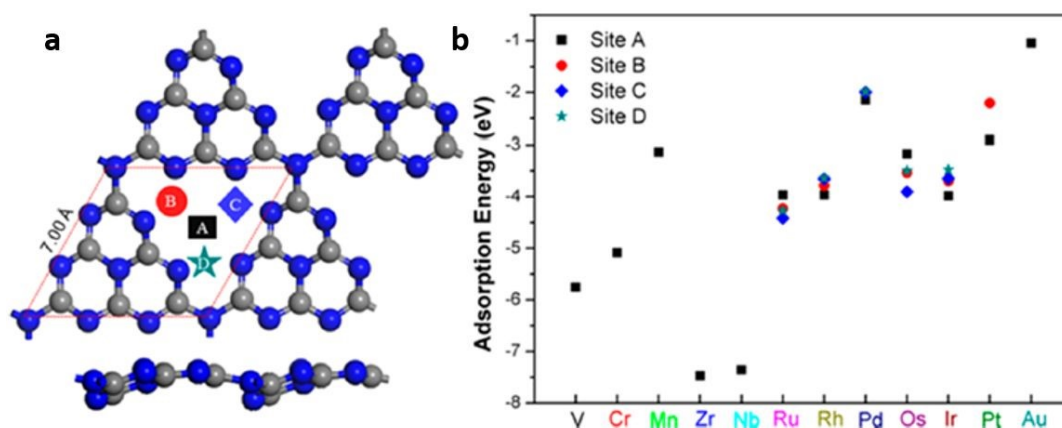


Figure 27. a) Possible adsorption sites for single metal atoms in g- C_3N_4 layer, b) Adsorption energies of various metal single atoms on available adsorption sites in the g- C_3N_4 surface. Reproduced with permission from ref. 115. Copyright 2020 American Chemical Society.

g- C_3N_4 containing single atom Cobalt (Co SACs) up to 23.58 wt.% loading was demonstrated to be an excellent catalyst for oxidation of ethylbenzene in the air with a high turn-over frequency of 19.6 h^{-1} and 97% selectivity for acetophenone formation. The catalytic pathway involves the formation of Co–O bond through O_2 adsorption while ethylbenzene adsorbs on the catalyst surface. The subsequent abstraction of the H atom from the CH_2 group of ethylbenzene produced acetophenone through the intermediates of phenylethyl radical and hydroperoxyl radical.¹¹⁶

The potential of g- C_3N_4 based ultra-high density copper single atom catalyst (UHD- Cu_1/PCN SAC) was demonstrated for catalysing the azide–alkyne cycloaddition reaction

between benzyl azide and 4-ethynylanisole at 60°C using water-*tert*-butanol (1:1) mixture as solvent. The effect of Cu content on the catalytic activity to yield 1-benzyl-5-(4-methoxyphenyl)-1H-1,2,3-triazole was investigated. As the Cu loading increased, the number of active sites as well as the site-specific activity for UHD-Cu1/PCN SAC also enhanced remarkably yielding 92% of 1,5-disubstituted triazole in 12h. However, no explanation was provided for the selective formation of the 1,5-disubstituted triazole rather than the 1,4-regioisomer.¹¹

Recently, single atom copper catalysts on mesoporous graphitic nitride (saCu-x@mpgC₃N₄), obtained by the template assisted direct synthesis involving sodium tricyanomethanide, CuCl₂·2H₂O, cyanamide and SiO₂ particles, were demonstrated to catalyse click cycloaddition between various phenylacetylene derivatives and in situ formed azides (from benzyl bromide, and sodium azide) (Figure 28 (a)). Cu-2@mpgC₃N₄ catalyst with 1.6 wt % of Cu loading exhibited a yield of 45% for 1-benzyl-4-phenyl-1H-1,2,3-triazole in DMF solvent at 130 °C for 30 min (Figure 28 (b-c)). The reaction mechanism evolved from the three possible coordinating structures (Figure 28 (e-g)), involved acetylene activation by adsorption on Cu(ads)/C₃N₄ with a minimal thermodynamic barrier of +0.09 eV relative to Cu(sub)/C₃N₄ (+0.48 eV) and Cu(ads)/NG (+0.66 eV). Subsequently, sodium azide reacts with the C atom of acetylene forming a stable linear intermediate over Cu(ads)/C₃N₄ with a free energy change of -4.19 eV compared to Cu(ads)/NG and Cu(sub)/C₃N₄ with more positive free energy values of -1.10 eV and -2.73 eV respectively. A triazolite pentacyclic ion attached to the Cu SAC was formed on the completion of cyclisation with free energies of -3.79 eV, -5.34 eV, -5.47 eV for Cu(ads)/NG, Cu(sub)/C₃N₄, and Cu(ads)/C₃N₄ respectively. The final step of catalyst regeneration was by the desorption of sodium triazolite molecule where the desorption energy barrier was highest for Cu(ads)/C₃N₄ (2.27 eV) compared to Cu(ads)/NG (0.59 eV) and Cu(sub)/C₃N₄ (2.14 eV) (Figure 28 (h-i)).¹¹⁷

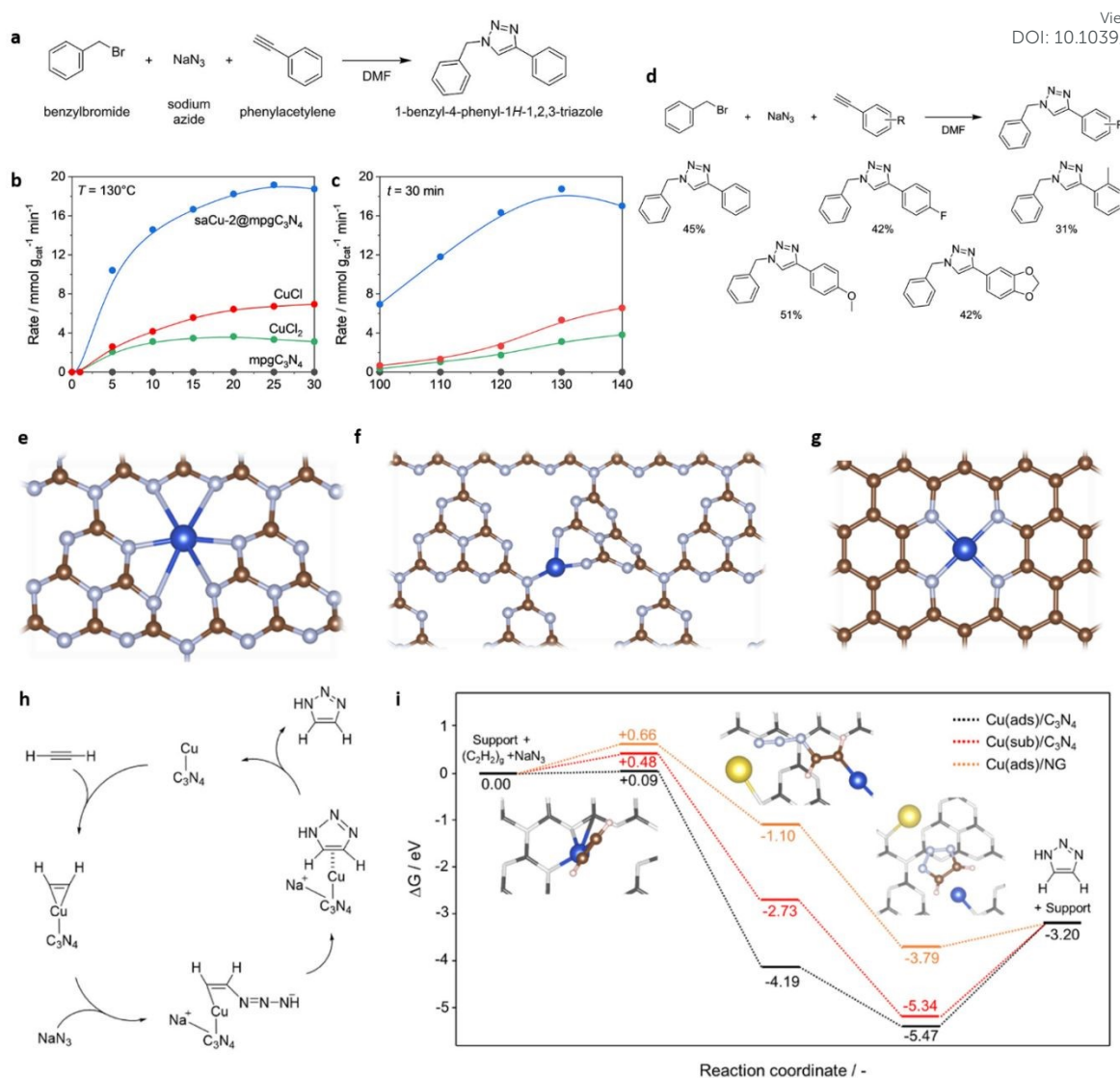


Figure 28. (a) Reaction scheme of cycloaddition, (b-c) The comparison of catalytic performance of mpgC₃N₄, CuCl₂, CuCl, and saCu-2@mpgC₃N₄ with respect to (b) time and (c) temperature, (e-g) The structural model for the Cu coordination in Cu-based SACs (e) Cu adsorbed in the heptazinic pore of C₃N₄ (Cu(ads)/C₃N₄), (f) Cu substituted the carbon in C₃N₄ (Cu(sub)/C₃N₄), and (g) Cu adsorbed on N-doped graphene at its dicarbon vacancy (Cu(ads)/NG), (h) Proposed reaction mechanism for click cycloaddition over supported Cu₁ active sites, (i) Reaction free-energy profile for (Cu(ads)/C₃N₄), (Cu(sub)/C₃N₄), and (Cu(ads)/NG) at 130 °C (inset: Structures of intermediates formed over Cu(ads)/C₃N₄). Reproduced with permission from ref. 117. Copyright 2022 The Authors. Published by American Chemical Society.

