

TOPICAL REVIEW

Graphitic carbon nitride based single-atom photocatalysts

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Single-atom photocatalysts, due to their high catalysis activity, selectivity and stability, become a hotspot in the field of photocatalysis. Graphitic carbon nitride (g-C₃N₄) is known as both a good support for single atoms and a star photocatalyst. Developing g-C₃N₄-based single-atom photocatalysts exhibits great potential in improving the photocatalytic performance. In this review, we summarize the recent progress in g-C₃N₄-based single-atom photocatalysts, mainly including preparation strategies, characterizations, and their photocatalytic applications. The significant roles of single atoms and catalysis mechanism in g-C₃N₄-based single-atom photocatalysts are analyzed. At last, the challenges and perspectives for exploring high-efficient g-C₃N₄-based single-atom photocatalysts are presented.

Keywords graphitic carbon nitride, single atoms, atomically dispersed sites, site-isolated catalysts, photocatalysis

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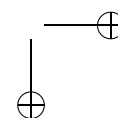
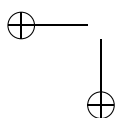
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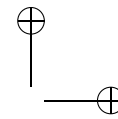
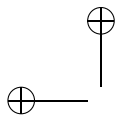
as a star photocatalyst, it has been widely used in various photocatalytic reactions [5–13]. However, due to its sluggish surface catalytic rates, insufficient light absorption capacity and high recombination rate of photogenerated electron/hole pairs, the photocatalytic performance is still far from the requirements [14–16]. Various effective modification methods have been applied, such as loading of metal cocatalyst [17–19], doping with heteroatoms [20–22], and compositing with other semiconductors [23, 24]. Generally, metal cocatalyst could easily meet the demands for improving photocatalytic activity of g-C₃N₄, mainly attributing to better separation of photogenerated charge carriers and higher surface catalysis activity of metal active sites [25, 26]. For example, Pt, the most typical noble metal cocatalyst, has been proven to be the most effective cocatalyst of g-C₃N₄ for various photocatalytic application [17, 27]. Unfortunately, the low reserves of noble metals greatly limit their price and widespread applications.

As we know, traditional heterogeneous catalysis plays an important role in driving oil refining, ammonia and fine chemical synthesis [8, 16, 28–30]. Generally, heterogeneous catalysts are composed of metal nanoparticles (especially noble metals, such as Pt, Ru) and metal oxide supports. Only the metal atoms exposed on the surface of metal nanoparticles are active in the catalysis reactions

Photocatalysis is one of the potential solutions to energy crisis and environmental pollution [1–3]. Since Wang *et al.* firstly reported graphitic carbon nitride (g-C₃N₄) for photocatalytic hydrogen generation from water splitting [4],

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[23, 31, 32]. The metal atomic utilization is low, and the actual catalytic activity of metal component has not been fully exploited. Furthermore, the heavy consumption of noble metal greatly increases the cost of heterogeneous catalysts. On this background, single-atom heterogeneous catalysts (SACs) containing metals atomically dispersed as isolated catalysis sites emerge. First, SACs exhibited higher catalytic activity than its counterpoint. Second, single-atom metal sites can achieve nearly 100% atomic utilization, greatly reducing the dosage of metal. Third, the single-atom model can more clearly study the real catalytic effect of the active site, facilitating the study of catalytic mechanisms [28, 29, 33–37].

In recent years, g-C₃N₄-based single-atom photocatalysts have been widely studied [3, 38–42]. Combined with the photo-response characters of g-C₃N₄ and the high catalytic activity of single-atom metal sites, they show great potential in the field of photocatalysis [16]. Single atoms are extremely small in size, resulting in a maximum surface free energy. Strong chemical interactions between the g-C₃N₄ support and single atoms are the key factor in the stability of SACs. g-C₃N₄ is an ideal support material for loading single atoms [36, 40, 41, 43]. The typical two-dimensional (2D) layered structure of g-C₃N₄ brings rich surface loading sites. The adjacent layers are connected by weak van der Waals force, the CN atoms in plane are hybridized with sp² to form a highly delocalized π -conjugated system [14]. The presence of lone-pair electrons in two-coordinated N atoms provides an opportunity for coordinating metal atoms. The rich lone-pair electrons of N atoms in the CN heterocycle can confine the highly active single metal atoms, resulting stable g-C₃N₄-based single-atom photocatalysts. Moreover, the modified g-C₃N₄ with more defects can also be good support for single atoms. The defects can play a positive role in the stability of single atoms, which can be ascribed to that the single atoms can be embedded into the defects of supports or bonded with adjacent N atoms. In addition, the physicochemical property of g-C₃N₄ support also changes with the aid of the loaded single atoms. The single atoms on g-C₃N₄ can optimize the band structure of g-C₃N₄, extending optical absorption range. The single metal atom can also accelerate the photogenerated charge separation of g-C₃N₄, which are beneficial for photocatalytic reactions.

In this review, we make a comprehensive review on the progress in the preparation, characterization and application of single atoms modified g-C₃N₄ photocatalysts. We focus on how to accurately characterize the single-atom active sites, and the main roles of the single-atom active site in photocatalytic reactions. This review aims to deepen the understanding of g-C₃N₄ based single-atom photocatalysts, with emphasis on the mechanism of photocatalytic reactions. Some perspectives and challenges on the design of g-C₃N₄ supported single-atom photocatalysts are also presented.

2 Main preparation methods of g-C₃N₄-based single-atom photocatalysts

For the single atoms loaded on g-C₃N₄ support, different synthesis methods will form different microscopic structures and active sites, which will ultimately affect their photocatalytic performance. At present, the widely used methods for preparing single atoms on g-C₃N₄ are wet chemical route, thermal copolymerization, atomic layer deposition and metal molecular complexes (Fig. 1). These methods all have their own convenience and advantages. Each preparation method is described in detail below.

2.1 Wet chemical route

Wet chemical route is the most common method to deposit single atoms on the surface of g-C₃N₄ supports, generally including two important steps: (i) the proper amount of metal precursor is fixed on the surface of g-C₃N₄ supports by means of impregnation, adsorption, coordination bonding, and deposition; (ii) appropriate reduction and activation steps are used to convert the surface-bound precursor into stable mono-disperse atoms on the surface of support. Figure 2 exhibits the typical process of single-atom metal supported on g-C₃N₄ by wet chemical route. The g-C₃N₄ with rich mesoporous can obtain higher surface area for better single-atom metal deposition. Mesoporous g-C₃N₄ (MCN) support was prepared by co-thermo-polymerization of g-C₃N₄ precursor and pore-forming template (such as SiO₂ spheres). Soluble metal salt uniformly adsorbed on the surface of MCN. A NaBH₄ reduction method was used for reduction and activation of single-atom metals on MCN [44].