Sleim et al demonstrated the complete conversion of CO to CO₂ by thermal oxidation at 184°C utilising single atoms of Cu incorporated on ultra-thin sheets of porous C₃N₄ (Cu-P-g-C₃N₄). The SAC developed was characterised by a high surface area of 240 m²g⁻¹ and contained 1.8 wt% of Cu atoms isolated through coordination with the nitrogen of C₃N₄. The Cu-N coordination sites bond weakly to the intermediates and products enabling faster reaction kinetics at relatively low temperature.¹¹⁸

The potential of metal embedded C₃N₄ catalysts (M@g-C₃N₄, where M stands for Mo, Ni, Co, Cu, Mn and Fe) were evaluated through first principles calculations and ab initio molecular dynamics (AIMD) simulations, for the catalytic hydrogenation of CO₂ to HCOOH, CO, and CH₃OH. The p orbitals of pyridinic N atoms in s-triazine-based graphitic C₃N₄ (gt-C₃N₄), bond strongly with the d (p) orbitals of single metal atoms activating H₂ and CO₂. The co-adsorbed state, thus formed, acts as intermediates to the hydrogenation of CO₂ to different C₁ products, with the metals Mn, Fe, Mn and Co providing superior catalytic performance compared to others. The binding energy (ΔEb) values of a metal single atom anchored on gt-C₃N₄ and the ΔEb values for all the M@g-C₃N₄ vary from -2.25 to -3.72 eV confirming the thermodynamic feasibility of metal incorporation on gt-C₃N₄. Furthermore, the thermal stability of the SACs was evaluated from AIMD simulations and estimating the energy barrier values for surface migration of metal atoms. Considering Co@g-C₃N₄ as a representative example, it was established that the framework structure was retained without bond fission and metal migration even after 10 ps AIMD stimulation. A high energy barrier of 2.11 eV ruled out the possibility of Co atom migration. Additionally, the evaluation of electronic properties through band structure analysis, charge density difference and electron spin density calculations indicated that Cu@g-C₃N₄ possessed metallic nature whereas all other metal atoms induced semiconducting properties. This was attributed to the availability of more valence electrons in Cu compared to the rest of the metals as well as to the strong hybridisation of Cu orbitals with neighbouring N orbitals resulting in a high Fermi level value of -2.02 eV relative to the range of -2.98 to -2.15 eV for other metal SACs. The hydrogenation of CO₂ starts with the adsorption of CO₂ and H₂ molecules in bidentate configuration. The adsorption energies (E_{ads}) of CO₂ over the metal atom, vary between -0.33 to -1.25 eV whereas E_{ads} of H₂ lies between -0.70 and -1.21 eV. The co-adsorption of CO₂ and H₂ is energetically more favourable for all M@g-C₃N₄, except for that of Mn. For the representative Co@g-C₃N₄ system, H₂ adsorption proceeds exothermic route with

an Eads value of 1.13 eV followed by the adsorption of CO₂ whereas co-adsorption occurs with the release of energy of 0.19 eV. CO₂ hydrogenation follows the Langmuir-Hinshelwood (L-H) mechanism which starts with the coadsorption of CO₂ and H₂. The CO₂ hydrogenation process follows various pathways to produce various products. The HCOO* pathway led to HCOOH formation. A reverse water-gas shift (RWGS) reaction pathway produces CO, whereas a mixed reaction pathway involving CO intermediate hydrogenation (CO-hydro) and RWGS results in CH₃OH formation. The hydrogenation of CO₂ led to the formation of CO intermediate with high Eads ranging from -2.07 to -2.61 eV which makes the desorption of CO difficult from the catalyst surface and thereby facilitates further hydrogenation to produce CH₃OH. In the case of Co@gt-C₃N₄ which was theoretically predicted to be the most efficient system for CO₂ hydrogenation, HCOOH formation occurs with the lowest energy barrier of 0.58 eV, whereas the formation of CO and CH₃OH occurs by overcoming an energy barrier of 0.67 eV and 0.95 – 1.19 eV respectively.¹¹⁹ The SACs demonstrated for thermal catalysis with the salient outputs are presented in Table 7.

Table 7 Summary of g-C₃N₄ SACs for thermal catalysis

System	Single atom & loading	Synthesis method	Catalytic application, Product yield/ Rate/Turnover frequency (TOF) & Selectivity	Coordination Site or Structure & oxidation state	Reference
[Pd]mpg-C ₃ N ₄	Pd 0.5 wt%	Post synthesis- Chemical reduction	Hydrogenation of alkynes & nitroarenes 1-hexyne to 1-hexene: Rate 1.41×10^3 $\text{mol}_{\text{product}} \text{mol}_{\text{Pd}}^{-1} \text{h}^{-1}$ & selectivity 90%, 2-methyl-3-butyne-2-ol to 2-methyl-3-buten-2- ol, 3-hexyne to cis-3- hexene, Nitrobenzene to aniline	Nitrogen	4
AgTCM-mpg-CN	Ag 1 wt%	Direct synthesis	Hydrogenation of 1- Hexyne to 1-Hexene, Rate $100 \text{ mol}_{\text{alkyne}} \text{h}^{-1}$ $\text{mol}_{\text{Ag}}^{-1}$, Selectivity 100%	Carbon or Nitrogen, +1	17
Au ₁ /mpg-C ₃ N ₄	Au 519 ppm	Post synthesis- Reduction under an inert atmosphere	Silane oxidation with water, PhMe ₂ SiH to PhMe ₂ SiOH, Yield 99 %, 30 min, selectivity >99.9%, TOF 50200 h^{-1}	Carbon or Nitrogen, +1	26

Pd-ECN	Pd 0.66 wt%	Microwave treatment (Post synthesis)	Suzuki coupling of bromobenzene with phenylboronic acid pinacol ester to form biphenyl, 63 % conversion, 90% selectivity, Rate $0.57 \text{ mmol}_{\text{product}} \text{ min}^{-1} \text{ g}_{\text{cat}}^{-1}$	Nitrogen, Pd ²⁺ /Pd ⁴⁺ ratio 0.82	111 View Article Online DOI: 10.1039/D2TA09776A
PtRuSA-CN	Pt 0.51 wt% Ru 0.45 wt%	Post synthesis-Photochemical reduction	CO oxidation 100% conversion at 150 °C	C-Pt-Ru-N	8
CuI@HCNS	Cu 0.85 wt%	Supramolecular preorganisation assisted direct synthesis	Non-oxygenative coupling of amines to imines using H ₂ O & light, Benzylamine to imine: 10583 $\mu\text{mol g}^{-1} \text{ h}^{-1}$, 96% selectivity	Cu ₁ N ₃ , +1	69
Cu-CN-x	Cu 8 wt%	Template free direct synthesis	Carboxylation of terminal alkynes using atmospheric CO ₂ ; Phenylacetylene to Phenylpropionic acid: Yield 97%, TOF 9.7 h ⁻¹	Nitrogen, +1	112
Pd ₁ /C ₃ N ₄	Pd 0.18 wt%	Post synthesis-Reduction under an inert atmosphere	a) Hydrogenation; i) Styrene to ethylbenzene: 98% conversion in 1.5 h, TOF: 834 h ⁻¹ , ii) Furfural to Furfuryl alcohol: 64% Conversion in 4 h, TOF: 146 h ⁻¹ , b) Hydrodechlorination of 4-chlorophenol to phenol: 99% conversion in 10 min, TOF: 13,333 h ⁻¹	Nitrogen, +1	113
Au ₁ /g-C ₃ N ₄	Au 0.414 wt%	Post synthesis	Hydrochlorination of acetylene to vinyl chloride: 70% conversion in 600 min	Au-N ₃ , +1	114
TM/g-C ₃ N ₄	V, Cr, Mn, Zr, Nb, Ru, Rh, Pd, Os, Ir, Pt, Au	DFT Study	Non-oxidative dehydrogenation of propane to propylene, Predicted highest activity & selectivity for V ₁ /g-C ₃ N ₄	-	115
Co SAC (Co SACs/CN)	Co 23.58 wt%	Direct synthesis	Aerobic oxidation of ethylbenzene to acetophenone: 62% conversion, 40 h, 99% selectivity, TOF: 19.6 h ⁻¹	Co-N ₂ , +2	116

UHD-Cu ₁ /PCN	Cu 23 wt%	Post synthesis – Reduction under an inert atmosphere	Azide–Alkyne cycloaddition reaction: Cycloaddition between benzyl azide & 4-ethynylanisole to form 1-benzyl-5-(4-methoxyphenyl)-1H-1,2,3-triazole, Yield 92%, 12h	Nitrogen, +1	¹¹ View Article Online DOI: 10.1039/D2TA09776A
saCu@mpg C ₃ N ₄	Cu 1.6 wt %	Template assisted direct synthesis	Click cycloaddition between phenylacetylene and in situ formed benzyl azide (from benzyl bromide, & sodium azide) to form 1-benzyl-4-phenyl-1H-1,2,3-triazole, Yield 45%, 30 min	Nitrogen, +1	¹¹⁷
Cu-P-g-C ₃ N ₄	Cu 1.8 wt%	Template free direct synthesis	Oxidation of CO to CO ₂ 100% conversion	Nitrogen, 0	¹¹⁸
M@gt-C ₃ N ₄	M = Mn, Fe, Co, Ni, Cu, and Mo	DFT Study	CO ₂ hydrogenation to HCOOH, CO, & CH ₃ OH, Co@gt-C ₃ N ₄ was theoretically predicted to be the most efficient system	Nitrogen	¹¹⁹

5.3 Electrocatalytic applications of g-C₃N₄ based SACs

Electrocatalysis is perceived to be a promising approach to meet the continuously increasing energy demand by employing various technologies, such as the electrolysis of water, CO₂ reduction, fuel cells, etc. The underlying electrochemical processes enable the sustainable utilisation of renewable electrical energy with appreciable energy conversion efficiencies. Precious metals (Pt, Ir, Ru, Rh, Pd, etc.) and their metal oxide-based catalysts are widely used in the field of electrocatalysis.¹²⁰ However less availability and high cost hinder their widespread application. The utilisation of single atom catalysts of precious & non-precious metals with high intrinsic activity, unique electronic structure, and high atom utilisation efficiency help to improve the electrocatalytic performance for various reactions (Figure 29).¹²¹

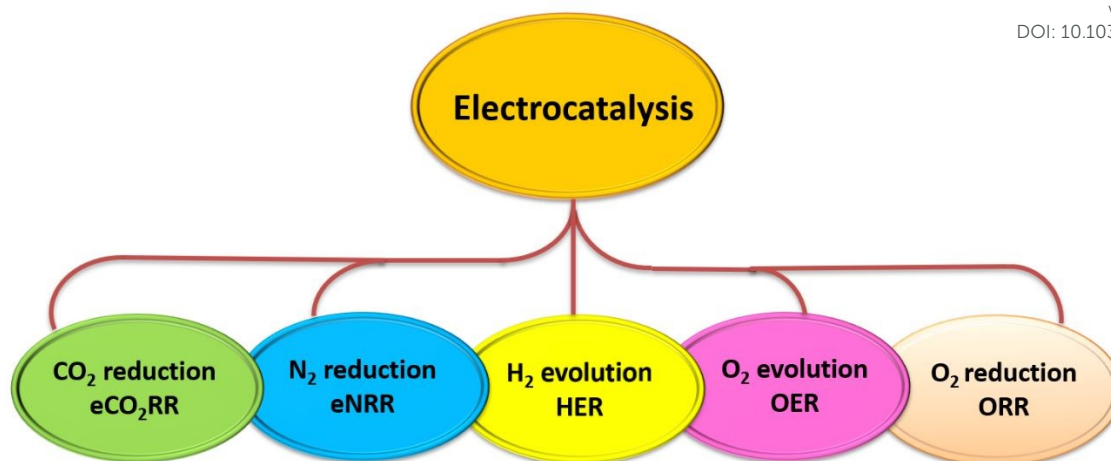
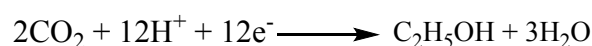
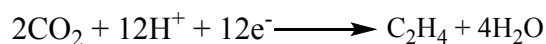
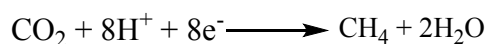
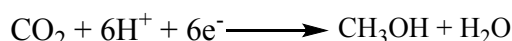
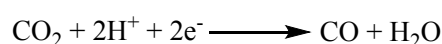
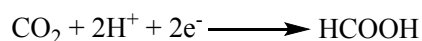


Figure 29. Various electrocatalytic reactions catalysing by g-C₃N₄ based SACs

5.3.1 Electrocatalytic CO₂ Reduction

Electrocatalytic reduction of CO₂ (eCO₂RR) to valuable feedstocks by utilising renewable electrical energy is an environmentally benign strategy to mitigate carbon emission, fossil fuel depletion, and reduce the climatic impact of the green-house effect.¹¹⁹ CO₂ reduction proceeds via multi electron-proton transfer steps and converts it to various products like CO, HCOOH, CH₄, CH₃OH, C₂H₅OH, and C₂H₄ and higher hydrocarbon etc¹²² as shown in the equations below.



Zhang et al developed Mn based SACs through thermal treatment of a precursor mix containing manganese acetate, dicyandiamide (DCD), and CNT under an inert atmosphere of N₂ at 600 °C. SACs with Mn-N₃ sites embedded in the mixed matrix of g-C₃N₄ with carbon nanotubes (Mn-C₃N₄/CNT) exhibited excellent eCO₂RR in aqueous electrolyte with 98.8 % of Faradaic efficiency (FE) and CO partial current density (*j*_{CO})

value of 14.0 mA cm^{-2} , at a low overpotential of 0.44 V . j_{CO} further improved to 18.6 and 29.7 mA cm^{-2} at an overpotential of 0.42 and 0.62 V , respectively by the usage of ionic liquid (IL) electrolyte. Theoretical studies and XAS analysis revealed that CO_2 can easily get adsorbed on Mn-N_3 active site which facilitated a low free energy barrier for COOH^* intermediate formation.¹²³

The potential of atomically dispersed Er atoms on $\text{g-C}_3\text{N}_4$ nanotubes described earlier for photocatalytic CO_2 reduction, has been evaluated for eCO_2RR . $\text{HD-Er}_1/\text{CN-NT}$ exhibited enhanced cathodic current compared to pure CN-NT and $\text{LD-Er}_1/\text{CN-NT}$.⁹

Yan Jiao et al used DFT calculations to predict different C-C coupling pathways for the eCO_2RR to C_2H_4 over $\text{Cu-C}_3\text{N}_4$ SACs utilising Cu/C or Cu/N dual active sites present in it. The reduction proceeded via 12 e^- and 12 proton transfer pathways at a potential of -0.764 V vs SHE. The first in the process is the protonation of a CO_2 molecule to $^*\text{COOH}$ at any of the three active sites of Cu , C , N present in the catalyst. DFT study and associated ΔG calculations divulged that the Cu active site with a ΔE of 0.37 eV is preferred to N active site with 1.47 eV . Even though active sites of C possess the lowest ΔE of 0.37 eV , it is difficult to facilitate C-C coupling as the reaction proceeds. Based on the sites and intermediates involved in the formation of C_2H_4 , 14 different pathways are suggested in two categories involving the Cu/N dual active sites and Cu/C dual active sites. The Cu/C pathway exhibited a better synergistic effect than Cu/N which is beneficial for possessing catalytic activity comparable to Cu (100).¹²⁴

Electrochemical CO_2 reduction to formate was demonstrated in exfoliated $\text{g-C}_3\text{N}_4$ (GCN) containing atomic dispersions of Cu (Cu-GCN). XANES analysis indicated the presence of both Cu^{2+} and Cu^+ with an average oxidation state of $+1.4$ confirming different Cu-N co-ordinations, Coupled with DFT calculations, the authors predicted a partially polymerised GCN that retained a few amino functional groups coordinated to Cu as the Cu atoms are expected to interact preferentially with pyridinic N atoms. The catalyst $\text{Cu-GCN}(20)$ exhibited CO_2RR activity in bicarbonate solution through the formation of formate as the only product in the liquid phase, with a faradaic efficiency of 12% and a current density of $14 \text{ mA/mg}_{\text{cat}}$. However, in the phosphate solution HER was predominant over CO_2RR and hydrogen was obtained as a result of HER rather than CO_2RR .¹²⁵

Ge et al successfully developed an efficient electrocatalyst (ZnSA-CN-G) for CO₂RR by dispersing zinc single atoms (ZnSA) on graphitic carbon nitride nanosheets (CN) and graphene (G) through the pyrolysis of a precursor mix containing DCDA, graphene-oxide nanosheets (GO nanosheets) and ZnCl₂. During the pyrolysis process at 700 °C, the conversion of DCDA to CN facilitated the atomic level dispersion of Zn single atoms to CN matrix with Zn-N coordination and GO was reduced to graphene. ZnSA-CN-G catalyst with a metal loading of 1.2 wt%, exhibited excellent conversion of CO₂ to CO with 87.1% of FE at a potential of -0.5 V vs RHE. The enhanced electrocatalytic activity is derived from the availability of abundant Zn single atoms as well as from the enhanced surface area & electrical conductivity of ZnSA-CN-G.¹²⁶

The electrocatalytic CO₂ reduction capabilities demonstrated for g-C₃N₄ based SACs are presented in Table 8.