Similarly, Vilé *et al.* [45] prepared mesoporous g-C₃N₄ with high specific surface area (155 m²/g) by co-thermo-polymerization of cyanamide and colloidal silica. Silica acted as template and pore former was removed after

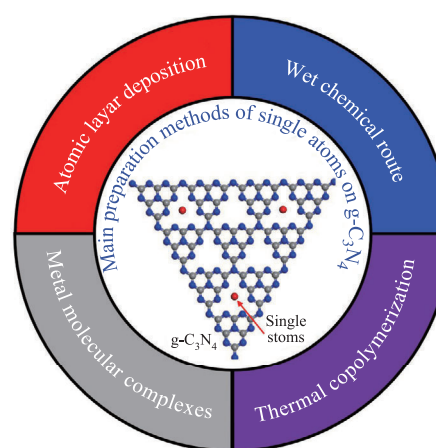
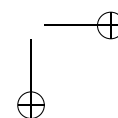
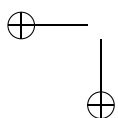


Fig. 1 Main methods for synthesizing single atoms on g-C₃N₄.



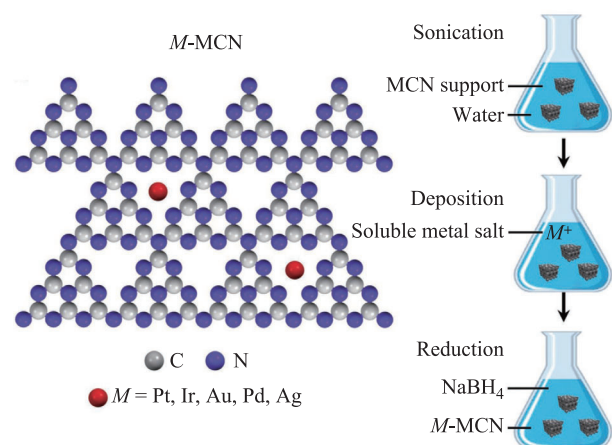


Fig. 2 Typical process of single-atom metal supported on $g\text{-C}_3\text{N}_4$ by wet chemical route [44].

thermo-polymerization. The mesoporous $g\text{-C}_3\text{N}_4$ was immersed in Pd precursor solution (an aqueous solution of PdCl_2 and NaCl), and then NaBH_4 solution was used to reduce Pd^{2+} and generate Pd single atom modified mesoporous $g\text{-C}_3\text{N}_4$. The different reduction and activation methods of single atoms are important steps in the preparation process. The surface adsorbed metal precursor on $g\text{-C}_3\text{N}_4$ can be transformed into single-atom metal by thermal-reduction with inert atmosphere. Tian *et al.* [46] used mesoporous $g\text{-C}_3\text{N}_4$ as support for single-atom deposition. The mesoporous $g\text{-C}_3\text{N}_4$ was prepared by the same method with Vile *et al.* [45]. Single-atom Ru was anchored on mesoporous $g\text{-C}_3\text{N}_4$ by wet-impregnation and thermal-reduction. Specifically, Ru precursor was firstly uniformly adsorbed on mesoporous $g\text{-C}_3\text{N}_4$, and then the Ru precursor loaded mesoporous $g\text{-C}_3\text{N}_4$ was pyrolyzed at 300°C under N_2 protection. Li *et al.* [47] reported single-atom Pt modified $g\text{-C}_3\text{N}_4$ by wet-impregnation deposition with low temperature (125°C) thermal reduction. Firstly, the metal precursor H_2PtCl_6 was uniformly dispersed on the surface of $g\text{-C}_3\text{N}_4$ by directly solution evaporation of $g\text{-C}_3\text{N}_4$ nanosheets dispersed H_2PtCl_6 solution, and then single-atom Pt was deposited on $g\text{-C}_3\text{N}_4$ by thermal reduction under the protection of Ar atmosphere at 125°C . Reductive atmosphere is also a good strategy for reduction and activation of single-atom metals. Chen *et al.* [48] prepared single-site Au on mpg- C_3N_4 by pre-impregnation HAuCl_4 on the surface of mpg- C_3N_4 and a following reduction in H_2/Ar atmosphere at 100°C . Other special method also be developed for reduction and activation of single-atom metals on $g\text{-C}_3\text{N}_4$. Liu *et al.* [49] synthesized single-atom Au anchored on $g\text{-C}_3\text{N}_4$ by wet-impregnation deposition with amine-induced-reduction strategy. Firstly, the support $g\text{-C}_3\text{N}_4$ was ammoniated treated. At the set pH value of the solution, the ammoniated $g\text{-C}_3\text{N}_4$ was positively charged, which can electrostatically adsorb AuCl_4^- with negatively charged. Then, the protonated amine can direct reduce Au^{3+} and form Au-N bonds on the surface

of $g\text{-C}_3\text{N}_4$ support. The different strategies of reduction and activation of single-atom metals on $g\text{-C}_3\text{N}_4$ supports in wet chemical route are summarized in Table 1.

The stability of loaded single atoms on the surface of $g\text{-C}_3\text{N}_4$ support is an important factor to obtain high-efficient single atoms modified $g\text{-C}_3\text{N}_4$ photocatalysts. Though high specific surface area and abundant nitrogen-based ligands make $g\text{-C}_3\text{N}_4$ an ideal support for stabilization of single atoms, heteroatoms doping can further enhance the stability of single atoms by ligand interaction between the single atoms and doping atoms. Chen *et al.* [50] firstly exfoliated bulk $g\text{-C}_3\text{N}_4$ into $g\text{-C}_3\text{N}_4$ nanosheets to get higher specific surface area, and then introduced heteroatom P doping into exfoliated $g\text{-C}_3\text{N}_4$ nanosheets. Pd single atoms were loaded on the modified $g\text{-C}_3\text{N}_4$ nanosheets by wet-impregnation deposition. The support (P doping modified $g\text{-C}_3\text{N}_4$ nanosheets) was firstly impregnated in $\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2$ solution for complete adsorption of Pd species. Then, the adsorbed Pd species converted into Pd single atoms on the surface of modified $g\text{-C}_3\text{N}_4$ nanosheets by microwave-assisted reduction. The modification of heteroatom P doping increased the surface electron density of $g\text{-C}_3\text{N}_4$, which reduced the oxidation state of the metal and stabilized the Pd single atoms on $g\text{-C}_3\text{N}_4$ by P ligand interaction. In addition to these noble metals single atoms, Liu *et al.* [51] prepared non-noble single-atom Co-based $g\text{-C}_3\text{N}_4$ by co-thermal-treatment of $\text{Co}(\text{NO}_3)_2$ and $g\text{-C}_3\text{N}_4$. To stabilize the Co single atoms, phosphidation treatment to form more stable Co_1P_4 on the surface of $g\text{-C}_3\text{N}_4$ was performed by co-calcination of $\text{NaH}_2\text{PO}_2\cdot\text{H}_2\text{O}$ and single-atom Co modified $g\text{-C}_3\text{N}_4$.

The confinement effect of supports can effectively prevent the agglomeration of single atoms and improve their dispersion stability. Single atoms dispersed on zeolite [27, 53, 54], mesoporous carbon [55] and metal organic frameworks (MOFs) [1] have been widely studied. These

Table 1 Reduction and activation strategies of single-atom metals on $g\text{-C}_3\text{N}_4$ supports in wet chemical route.

Samples	Reduction and activation strategies	Ref.
$\text{M}@g\text{-C}_3\text{N}_4$ (M = Pt, Ir, Au, Pd, Ag)	NaBH_4 solution	[44]
$\text{Pd}@g\text{-C}_3\text{N}_4$	NaBH_4 solution	[45]
$\text{Ru}@g\text{-C}_3\text{N}_4$	300°C thermal-reduction under N_2 atmosphere	[46]
$\text{Pt}@g\text{-C}_3\text{N}_4$	125°C thermal-reduction under Ar atmosphere	[47]
$\text{Au}@g\text{-C}_3\text{N}_4$	100°C thermal-reduction under H_2/Ar atmosphere	[48]
$\text{Au}@g\text{-C}_3\text{N}_4$	amine-induced reduction	[49]
$\text{Pd}_1\text{P}_4@g\text{-C}_3\text{N}_4$	microwave-assisted reduction	[50]
$\text{Co}_1\text{P}_4@g\text{-C}_3\text{N}_4$	300°C thermal-reduction under Ar atmosphere with NaH_2PO_2	[51]
$\text{Pt}@g\text{-C}_3\text{N}_4$	icing-assisted photoreduction	[52]
$\text{Pt}@g\text{-C}_3\text{N}_4$	photoreduction with H_2PtCl_6 aqueous solution dropwise	[17]

supports provided confined pores for single atoms reduction/activation process, which greatly prevented nucleation and crystal growth. During the wet-chemical routes, the nucleation and crystal growth process depend on the diffusion of ions and atoms. Freezing precursor solution to prevent the diffusion of ions and atoms can greatly inhibit the nucleation and growth process. The ice lattice can naturally confine the dispersed single atoms. Wei *et al.* [56] firstly reported synthesis atomically dispersed Pt metal by directly irradiation of freezing H_2PtCl_6 aqueous solution, no support was required. The single-atom Pt was derived from photodecomposition of H_2PtCl_6 . Zhou *et al.* [52] prepared single-atom Pt modified $\text{g-C}_3\text{N}_4$ by icing-assisted in-situ photocatalytic reduction method [57]. $\text{g-C}_3\text{N}_4$ acted as support and provided photogenerated electrons for in-situ reduction of the adsorbed PtCl_6^{2-} . Compared with the traditional photo-reduction method, freezing dramatically reduced the size of Pt metal, single-atom Pt can be in-situ deposited on the surface of $\text{g-C}_3\text{N}_4$. Similarly, for inhibiting the nucleation and growth of metal during the photo-reduction process, Zhu *et al.* [17] added H_2PtCl_6 aqueous solution into $\text{g-C}_3\text{N}_4$ suspension dropwise under visible light irradiation. The addition of H_2PtCl_6 aqueous solution drop by drop greatly prevent the growth of Pt metal grains. Atomically dispersed Pt can be observed on the surface of $\text{g-C}_3\text{N}_4$. Noteworthily, the high adding amount of H_2PtCl_6 aqueous solution will lead to big size of Pt nanoparticle, no single-atom Pt can be obtained.

2.2 Thermal copolymerization

Copolymerization of metal precursors and $\text{g-C}_3\text{N}_4$ precursors can directly obtain single-atom metal on the surface of $\text{g-C}_3\text{N}_4$. Generally, $\text{g-C}_3\text{N}_4$ can be easily synthesized by thermal polymerization of carbon, nitrogen-rich small molecules precursors. Oh *et al.* [58] directly thermally treated dicyandiamide and FeCl_2 at 600°C for 4 h to prepare single Fe atoms modified $\text{g-C}_3\text{N}_4$. As shown in Fig. 3(a), the thermal copolymerization reactions obtained single-atom Fe loaded on $\text{g-C}_3\text{N}_4$. The TEM image [Fig. 3(b)] shows arbitrary and nonperiodic morphology of $\text{Fe@g-C}_3\text{N}_4$. Figures 3(c) and (d) exhibit the crystalline nature of $\text{g-C}_3\text{N}_4$. The introduction of single-atom Fe into $\text{g-C}_3\text{N}_4$ did not change the main stacking of heptazine chain layer structure of $\text{g-C}_3\text{N}_4$ supports. Li *et al.* [59] reported single Mn atoms located on $\text{g-C}_3\text{N}_4$ by direct calcination of the mixture of KMnO_4 and urea in an inert gas. Chen *et al.* [60] firstly prepared silver tricyanomethanide (AgTCM) [61, 62] as metal precursors, and then one-step direct calcination of cyanamide, AgTCM and silica at 550°C . After the thermal copolymerization, the silica templates were removed and single-atom dispersed Ag on mesoporous $\text{g-C}_3\text{N}_4$ can be obtained. Li *et al.* [63] prepared single-atom Pt or Cu modified $\text{g-C}_3\text{N}_4$ by thermal copolymerization of dicyandiamide and metal precursors ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ or CuCl_2) at 550°C . Chen *et al.* [44] prepared a series of single-atom metals on $\text{g-C}_3\text{N}_4$ by firstly