Table 8 Summary of g-C₃N₄ SACs for electrocatalytic CO₂ reduction

System	Single atom & Loading	Synthesis method	Products, FE, current density (<i>j</i>) & Overpotential	Coordination site or Structure & Oxidation state	Reference
Mn-C ₃ N ₄ /CNT	Mn 0.17 wt%	Template free direct synthesis	CO, FE 98.8 %, <i>j</i> _{CO} 14.0 mA cm ⁻² at 0.44 V	Mn-N ₃ , +2	123
Er ₁ /CN-NT	Er 18.4 wt%	Freeze drying assisted direct synthesis	HD-Er ₁ /CN-NT exhibited higher cathodic current than LD-Er ₁ /CN-NT & CN-NT	Er-N ₃ , +1	9
Cu-C ₃ N ₄	Cu	DFT Study	C ₂ H ₄ , Predicted Cu/C active sites favours C ₂ H ₄ formation than Cu/N	-	124
Cu-GCN(20)	Cu 20 wt%	Chemical reduction assisted post synthesis	Formate (HCOO ⁻), FE 12%,	Nitrogen, +1 & +2	125
ZnSA-CN-G	Zn, 1.2 wt%	Freeze drying assisted direct synthesis	CO, FE 87.1% at -0.5 V	Nitrogen, Oxidation state in between 0 & +2	126

5.3.2 Electrocatalytic Nitrogen Reduction Reaction (eNRR)

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The large-scale commercial synthesis of ammonia is currently realised through the traditional Haber Bosch process which is a high temperature, high pressure route and consequently is highly energy intensive and environmentally non-friendly.¹²⁷ The conversion of N_2 to NH_3 through electrochemical means is an attractive option by virtue of the milder conditions of operation and low energy requirements. Electrocatalytic nitrogen reduction reaction (eNRR), analogous to nitrogen fixation by nitrogenase enzymes, is the most sustainable pathway for ammonia production. Bulk catalysts like Fe and Rh are demonstrated for eNRR but with low efficiency, poor selectivity and slow kinetics.¹²⁸ Single atom catalysts with an optimal concentration of highly active metal sites have shown the potential to be highly effective for eNRR through improved selectivity, kinetics and efficiency.^{87, 129}

eNRR is a six-electron reaction progressing in both associative and dissociative mechanisms. The former involves the release of NH_3 simultaneously with $N \equiv N$ bond cleavage and proceeds through the distal, alternating, and enzymatic pathways. In the dissociative route, $N \equiv N$ cleaves into two separate N atoms before hydrogenation. The reduction process is initiated by the adsorption of N_2 to metal atoms and the adsorption energy calculations suggest that it proceeds preferably via an end on configuration.¹³⁰ Computing ΔG associated with the formation of possible species (N_2H^* , $N_2H_2^*$, $N_2H_3^*$, $N_2H_4^*$, N^* , NH^* , and NH_2^*) and identification of the potential determining step (PDS) through different pathways facilitate mechanisms to evaluate the efficiency of the catalyst.¹³¹

In one of the initial reports on SACs based on $g-C_3N_4$, Zhao and Chen employed DFT based computational studies to investigate the effectiveness of a variety of single atoms (Ag, Ru, Pd, Rh, Au, Pt, W, Ni, Ti, Mo, Cr, Mn, Co, and Fe) on C_3N_4 for eNRR (Figure 30 (a)). The structural stabilities of the catalysts were computed from the energy of the adsorption of the metal atoms on $g-C_3N_4$ (Figure 30 (b)). Single atoms of Ti, Mn, Pd, Ag, Au and W were adsorbed on the six-fold cavity of $g-C_3N_4$ with metal-N bond lengths varying in the range of 2.28-2.51 Å. The group comprising of Cr, Ni, Fe, Co, Cu, Mo, Ru, Rh, and Pt were anchored favourably at the corner of the same cavity with metal-N bond lengths of 1.90-2.11 Å. The difference in adsorption sites was ascribed to the differences in atomic radii and electronegativity values. Electron transfer from metal

atoms to C_3N_4 induces positive charges on metals facilitating eNRR and suppressing the competitive HER.¹³²

Ding et al compared the suitability of g- C_3N_4 and graphene, as support layers with differences in their coordination environment, for incorporating single atoms of V, Nb, and Ta (Figure 30(c)). Their subsequent use as electrocatalysts for nitrogen reduction was evaluated based on the ability of the catalyst to adsorb nitrogen for the activation of $N \equiv N$, the creation of a stable N_2H^* adsorption on the catalyst and the destabilisation of NH_2^* . The reactivity screening revealed that V, Nb, and Ta anchored onto graphene support, could only weakly stabilise the NH_2^* species and hence were considered to be unsuitable for eNRR. The binding energy of single atoms on C_3N_4 was used to ascertain the structural stability of SACs. The values ranging from -6.48 to -7.58 eV confirmed that the C_3N_4 layers with the corner vacancy are best suited to facilitate the anchoring of TM atoms. The band gap and spin density distribution calculations indicated strong N_2 adsorption capacity for TMs on C_3N_4 . The E_g of C_3N_4 lowered significantly from 2.84 eV to 1.36 eV (Ta/ C_3N_4) and 1.35 eV (Nb/ C_3N_4). Among the three TMs evaluated, SACs based on Nb/ C_3N_4 were shown to possess the highest catalytic efficiency with high selectivity for NRR compared to HER by virtue of the ΔG_{max} of 0.05 eV realised through a distal mechanism.¹³³

Singh et al employed density functional theory for the design of transition metal (TM) anchored heptazine-derived graphitic C_4N_3 (h- C_4N_3) based SACs. The catalytic efficiency was gauged by the ability of a metal to facilitate HER through the adsorption and protonation of nitrogen. The number of valence electrons of TM was identified to be an indicator to predict the catalytic efficiency of SACs. Among the carbon nitrides, h- C_4N_3 formed by the replacement of two N atoms with C atoms was identified to be a better support than C_3N_4 , as the former is metallic offering a free flow of electrons (Figure 30(d)). 27 transition metals anchored SACs were investigated and the evaluation of N_2 adsorption energies qualified Sc, Co, Ni, Zr, Nb, Mo, Ru, Ta, W, and Os for eNRR (Figure 30(e-f)). Subsequently, considering the feasibility of protonation of N_2^* to N_2H^* intermediate, only 3 of the 27 TMs namely Mo, W and Ta were found comparatively more effective. Among the three qualified, only Mo and W showed higher selectivity for eNRR and the highest efficiency was accorded to Mo based SACs by virtue of their extremely low overpotential of 0.02 eV versus SHE. The estimated Faradaic efficiency was 97.3% for Mo-SAC. Thermodynamic analysis of the reduction pathways (distal,

alternating and mixed) suggested that the most favourable mechanism for the conversion of N_2 to NH_3 by Mo-SAC is the mixed mode with a limiting potential of -0.18 eV vs SHE. The potential limiting step (PLS) for this mechanism is the conversion of $N_2H_2^*$ to $NH-NH_2^*$ intermediate.¹³⁴

Wang et al evaluated the catalytic performance of atomically dispersed Au on C_3N_4 for the electrochemical reduction of N_2 to NH_4^+ in an aqueous sulphuric acid solution. A high ammonium yield rate of $1,305 \mu g h^{-1} mg_{Au}^{-1}$ had been realised and the yield was roughly 22.5 times more than that obtained by employing Au nanoparticles as catalysts. The direct eNRR to NH_4^+ was thus demonstrated with an energy utilisation rate of $4.02 mmol kJ^{-1}$. DFT calculations revealed that the mechanistic pathway involves an alternating mechanism with the reduction of N_2 to $*NNH$ as the rate determining step with a positive ΔG value of 1.33 eV for Au- C_3N_4 SACs compared to a higher ΔG value of 2.01 eV for Au nanoparticles (Figure 30 (g-h)). The electron density difference due to the anchoring of Au on g- C_3N_4 also favoured stronger binding interaction between Au and $*NNH$ (Figure 30(i)). Bader charge population analysis confirmed charge transfer from Au to C_3N_4 leading to the shifting of the d-orbital position towards the Fermi level enabling enhanced interaction with intermediates. The selectivity of Au- C_3N_4 SACs towards NRR, compared to HER, was ascertained based on the thermodynamic limiting potentials which was computed to be -0.88 V for SACs relative to -1.67 for Au nanoparticles-based catalysts (Figure 30(j)).¹³⁵

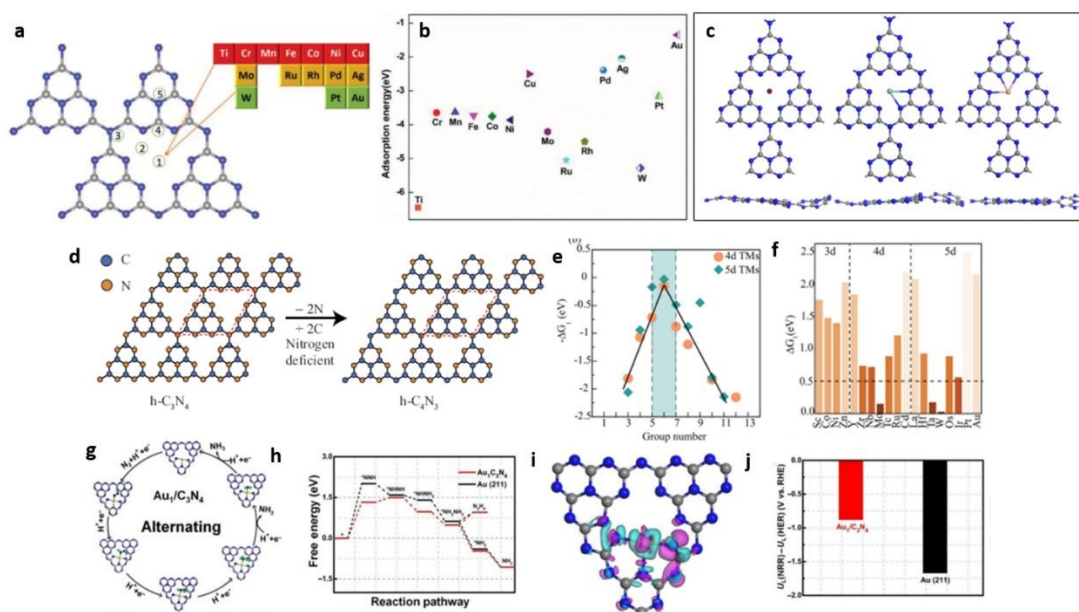


Figure 30. (a) g-C₃N₄ monolayer structure with possible coordination sites for single metal atoms and their (b) adsorption energies (calculated) HER. Reproduced with permission from ref. 132. Copyright 2018 John Wiley and Sons. (c) Optimised monolayer g-C₃N₄ structure with V, Nb, Ta single atoms. Reproduced with permission from ref. 133. Copyright 2020 American Chemical Society. (d) Structural transformation of h-C₃N₄ to h-C₄N₃, (e) $-\Delta G_1$ versus group number for 4d and 5d TMs (f) ΔG_1 for the screened TM-SACs. Reproduced with permission from ref. 134. Copyright 2021 American Chemical Society. (g) Alternating mechanism of NRR on Au₁/C₃N₄ with optimised structures of various intermediates, (h) Free energy profile of NRR using Au₁/C₃N₄ and Au (211), (i) Change in electron density induced by anchored Au atom on g-C₃N₄ (Cyan and pink colour indicate accumulation and depletion of electron density respectively), (j) Limiting potential difference in NRR and HER. Reproduced with permission from ref. 135. Copyright 2018 Elsevier. g-C₃N₄ based SACs demonstrated for eNRR application are listed in table 9.

Table 9 Summary of g-C₃N₄ SACs for electrocatalytic nitrogen reduction Reaction

System	Single atom & loading	Synthesis method	Rate, FE, Limiting potential	Coordination site or structure & oxidation state	Reference
TM@C ₃ N ₄	TM = Ag, Ru, Pd, Rh, Au, Pt, W, Ni, Ti, Mo, Cr, Mn, Co, Fe	DFT study	W@C ₃ N ₄ is predicted to exhibit the highest NRR activity with a limiting potential of -0.35 V	Nitrogen	132
TM/CN	TM = V, Nb, Ta	DFT study	Nb/CN is predicted to exhibit highest NRR activity with a low ΔG_{\max} (0.05 eV)	Nitrogen	133
TM-SAC (TM/h-C ₄ N ₃)	TM = Sc, Co, Ni, Zr, Nb, Mo, Ru, Ta, W, and Os	DFT study	Mo-SAC is predicted to be the most effective eNRR catalyst with an ultralow overpotential value of 0.02 V & high FE	Nitrogen	134
Au-C ₃ N ₄	Au 0.15%,	Post synthesis – Reduction under inert atmosphere	Rate: 1,305 $\mu\text{g h}^{-1} \text{mg}_{\text{Au}}^{-1}$, FE: 11.1% at -0.10 V	Nitrogen, +1	135

5.3.3 Electrocatalytic hydrogen evolution

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Hydrogen is a clean source of energy with high energy density and is considered to be the fuel of the future. Green hydrogen produced through economically viable water electrolysis enables sustainable energy generation without carbon footprints. The efficient production of high-purity green hydrogen via electrocatalysis is being pursued by researchers worldwide. Electrocatalytic hydrogen evolution is thus a promising pathway in the efforts for affordable hydrogen generation. SACs have been recently demonstrated to be efficient HER electrocatalysts for hydrogen generation.¹³⁶

Dai et al employed computational studies to explore the potential of transition metal (TM= Ti, V, Cr, Mn, Fe, Co and Ni) based SACs on holey g-C₃N₄ (TM/g-CN) for overall water splitting (HER & OER). Among the various TM/g-CN SACs designed, Co₁/g-CN and Ni₁/g-CN were predicted to perform as the most efficient bifunctional electrocatalysts owing to the strong interaction between the intermediates and catalysts as governed by the d band centre of the metal atoms. The calculations indicated that Co₁/g-CN and Ni₁/g-CN SACs can attain over potential values of 0.15 V and 0.12 V respectively for HER. Values are comparable with that of Pt reference catalyst with 0.09 V overpotential value.¹³⁷

Single Atom Co dispersed over g-C₃N₄ matrix coupled with RGO and having a metal loading of 6 wt% (Co-g-C₃N₄/rGO SACs, Co-CNG) are shown to perform (10 mA cm⁻²; ~47 mV) at par with commercial Pt/C catalysts for electrocatalytic HER (10 mA cm⁻² at ~48 mV). The Co-CNG was better than the commercial Pt/C catalyst with 4 times higher mass activity with 500 h durability (Figure 31 (a-e)). DFT studies supplemented the experimental observations and the superior HER activity of Co-CNG was ascribed to the presence of 20% and 80% of Co-N and Co-3N type coordination structures respectively. Coordination engineering is thus promoted as a pathway to boost HER for Co-N site than Co-3N model by virtue of the unique electronic structure, downshift of d-band centres and low free energy barriers (Figure 31 (f-i)).¹³⁸

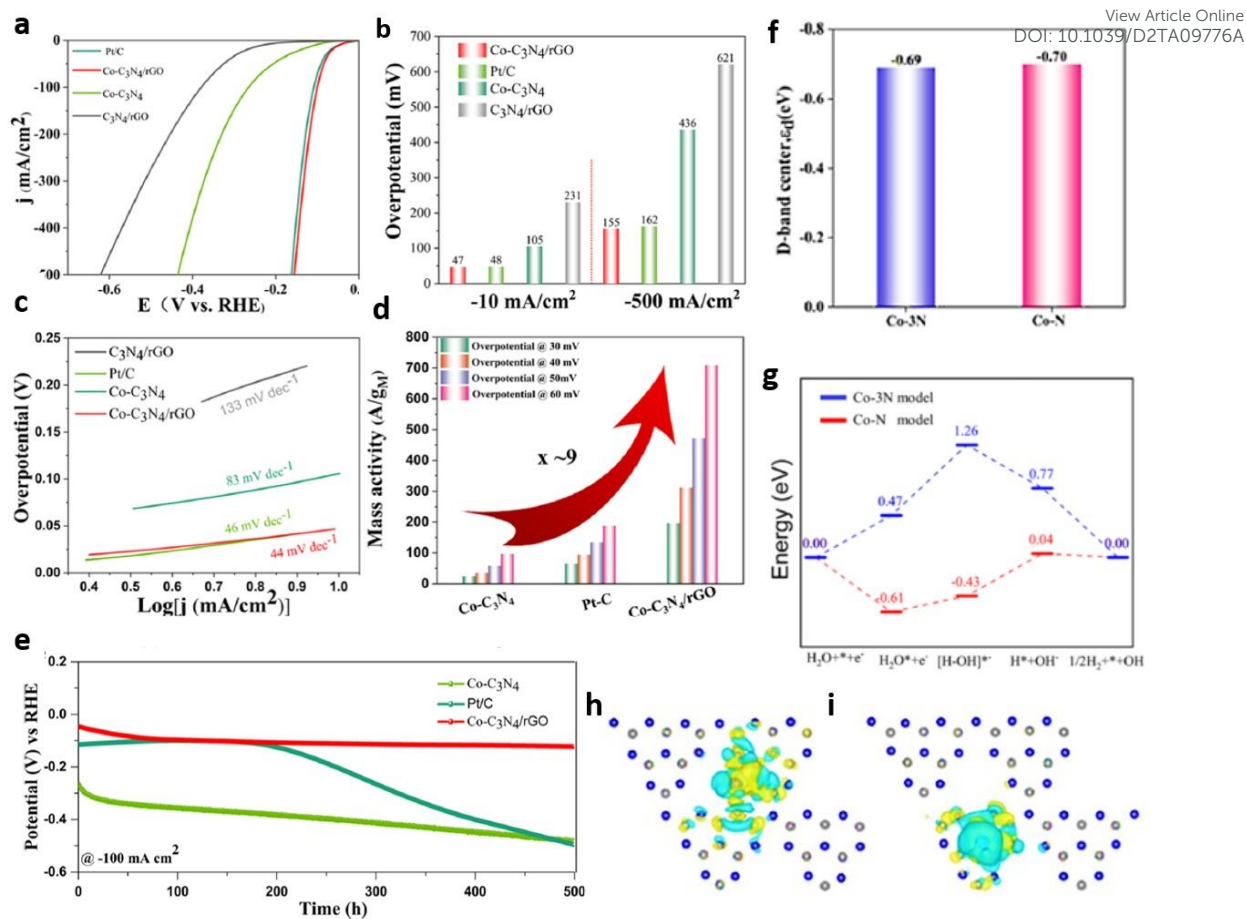


Figure 31. Data elucidation of HER activity, (a) LSV curves in 1.0 m KOH, at a scan rate of 5 mVs^{-1} for Co- $\text{C}_3\text{N}_4/\text{rGO}$, Co- C_3N_4 , $\text{C}_3\text{N}_4/\text{rGO}$, and Pt/C, (b) Overpotential values of the developed catalysts for a current density of -10 and -500 mA cm^{-2} , (c) Tafel plots, (d) Mass activity of the developed catalyst in comparison with Pt/C, at different overpotentials (e) Time-dependent overpotential curves of Co- $\text{C}_3\text{N}_4/\text{rGO}$, Co- C_3N_4 , in comparison with Pt/C. Co-N and Co-3N systems with (f) d-band centers, (g) Energy profiles, charge density differences in structures of (h) Co-N3, (i) Co-N1. Reproduced with permission from ref. 138. Copyright 2022 American Chemical Society.

The electrocatalytic hydrogen evolution reported for g- C_3N_4 based SACs is summarised in table 10.