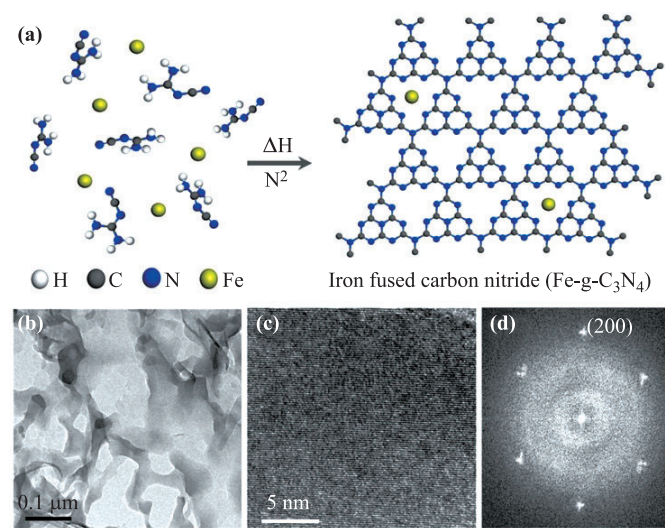


Fig. 3 (a) Thermal copolymerization process of metal precursor FeCl_2 and $\text{g-C}_3\text{N}_4$ precursor dicyandiamide to prepared single-atom Fe functionalized $\text{g-C}_3\text{N}_4$. TEM image (b) and well-defined local structure (c) of single-atom Fe modified $\text{g-C}_3\text{N}_4$. (d) Selected area electron diffraction electron of $\text{g-C}_3\text{N}_4$ (002) orientation [58].

mixture of soluble metal salt precursor, $\text{g-C}_3\text{N}_4$ precursor and colloidal silica template. During the process of co-thermo-polymerization, the reducing atmosphere released by $\text{g-C}_3\text{N}_4$ precursor can reduce/activate metal salt precursor to obtain single-atom metals. After removal of the SiO_2 template, single-atom metals modified mesoporous $\text{g-C}_3\text{N}_4$ can be obtained.

2.3 Atomic layer deposition

Atomic layer deposition (ALD) technique is one of the effective means to accurately deposit single-atom metals on $\text{g-C}_3\text{N}_4$ support. Cao *et al.* [64] deposited single-atom Co on the surface of P-doped $\text{g-C}_3\text{N}_4$ (PCN) by ALD using cobalt bis(cyclopentadienyl) (Cp) as metal precursor. As shown in Fig. 4(a), the support (PCN) was prepared by phosphidation treatment of pure $\text{g-C}_3\text{N}_4$. ALD can anchor atomic Co on PCN with residual surface Cp ligand due to the unsaturated two-coordinated N atoms. Further O_3 treatment eliminated excess Cp ligands. The whole treatment process did not change the main morphology and structure of $\text{g-C}_3\text{N}_4$ [Fig. 4(b)]. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images [Figs. 4(c) and (d)] exhibit the stable single-atom Co on the surface of PCN.

2.4 Metal molecular complexes

Metal atoms in the metal molecular complexes are protected by the surrounding ligands, are another form of atomically dispersed metal site. Compositing metal molecular complexes with $\text{g-C}_3\text{N}_4$ have been studied for improv-

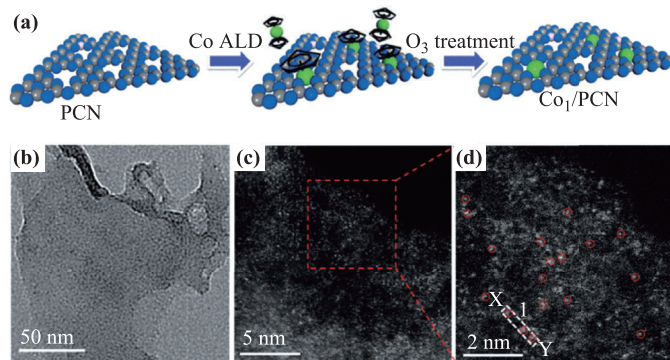


Fig. 4 (a) Illustration of the synthesis process of single-atom Co on the surface of P-doped $g\text{-C}_3\text{N}_4$ by ALD and O_3 treatment. (b) TEM and (c) HAADF-STEM images of single-atom Co on PCN. (d) magnification image of (c). The red circles in (d) represent atomically dispersed Co atoms [64].

ing the photocatalytic performance of $g\text{-C}_3\text{N}_4$ [65–67]. Kumar *et al.* [65] reported cobalt phthalocyanine grafted to $g\text{-C}_3\text{N}_4$ by simple adsorption effect. As shown in Fig. 5, CoPc with surface $-\text{COOH}$ and $g\text{-C}_3\text{N}_4$ were firstly synthesized separately. Phthalocyanine molecules are easily agglomerated due to their strong $\pi\text{-}\pi$ interactions. Increasing the dispersion to reduce the agglomeration is an important strategy to realize the metal single-atom dispersion. The obtained CoPc-COOH and $g\text{-C}_3\text{N}_4$ were mixture and stirred in N, N-dimethylformamide (DMF) solution due to the good dispersion of CoPc-COOH in DMF. The adsorbed CoPc-COOH on the surface of $g\text{-C}_3\text{N}_4$ can be obtained, and atomically dispersed Co site on $g\text{-C}_3\text{N}_4$ greatly improved the selective photocatalytic conversion of CO_2 to methanol. Concentrated sulfuric acid is another dispersion solvent of phthalocyanine molecules. Shi *et al.* [66] prepared iron(II) phthalocyanine (FePc) composited with $g\text{-C}_3\text{N}_4$ by easy exfoliation and adsorption method. In order to get good dispersion and close contact of FePc

and $g\text{-C}_3\text{N}_4$. Concentrated sulfuric acids were used as dispersion solvents, both FePc and $g\text{-C}_3\text{N}_4$ nanosheets can be obtained and composited by the exfoliation and adsorption effects.