System	Single atom &	Synthesis method	Current density (j) & overpotential	Coordination site or	Reference
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loading		structure & oxidation state			
TM/g-CN	TM = Ti, V, Cr, Mn, Fe, Co, Ni	DFT study	Co ₁ /g-CN & Ni ₁ /g-CN SACs are predicted to be the most effective HER catalysts with over potential values of 0.15 V and 0.12 V respectively	Nitrogen	137
Co-gC ₃ N ₄ /rGO (Co-CNG)	Co 6 wt%	Template free direct synthesis	10 mA cm ⁻² , 47 mV	20% Co-N & 80% Co-3N type coordination	138

Table 10 Summary of g-C₃N₄ SACs for electrocatalytic hydrogen evolution

5.3.4 Electrocatalytic oxygen evolution reaction & oxygen reduction reaction (OER & ORR)

Technologies for renewable energy sources such as fuel cells, hydrogen generation by water splitting, etc. rely on the fundamental reactions of oxygen evolution and oxygen reduction (OER and ORR). Conventionally noble metals (Pt) and oxides (RuO₂) are the benchmark catalyst for highly efficient ORR and OER.¹³⁹ However, the widespread use of such catalysts is largely hindered due to their unaffordable cost coupled with poor selectivity and stability. Additionally, as the reactions are of competing nature due to its reversibility, catalysing both by the use of a single catalyst is non-realisable.^{140, 141} It is therefore desirable to develop bifunctional catalysts with appreciable OER and ORR activities. SACs due to their desirable attributes in terms of structural and electronic properties can function to perform the dual roles of catalysing OER and ORR reactions.

In one of the earlier works, Park et al developed molecularly dispersed nickel on C₃N₄ matrix (Ni-CN) by employing a direct synthetic methodology involving the precursors of melamine and Ni(II) chloride hexahydrate precursors. The optimised catalyst displayed OER activity with an onset potential of 1.54 V (vs. RHE) which was 80 mV less positive than g-C₃N₄. Atomic dispersions of Ni species on C₃N₄ through Ni-N bonding were confirmed by EXAFS analysis.¹⁴²

Qiao et al developed organometallic complexes of graphitic carbon nitride (g-C₃N₄) with transition metals (M-C₃N₄) as electrocatalysts for both OER & ORR activities.

Theoretical studies predicted that among the 3d transition metal centres, (M-C₃N₄, where M = Cr, Mn, Fe, Co, Ni, Cu, Zn) Fe, Ni and Co possess the potential to exhibit bifunctional activity toward reversible ORR/OER processes due to high stability of structures. The representative catalyst of Co-C₃N₄ with multi-walled carbon nanotubes (CNT) exhibited higher electrode conductivity exposing all the electrocatalytically active sites of Co-C₃N₄. An onset potential of 0.9 V and a diffusion limited current density of ~ 5 mA cm⁻² in O₂-saturated 0.1 M KOH solution was obtained for the Co-C₃N₄/CNT catalyst via 4e⁻ dominated ORR pathway. The catalyst also showed an onset potential of ~1.5 V and an anodic current density of 10 mA cm⁻² at 1.61 V for OER activity in N₂-saturated 1 M KOH solution. The excellent bifunctional performance of Co-C₃N₄/CNT catalysts was at par with precious metal benchmarks and was attributed to the presence of Co-N₂ active sites.¹⁴³

Liu et al developed SAC based electrocatalyst by stabilising Au₁N_x single-sites on g-C₃N₄ (Au₁N_x single-site/C₃N₄) via a post synthesis strategy involving electrostatic adsorption. Au₁N_x single-site/C₃N₄ exhibited excellent catalytic activity with good durability for ORR and OER with mass activity values of ~9000 A•g_{Au}⁻¹ and ~1500 A•g_{Au}⁻¹ at a half-wave potential (E_{1/2}) of 0.76 V and at an overpotential 0.45 V respectively. The catalytic performances were 20 and 26 times higher than the conventional Pt/C and RuO₂ benchmarks. DFT calculations coupled with analysis of the electronic structure revealed the injection of electrons from Au₁N_x site to g-C₃N₄ enabling the formation of an additional energy level near the Fermi level. This promotes faster redox kinetics for highly efficient OER and ORR reactions. Moreover, the presence of mobile electrons near the Fermi level facilitated surface adsorption of the key intermediates *OO and *OH on Au₁N_x single-sites with a theoretical binding energy of 1.3 and 1.5 eV, close to that Pt and RuO₂ (1.4 eV and 1.7 eV).²²

In a noteworthy contribution, Sun et al prepared Fe, N doped hollow carbon catalyst (C-FeHZ8@g-C₃N₄) by the pyrolysis of a precursor mixture containing ZIF-8, C₃N₄ and ferric acetyl acetonate. The Fe-N₄ atomic level coordination was affected by C₃N₄ and ferric acetylacetonate as N and Fe precursors respectively. The optimised catalyst exhibited high ORR activity with E_{1/2} values of 0.18 and 0.845 V in acidic and alkaline conditions. The use of C₃N₄ prevented agglomeration of Fe during high-temperature pyrolysis and facilitated the formation of Fe-N_x sites through its cyano products formed

during decomposition at 950 °C. The incorporation of g-C₃N₄ during the synthesis provides an effective pathway for the stabilisation of single atoms in Fe-C-N catalyst.¹⁴⁴

Wang and co-workers developed a hybrid ORR-OER electrocatalyst (NGM-CN-Fe) with atomic Fe-N_x between g-C₃N₄ and graphene and were utilised as a material for air electrode cathode in Zn-air battery (ZAB). Fe is atomically dispersed over g-C₃N₄ (bulk CN-Fe) through template free direct synthesis involving dicyandiamide (DCDA) and ferric chloride precursors. Exfoliated porous CN-Fe nanosheets derived from bulk CN-Fe through sonication were subjected to hydrothermal treatment in presence of graphene nanomesh and annealed at 600 °C to form hybrid NGM-CN-Fe SAC. The catalyst exhibited superior ORR activity with a current density of -6.42 mA cm⁻² at an improved onset potential of nearly 0.00 V which is 13 times larger than that of atomic Fe dispersed g-C₃N₄ (CN-Fe). Both pure g-C₃N₄ (CN) and CN-Fe displayed an onset potential around -0.26 V and the current density was -0.45 mA cm⁻² at -0.5 V. In comparison with commercial Pt-C (20 wt%) catalyst, NGM-CN-Fe exhibited a comparable onset potential, better half-wave potential with 20 mV improvement & enhanced current density. The superior activity of NGM-CN-Fe SAC is attributed to the existence of Fe-N_{4.1} coordination sites via atomic Fe-bridged coordination between g-C₃N₄ and nitrogen-doped graphene nanomesh.¹⁴⁵

Li et al demonstrated the development of OER catalyst with highly dispersed Co atoms over the hierarchical structure of g-C₃N₄ and carbon spheres (C₃N₄@CS), where ultrathin g-C₃N₄ aided the atomic level dispersion of Co atoms. As the electrocatalytic performance of the SACs is influenced by the chemical bonding between the support and single atoms, catalysts with Co-O coordination (Co-O-C₃N₄@CS), and Co-N coordination (Co-C₃N₄@CS), were precisely synthesised by changing the calcination atmosphere from air to argon. Co-O-C₃N₄@CS and Co-C₃N₄@CS catalysts exhibited appreciable OER activity and delivered overpotentials of 0.23 V at 10 mA cm⁻² and 0.47 V at 50 mA cm⁻², respectively in alkaline media. The Co-O-C₃N₄@CS exhibited higher OER performance, at low overpotentials, as the higher electronegativity of O, compared to N, accelerated the adsorption of oxygen species. However, at high overpotentials the activity worsened due to unfavourable desorption energies.¹⁴⁶

Employing first principle calculations, Guo et al established the suitability of a single transition metal atom dispersed g-C₃N₄ catalyst for ORR. The adsorption energy of the

key intermediate OH (ΔE_{*OH}) and the d-band centres form the basis of predicting the overpotential for ORR. The study predicted that among the various TM/g-C₃N₄ catalyst, Pd/g-C₃N₄ exhibited a low overpotential value of 0.46 V qualifying it to be an effective substituent for the conventional Pt catalyst.¹⁴⁷

N-doped porous carbon containing Fe atoms (Fe-g-C₃N₄/HPNCs, 2.15 wt%) coordinated to C₃N₄ matrix was demonstrated to be an effective ORR electrocatalyst, with an E_{1/2} of 0.902 V, outperforming the commercial Pt/C catalysts. The hierarchical structure characterised by a micro-mesoporous architecture enabled increased mass transport to the catalytically active single atomic Fe-N₂ sites favouring enhanced ORR activity with appreciable durability.¹⁴⁸

The potential of Co₁/g-CN and Ni₁/g-CN SACs described earlier for overall water splitting, have been evaluated for OER. The theoretical calculations predicted that Co₁/g-CN and Ni₁/g-CN SACs can exhibit over potential values of 0.61 V and 0.40 V respectively for OER reactions that are comparable with that of IrO₂ reference catalysts with 0.55 V overpotential value.¹³⁷

By combining DFT with machine learning Guo et al predicted the possibility of developing highly efficient OER and ORR bifunctional catalysts based on single atom transition metal (TM) dispersed over g-C₃N₄ (Figure 32 (a-b)). The defects induced by the nitrogen vacancies in g-C₃N₄ (VN-CN) facilitate a strong RMSI with TM single atoms providing stability for TM/VN-CN. Among various TMs, Rh/VN-CN indicated low overpotentials of 0.43 and 0.32 V for ORR and OER respectively (Figure 32 (c-h)).¹⁰

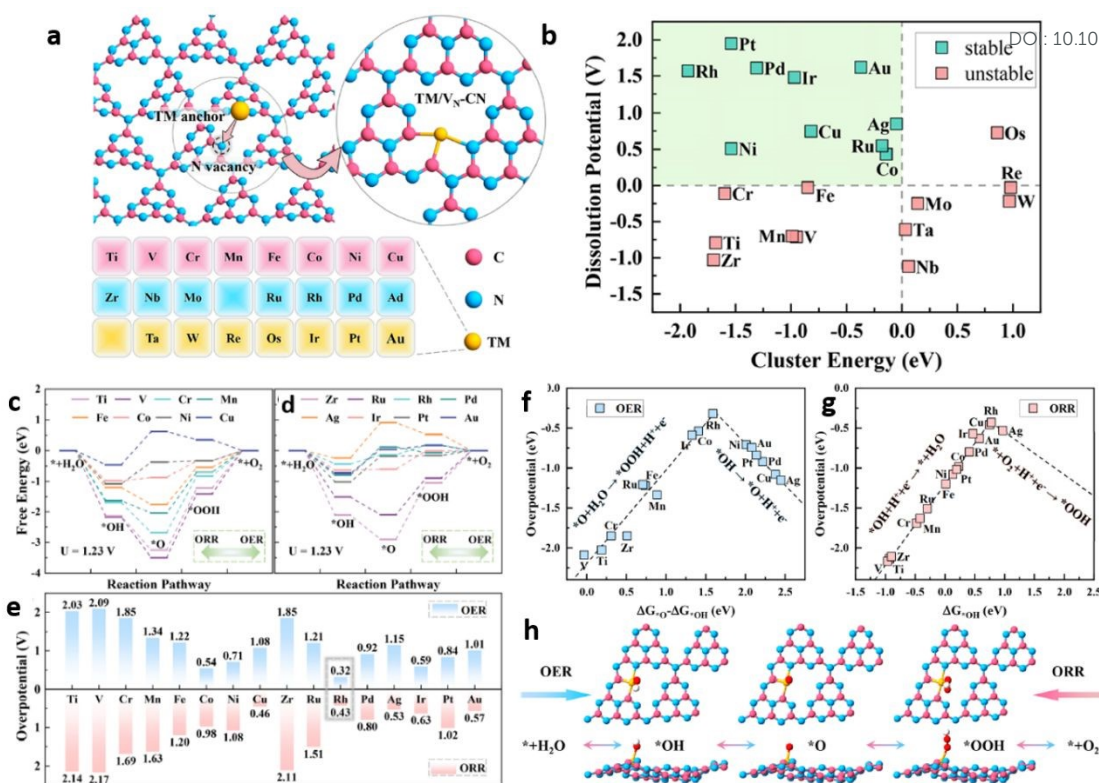


Figure 32. (a) Schematic representation of various transition metals (TM) based SACs on VN-CN, (b) Stability of TM/V_N-CN based on Cluster energy ($E_{\text{Clus}} < 0$ eV) and dissolution potential ($U_{\text{diss}} > 0$ eV), The free energy diagrams of TM/VN-CN (c) from Ti to Cu and (d) from Zr to Au related to both OER and ORR at the equilibrium potential of 1.23, (e) The OER and ORR overpotentials of TM/VN-CN (from Ti to Au), The volcano plots of (f) OER ($-\eta_{\text{OER}}$ vs $\Delta G^*O - \Delta G^*OH$) and (g) ORR ($-\eta_{\text{ORR}}$ vs ΔG^*OH) on TM/VN-CN, (h) OER and ORR intermediate structures adsorbed on Rh/VN-CN. Reproduced with permission from ref. 10. Copyright 2021 American Chemical Society.

Peng et al demonstrated the development of Fe, N co-doped carbon (Fe/N/C) using Fe coordinated $g\text{-C}_3\text{N}_4$ and glucose as precursors. The intense mixing of urea-derived $g\text{-C}_3\text{N}_4$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and glucose under ultrasonication resulted in the formation of Fe coordinated $g\text{-C}_3\text{N}_4$ matrix. The adsorbed glucose on hydrothermal treatment, formed linear and/or branchlike oligosaccharides. Carbonisation at 1100 °C resulted in the conversion of $g\text{-C}_3\text{N}_4$ -coordinated Fe embedded in glucose-derived carbon to porous Fe/N/C. The pyridinic N atoms of heptazine rings (known as N pots) in the $g\text{-C}_3\text{N}_4$ matrix can prevent the aggregation of the metal species during high-temperature pyrolysis by realising coordination between lone pairs of electron and metal species. The negative adsorption energy values calculated via DFT studies for Fe^{3+} ion (-38.26 eV) and Fe atom

(-3.54 eV) on the N pots further substantiated the role of g-C₃N₄ in realising atomic level dispersion of Fe on carbon matrix. Fe/N/C-575-A (Fe/N/C-575 sample after the ORR catalytic activation steps such as acid leaching and second annealing) exhibited good ORR activity with large onset potential ($E_{\text{onset}} = 0.972$ V and half-wave potential ($E_{1/2} = 0.890$ V) with a mass specific activity (j_m) of 9.103 mA mg⁻¹ at 0.9 V. The availability of a large number of Fe-N₄ active sites over the high surface area matrix, synergistic activity of Fe single atoms with N-C nanosheets, and the enhanced mass transfer due to high porosity collectively contributed towards the enhanced ORR performance of Fe/N/C-575-A catalyst.¹⁴⁹

Xu et al demonstrated a facile template strategy for the development of ORR electrocatalyst based on N-doped graphene containing up to 14.0 wt% of Co single atoms and atomic clusters. The catalyst CoSAs/AC@NG was obtained by the pyrolysis of dicyandiamide with the formation of layered g-C₃N₄ as the sacrificial template with abundant N anchoring sites to realise the single Co atom loading. The catalyst was synthesised by the low-temperature pyrolysis (550 °C) of a precursor mix of glucose, dicyandiamide (DCDA) and CoCl₂·6H₂O followed by a high-temperature annealing at 800 °C for the conversion of g-C₃N₄ to porous carbon. The numerous defective sites and high N content acted as the anchoring sites for Co single atoms and the transformation of intermediate products to conductive carbon led to the in-situ formation of high-density cobalt single atoms in nitrogen-doped graphene (Co SAs/AC@NG). XANES analysis revealed that the valence state of cobalt is close to +2 as the Co K-edge absorption position of Co SAs/AC@NG varied with that of Co foil but was similar to that of CoO. The EXAFS spectral analysis of the catalyst confirmed Co-N(O) coordination through a major peak at ≈1.41 Å, and a weak peak at 2.22 Å, indicating the presence also of Co clusters. The EXAFS fittings suggested an average coordination number of 3.7±0.3 for Co-N(O). It was inferred from the XPS and XAS analysis that the most dominant active sites in Co SAs/AC@NG are likely to be the Co-N₄ moiety (Figure 33 (a-g)). Co₄₀SAs/AC@NG with $E_{1/2}$ of 0.890 V, kinetic current density (J_k) of 17.070 mA cm⁻² and mass activity of 305 A g⁻¹ at 0.85 V outperformed the commercial Pt/C (J_k of 4.845 and mass activity of 60.5 A g⁻¹) for ORR reaction (Figure 33 (h-i)). Additionally, Co₄₀SAs/AC@NG exhibited excellent performance in Zn-air battery as an air electrode material with a high-peak power density value of 221 mW cm⁻² and with high cycling stability.¹⁵⁰