Summing up, in order to get single-atom metals loading on the $g\text{-C}_3\text{N}_4$ support, the metal precursor should firstly uniformly adsorb on the surface of $g\text{-C}_3\text{N}_4$ -based support or $g\text{-C}_3\text{N}_4$ precursor. Then, various post-treatments are used to reduce/activate and anchor single-atom species on the supports. The low loading amount of metals and high specific surface area of $g\text{-C}_3\text{N}_4$ -based supports are necessary conditions to obtain single-atom metals supported on $g\text{-C}_3\text{N}_4$ photocatalysts [44].

Although there are many methods to prepare single-atom photocatalysts, their low yield and low metal loading greatly limit their practical applications. Large-scale preparation of single-atom photocatalysts with high metal loading is still difficult [50, 68–70]. Yang *et al.* [70] reported a universal ligand mediated method for large scale synthesis of transition metal single atom catalysts on carbon black support. The obtained carbon-supported metal single atom catalysts are >1 kg scale. Zheng *et al.* [68] reported an ion adsorption process to prepare earth-abundant Ni single-atom catalysts on commercial carbon black with gram scale. Chen *et al.* [50] studied the scalability of single-atom catalysts on $g\text{-C}_3\text{N}_4$. The choice of precursor, synthesis condition, thermal exfoliation time, and metal deposition method is the key criteria for large-scale preparation and application of $g\text{-C}_3\text{N}_4$ based single-atom photocatalysts.

3 Strong characterizations of single-atom sites

How to determine the existence and spatial distribution of single atom on the support is the key to understand and

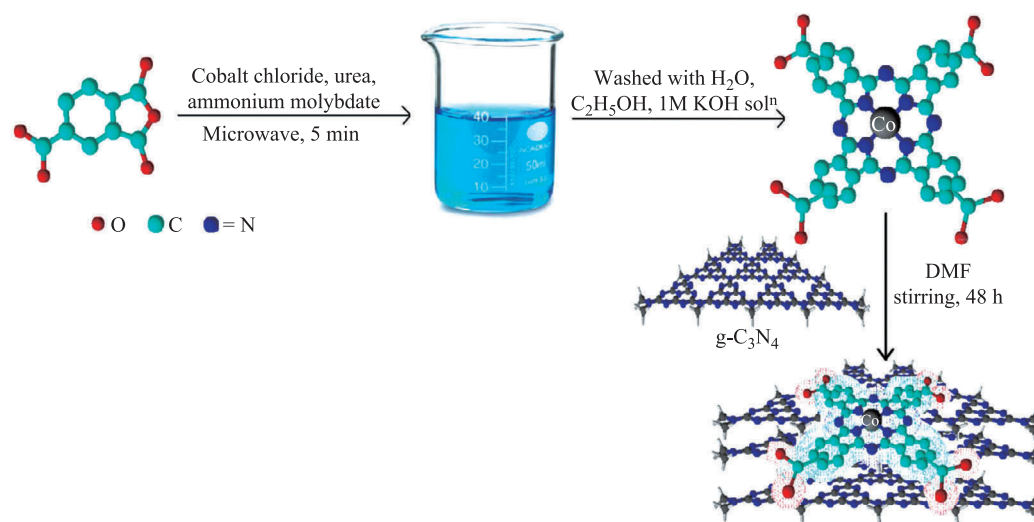


Fig. 5 Synthesis process of CoPc and CoPc modified $g\text{-C}_3\text{N}_4$ photocatalyst [65].

develop single-atom photocatalysts. The most intuitive and convincing tool is electron microscopy techniques, such as HAADF-STEM with spherical aberration correction, which can directly observe the morphology and sub-nanoscale size of single atom [46]. Tian *et al.* [46] performed aberration-corrected (AC) HAADF-STEM measurement to directly analyze the morphology and size of single-atom Ru loaded on g-C₃N₄. As shown in Fig. 6, many small bright spots are uniformly dispersed on the surface of g-C₃N₄ support. These bright spots can be ascribed to Ru atoms due to the Z-contrast difference of Ru atoms and C/N atoms. The ultra-small size of Ru atom indicated that Ru atoms are atomically dispersed.

Three-dimensional (3D) atom probe tomography (APT) technology with atomic resolution can also directly identify the presence and uniform dispersion of single atoms [71]. Jiang *et al.* [71] used 3D APT technology to directly identify the single-atom Ni sites in graphene support. As shown in Fig. 7, each pixel represents one single atom. The distance between different atoms can be obtained directly, so the coordination environment of metal atoms can be analyzed. Figure 7(c) exhibits the statistics of the surrounding coordination of Ni atoms, further proves the presence of single-atom Ni atoms.

X-ray absorption near edge structure (XANES) spectroscopy, and extended X-ray absorption fine structure spectroscopy (EXAFS) can directly determine the chemical state and coordination environment of atoms with

high sensitivity [47]. Li *et al.* [47] reported single-atom Pt as cocatalyst on the surface of g-C₃N₄ (Pt-CN) for photocatalytic H₂ generation. The Fourier transforms (FT) EXAFS curves shown in Fig. 8(a) prove that no Pt–Pt bonds can be detected in sample, only obvious Pt–C/N signal can be observed, further confirming the presence of single-atom Pt. Figures 8(b) and (c) determine the possible structural models of Pt-CN by the fitting of experimental EXAFS data.

Infrared spectroscopy with appropriate probe molecules, such as CO, NO, NH₃, and pyridine, can also be used to assess the existence of single metal atom [72, 73]. The content percentage of single metal atom dispersed on the surface of support can be quantitatively analyzed. Ding *et al.* [73] used infrared spectroscopy to fast and conveniently characterize the single-atom Pt on mesoporous zeolite HZSM-5. The stretching frequencies of CO when adsorbed to different Pt species sites are different. Single-atom Pt coordinated with O atoms of supported will result in a cationic charge state of Pt. The stretching frequency of CO adsorbed to single-atom Pt will exhibit higher wavenumber than CO adsorbed to Pt nanoparticles. As shown in Fig. 9, two different absorption bands can be observed, which can be ascribed to CO on single-atom Pt and linear CO on Pt nanoparticles. Moreover, higher Pt loading can lead to more Pt nanoparticles, and higher FTIR intensity of CO adsorbed to Pt nanoparticles. The ratio of absorption band areas can quantitatively identify the ratio of single-atom Pt to Pt nanoparticles.