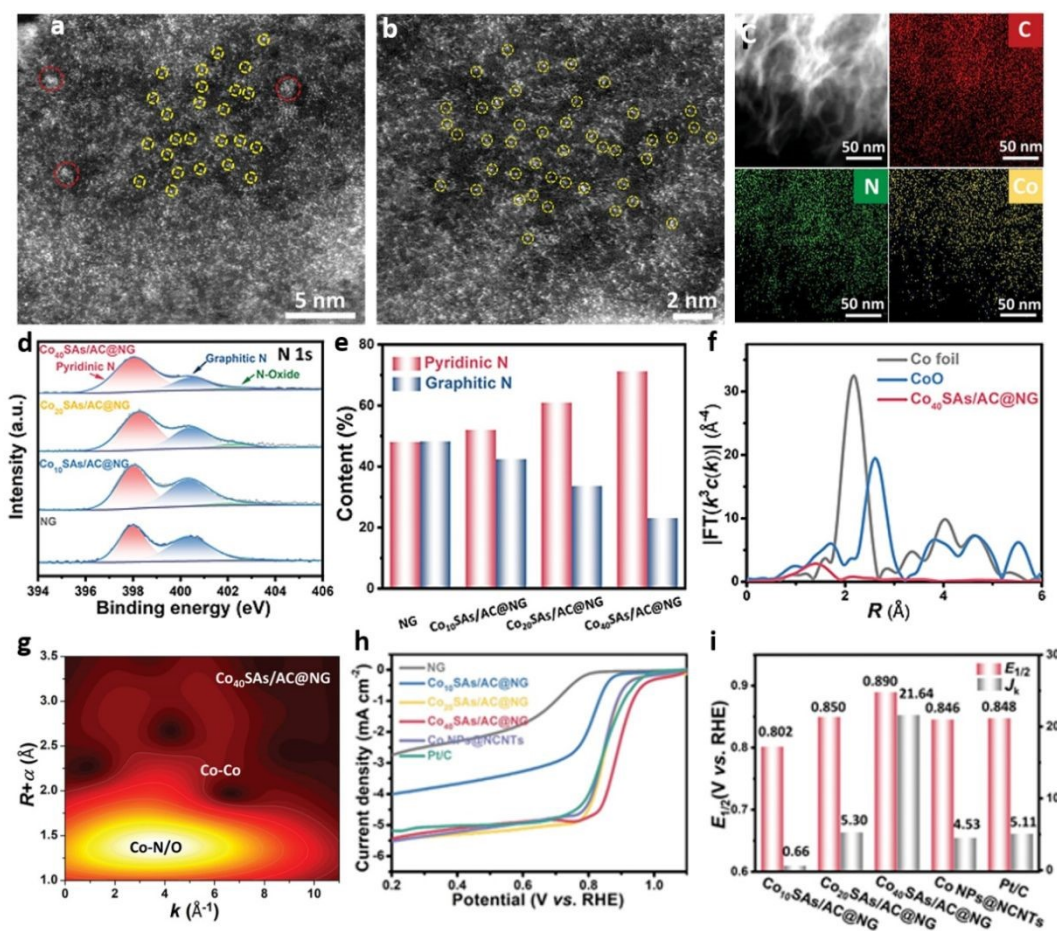


Figure 33. (a-b) HAADF-STEM images of $\text{Co}_{40}\text{SAs}/\text{AC}@/\text{NG}$ catalyst (Aberration-corrected), (c) EDS mappings of $\text{Co}_{40}\text{SAs}/\text{AC}@/\text{NG}$ by HAADF-STEM; Yellow and red circles represent Co single atoms and Co clusters respectively, (d) XPS N 1s spectra of NG and $\text{CoSAs}/\text{AC}@/\text{NG}$, (e) N content of NG and $\text{CoSAs}/\text{AC}@/\text{NG}$, (f-g) EXAFS spectra and WT-EXAFS plots of $\text{Co}_{40}\text{SAs}/\text{AC}@/\text{NG}$, (h-i) Comparison of RDE polarisation curves at a scan rate of 5 mV s^{-1} at 1600 rpm , J_k values at 0.85 V & $E_{1/2}$ values of the samples for ORR activity in O_2 -saturated 0.1 M KOH solution. Reproduced with permission from ref. 150. Copyright 2022 John Wiley and Sons.

Table 11 lists the OER and ORR applications of $g\text{-C}_3\text{N}_4$ based SACs.

Table 11 Summary of g-C₃N₄ SACs for electrocatalytic oxygen evolution reaction & oxygen reduction reaction (OER & ORR)

System	Single atom & loading	Synthesis method	OER & ORR activity (Onset potential, E _{1/2} , Current density, Mass activity)	Coordination site or structure & oxidation state	Reference
Ni-CN	Ni 2.4 at%	Template free direct synthesis	OER: Onset potential 1.54 eV	Nitrogen	142
M-C ₃ N ₄ /CNT	M= Cr, Mn, Fe, Co, Ni, Cu, Zn; Co: 0.2 at%	Template free direct synthesis	Co-C ₃ N ₄ /CNT ORR: Onset potential: 0.9 V, Current density: 5 mA/cm ² , ORR: Onset potential: 1.5 V, Current density: 10 mA/cm ² at 1.6 V	Co-N ₂ , +2	143
Au ₁ N _x /C ₃ N ₄	Au 0.7 wt%	Post synthesis-electrostatic adsorption	ORR: Mass activity of 9000 A•g _{Au} ⁻¹ at E _{1/2} of 0.76 V, OER: Mass activity of 1500 A•g _{Au} ⁻¹ at overpotential 0.45 V.	Au ₁ N _x , +1	22
C-FeHZ8 @g-C ₃ N ₄	Fe 3.17 wt%	g-C ₃ N ₄ as a fugitive template	ORR: E _{1/2} : 0.18 V in acidic condition 0.845 V in alkaline condition	Fe-N ₄ , +2	144
NCM-CN-Fe	Fe	g-C ₃ N ₄ as a fugitive template	ORR: Onset potential: 0.0V Current density - 6.42 mA/cm ²	Fe-N _{4,1}	145
Co-O-C ₃ N ₄ @CS & Co-C ₃ N ₄ @CS	Co 0.13 & 0.09 wt%	Post synthesis	OER: Co-O-C ₃ N ₄ @CS: Over potential 0.23 V Current density: 10 mA/cm ² Co-C ₃ N ₄ @CS: Over potential 0.47 V Current density: 50 mA/cm ²	Co-O & Co-N	146
TM/g-C ₃ N ₄	TM = Ti - Au	DFT Study	Pd/g-C ₃ N ₄ is predicted to exhibit good ORR activity with an overpotential of 0.46 V	-	147

Fe-g-C ₃ N ₄ /HPNCPS	Fe 2.15 wt%	g-C ₃ N ₄ as a fugitive template	ORR: E _{1/2} : 0.902 V	Fe-N ₂ , Oxidation state in between 0 & +3	148 View Article Online DOI: 10.1039/D2TA09776A
TM/g-CN	TM = Ti, V, Cr, Mn, Fe, Co, Ni	DFT study	Co ₁ /g-CN & Ni ₁ /g-CN SACs are predicted to be the most effective OER catalysts with over potential values of 0.61 V and 0.40 V respectively	Nitrogen	137
TM/V _N -CN	TM = Ti to Au	DFT Study	Rh/V _N CN is predicted to have optimal activity with overpotential values of 0.32 and 0.43 V for OER & ORR respectively	C/N	10
Fe/N/C	Fe 1.5 wt%	g-C ₃ N ₄ as a fugitive template	ORR: Onset potential: 0.972 V, E _{1/2} : 0.89 V, Mass specific activity: 9.103 mA/mg @ 0.9 V	Fe-N ₄ , +2	149
CoSAs/AC@NG	Co 14 wt%	g-C ₃ N ₄ as a fugitive template	ORR: E _{1/2} : 0.890 V, kinetic current density (Jk): 17.07 mA cm ⁻² , Mass activity: 305 A g ⁻¹ at 0.85 V	Co-N ₄ , +2	150

6 Conclusion and future perspectives

Single atom catalysts have emerged as potential systems with attractive features for a multitude of applications. The use of g-C₃N₄ as an efficient matrix for the development of SACs has been hitherto established to a fair level of certainty. The ease of anchoring single atoms on the matrix through abundant nitrogen sites in g-C₃N₄ facilitated the development of a variety of SACs for applications in different domains of catalysis. Advanced analytical tools like EXAFS, XANES, aberration corrected HAADF-STEM and EELS are used to confirm the single atom formation with a positive (partial/full) oxidation state. Computational studies have also been employed to validate the geometrical and coordination structures as well as to elucidate and predict the catalytic mechanisms.

Conventional approaches of synthesising g-C₃N₄ based SACs like wet chemical reduction, high-temperature heat treatment of precursor mix under an inert atmosphere, and supramolecular self-assembly techniques are presumed to be advantageous over hardware

intensive atomic layer deposition method (ALD). Even though precise control of single atom dispersion is possible in ALD, metal loading realisable is relatively low. The scale up possibilities in kilogram batches have been recently demonstrated in a multistep high temperature treatment under an inert atmosphere. Single atoms of 15 transition metals in ultra-high density have been developed on g-C₃N₄ support. The process is thus amenable for large-scale production in appreciable yields. Downsizing metal species to single atoms significantly improves metal utilisation efficiency imparting desirable catalytic properties. However, enhanced metal-support interaction, though beneficial for catalyst stability, often impedes catalytic activity due to unfavourable product desorption. A balance has to be thus established between catalyst stability and activity for which an in-depth analysis of the metal support interaction and mechanistic reaction pathways are essential. Real-time analysis involving operando techniques has to be explored further for g-C₃N₄ based SACs.

The use of synchrotron based spectroscopic tools is an essential requirement to elucidate the metal oxidation state and coordination structure in SACs. Apart from this catalyst characterisation, the study of the catalytic mechanism necessitates real-time analysis as mentioned before, the accessibility of which is scarce.

Of the reported systems thus far, g-C₃N₄ SACs are primarily based on single metal systems predominantly of precious metals. The techno-economic feasibility of such systems for large-scale applications is limited due to cost and availability. The shortcoming can presumably be circumvented by the use of dual or multiple metals as atomic dispersions over g-C₃N₄. This can be realised by substituting precious metals partly with non-precious ones to balance affordability with catalytic performance. This is particularly true for applications demanding multi-site synergism like CO₂ reduction and organic transformations. For example, in photocatalytic CO₂ reduction SAC with single sites normally facilitates the reduction of CO₂ to C₁ products like HCOOH, CO, CH₃OH, HCHO, CH₄, etc. The product selectivity mainly depends upon the stability of the intermediates formed during the multi-electron proton transfer. SACs with multiple metal sites can offer better stability to the intermediates compared to single metal sites thereby promoting extended electron proton transfer as well as C-C coupling to produce higher hydrocarbons. Along with dual metal sites, it is also feasible to incorporate single atom alloy catalysts based on g-C₃N₄ for enhanced activity by tuning electron density distributions around the multi centers.

Researchers have already employed DFT calculations to prove the efficiency of g-C₃N₄ based SACs for electrocatalytic applications such as CO₂ reduction, N₂ reduction, etc but the experimental verification of the hypothesis is still required. The poor conductivity of g-C₃N₄ support may impede its electrocatalytic activity to a larger extent and it may be advantageous to develop hybrid matrices incorporating materials of high electrical conductivity and charge transfer capacity (Graphene, N-doped carbon, etc.).

One area of high practical relevance for the use g-C₃N₄ based SACs is believed to be organic reaction catalysis as a majority of the industrially relevant reactions employ homogeneous catalysts for enhanced kinetics and high yield. Recovery of the catalyst, particularly of precious metal compositions is vital for recyclability and cost effectiveness. g-C₃N₄ SACs are affordable solutions to bridge this gap and are presumed to be of high practical viability even though most of the works reported still employ Pt, Pd, Au based SACs. However, the recent report on the large-scale synthesis of g-C₃N₄ Cu SAC and its demonstration for organic transformation opens up myriad possibilities for the industrial utilisation of SACs. Nevertheless, this would necessitate a thorough understanding of the underlying mechanisms leading to the regiospecificity and selectivity of products. This review comprehensively analysed the developments in g-C₃N₄ based SACs and overviewed the synthesis, characterisation, analysis and applications.

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