Other characterizations can also indirectly characterize the existence of single atoms. For example, the absence of Pd XRD reflection peak indicated the high dispersion

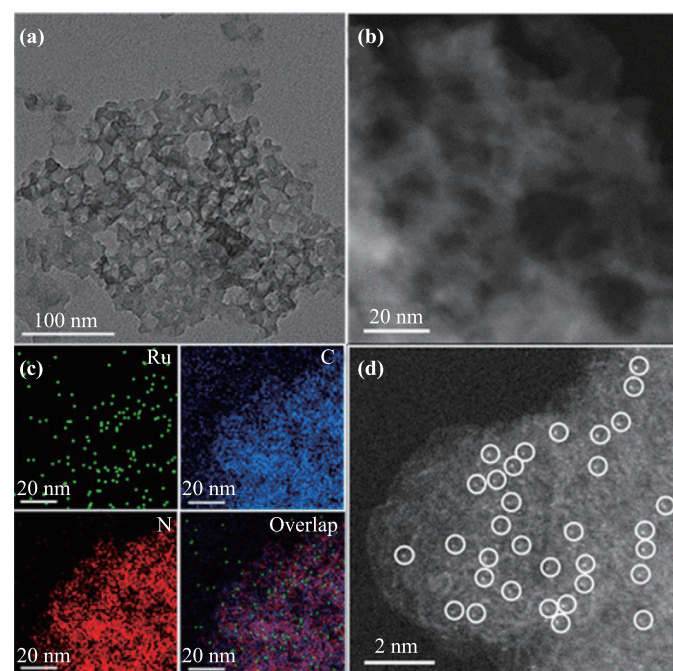


Fig. 6 TEM (a) and HAADF-STEM (b) images of the Ru loaded on g-C₃N₄ sample. (c) EDX element maps of Ru, C, and N atoms on the Ru loaded on g-C₃N₄ sample. (d) AC HAADF-STEM images of the Ru loaded on g-C₃N₄ sample [46].

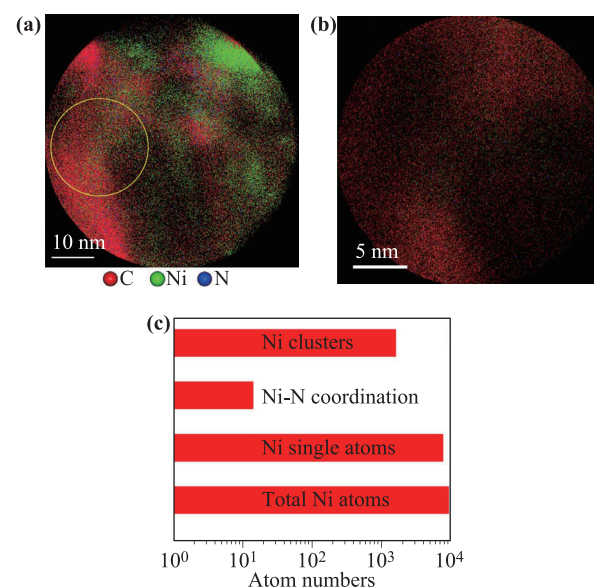


Fig. 7 (a) 2D atom map of Ni atom modified N-doped graphene. (b) Enlarge atom map of the yellow circle shown in (a). (c) The statistics of Ni atom in the selected area shown in (b) [71].

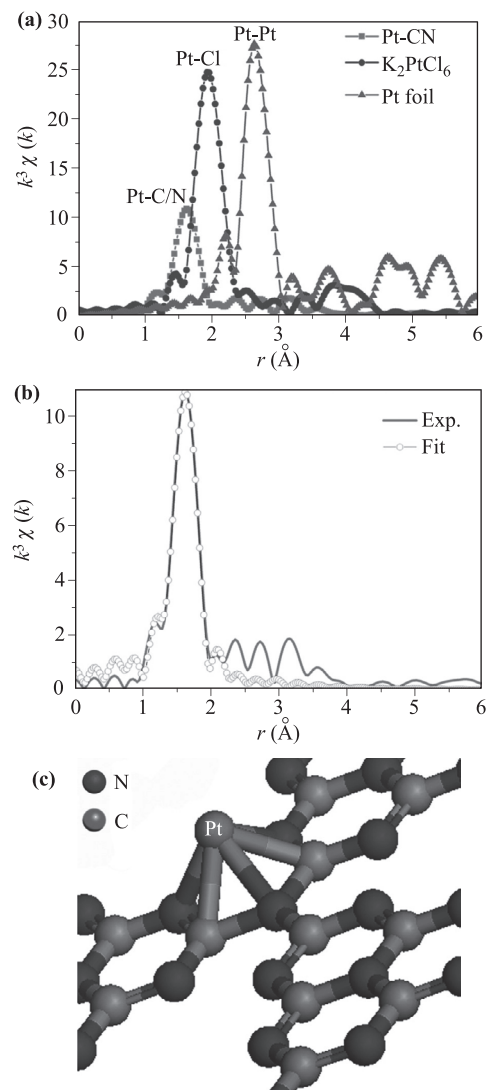


Fig. 8 (a) Fourier transform EXAFS curves of the Pt L3-edge oscillations of Pt-CN, K_2PtCl_6 , and Pt foil. (b) Experimental data and the fitting curves of the Pt-CN. (c) The possible schematic models of Pt-CN [47].

of Pd [50], which is necessary for single Pd atom dispersed on $g-C_3N_4$. The stable existence of single atoms requires strong interaction between single atoms and supports, which makes it impossible for single atoms to exist in zero valence state. Using X-ray photoelectron spectroscopy (XPS) to analyze the valence state of metal atoms is also a good indirect method [50].

4 Main roles of single atoms on $g-C_3N_4$ in photocatalytic reactions

For an excellent photocatalyst, activity, selectivity and stability are three important factors that must be considered. The low photocatalytic activity of $g-C_3N_4$ can be attributed to: i) insufficiency light absorption performance;

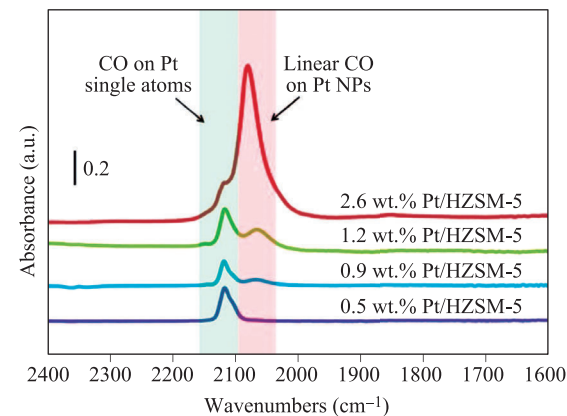


Fig. 9 FTIR spectra of CO adsorbed at Pt/HZSM-5 with different Pt loading [73].

ii) sluggish surface catalytic kinetics; iii) low utilization efficiency of photogenerated charge carriers. Single-atom metals on the surface can act as efficient active sites for catalysis reactions, which greatly improve the reaction kinetics. Moreover, the intrinsic properties of $g-C_3N_4$ can be changed by the loading of single-atom metals, so that the effect of light absorption and separation of photogenerated charge carriers can be improved.

Generally, only N atoms in $g-C_3N_4$ can bond with metal atoms due to the unsaturated coordination of N atoms. Three types of N atoms can be used to interact with metal atoms, namely two-coordinate N ($N-C_2$), tri-coordinate N ($N-C_3$) and surface amino N ($N-H_x$). The local bond coordination of single atom metals at $g-C_3N_4$ interface is important structure factor to analyze the photocatalytic performance. Oh *et al.* [58] proved the coordination of divalent Fe atom in $g-C_3N_4$ by detailed experimental and computational evidences. Solid-state nuclear magnetic resonance (NMR) spectroscopy of $g-C_3N_4$ and Fe modified $g-C_3N_4$ (Fe- $g-C_3N_4$) are shown in Fig. 10. Clearly, no obvious difference can be observed in the ^{13}C spectra [Fig. 10(a)]. Just the chemical shift of ^{15}N in Fe- $g-C_3N_4$ changed in peak 3 region (from 165.3 to 160.9 ppm) compared with the pure $g-C_3N_4$. Cross-polarization magic angle spinning (CP-MAS) NMR spectroscopy [Figs. 10(c) and (d)] were used to further determine the attribution of the peaks. As indicated in the chemical structure diagram of $g-C_3N_4$ [Fig. 10(d)], The peaks labeled with different colors correspond to atoms of different colors in $g-C_3N_4$. The signals of peak 3 regions come from two-coordinate N [N atoms in the red circle in Fig. 10(d)] in the $g-C_3N_4$ structure. The NMR characterizations confirmed that Fe atoms coordinated with two-coordinated N atoms. Further theoretical calculation proved that the cavities of $g-C_3N_4$ were the most favorable Fe adsorption sites with strong binding energy. The Fe single atoms coordinated with two-coordinated N in the cavities of $g-C_3N_4$. Similarly, Li *et al.* [59] proved metal atoms bond with the surface amino N ($N-H_x$) to form $NH-Mn^{II}$ in single atom Mn modified

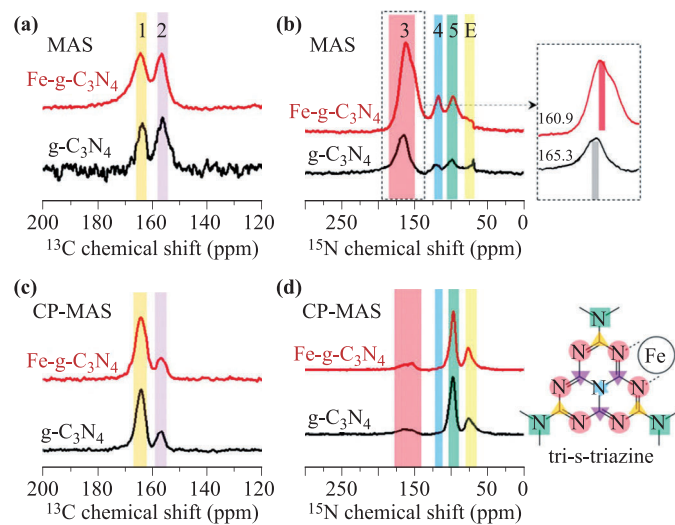


Fig. 10 Solid-state ^{13}C (a) and ^{15}N (b) magic angle spinning NMR spectra of $\text{g-C}_3\text{N}_4$ and $\text{Fe-g-C}_3\text{N}_4$. Cross-polarization magic angle spinning (CP-MAS) setup in (c) ^{13}C and (d) ^{15}N for $\text{g-C}_3\text{N}_4$ and $\text{Fe-g-C}_3\text{N}_4$ [58].

$\text{g-C}_3\text{N}_4$ by XPS and Mn K-edge XANES spectra. Non-metal P atoms doping in $\text{g-C}_3\text{N}_4$ structure for stabilizing isolated metal species is efficient tactic to obtain structurally stable single atoms on $\text{g-C}_3\text{N}_4$. Liu *et al.* [51] reported single $\text{Co}_1\text{-P}_4$ sites on the surface of $\text{g-C}_3\text{N}_4$ by a facile phosphidation method. XPS spectra proved that P atoms substituted C atoms of $\text{g-C}_3\text{N}_4$ to form stable P–N bonds. XANES spectra suggested Co atom were co-

ordinated with four P atoms. The obtained $\text{Co}_1\text{-P}_4$ sites greatly suppressed the recombination of photogenerated charge carriers in $\text{g-C}_3\text{N}_4$, and improved the H_2O adsorption and activation. As a result, the $\text{g-C}_3\text{N}_4$ with $\text{Co}_1\text{-P}_4$ active sites exhibited high activity in photocatalytic overall water splitting.

The single-atom metal coordinated with the N atoms in the $\text{g-C}_3\text{N}_4$ can greatly influence the intrinsic band structure of $\text{g-C}_3\text{N}_4$, and bring change of physicochemical property [9, 62, 74, 75]. Li *et al.* [63] reported single-atom Pt modified $\text{g-C}_3\text{N}_4$ for photocatalytic H_2 generation. The introduction of Pt can realize metal-to-ligand charge transfer (MLCT) between Pt and $\text{g-C}_3\text{N}_4$. As shown in Fig. 11(a), a new hybrid HOMO can be obtained after single-atom Pt modification. The MLCT process can absorb photons with energy greater than 1.8 eV [Fig. 11(b)]. Figure 11(c) exhibits the photoexcited charge density transition from Pt-induced hybrid HOMO to the LUMO of Pt modified $\text{g-C}_3\text{N}_4$. The new MLCT broadens the light absorption of $\text{g-C}_3\text{N}_4$, and then improves the visible-near-infrared photocatalytic H_2 generation activity.

The single-atom modification on $\text{g-C}_3\text{N}_4$ can greatly improve the separation efficiency of photogenerated charge carriers, which is beneficial for the photocatalytic reactions [9, 51, 76, 77]. Cao *et al.* [78] found that the single-atom Pd cannot only act as active sites for photocatalytic H_2 generation, but also directional charge transfer channels for photogenerated charge carriers in $\text{g-C}_3\text{N}_4$. As shown in Fig. 12(a), the single-atom Pd intercalated

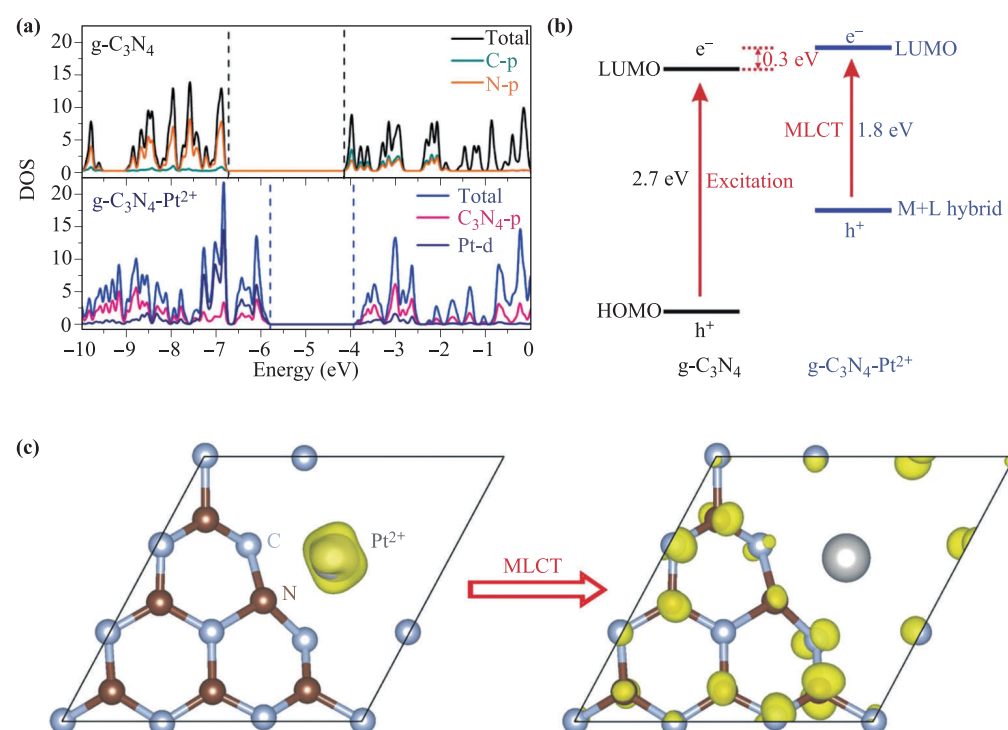


Fig. 11 DOS (a) and band alignment (b) of $\text{g-C}_3\text{N}_4$ and Pt^{2+} modified $\text{g-C}_3\text{N}_4$. (c) Photoexcited MLCT process from the Pt^{2+} -induced hybrid HOMO states to the LUMO of $\text{g-C}_3\text{N}_4\text{-Pt}^{2+}$. The yellow bubble represents electron population [63].

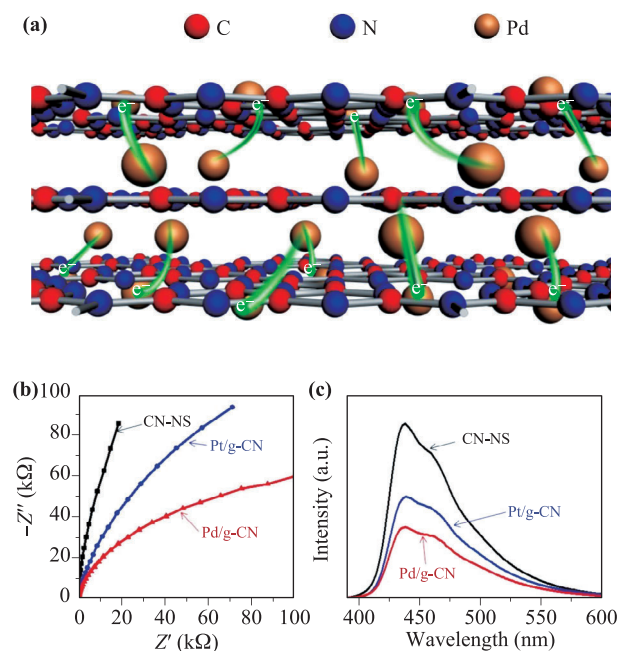


Fig. 12 (a) Schematic diagram of Pd atoms intercalated and surface anchored on Pd/g-CN hybrid. (b) Electrochemical impedance spectra (EIS) Nyquist plots of g-C₃N₄ nanosheets (CN-NS), Pd/g-CN and Pt/g-CN hybrid electrodes. (c) Steady-state photoluminescence (PL) spectra of CN-NS, Pd/g-CN and Pt/g-CN hybrids [78].

between layers as a bridge for electron transport, providing a new charge transfer channel. Figures 12(b) and (c) exhibit that the transfer efficiency of photogenerated charge carriers greatly improved. As a result, better photocatalytic H₂ generation activity can be obtained after single-atom Pd anchored on g-C₃N₄.

The strong interaction between single-atom metals and g-C₃N₄ not only affects the intrinsic property of g-C₃N₄, but also changes the electronic structure of the single-atom

metal itself, thus affecting the intrinsic catalytic activity of the metal active site. Cao *et al.* [79] reported single-atom Pt anchored on g-C₃N₄ with stable Pt₁-N₄ moiety for photocatalytic H₂ generation. The strong interaction of Pt atoms with N atoms in g-C₃N₄ changed the distribution of Pt valence electrons, and obtained more unoccupied 5d orbitals of Pt atoms. The more unoccupied 5d orbitals of Pt can result in the shift of d-band center, and then optimize the binding energy of H and lowers absorption free energy (ΔG_{H^*}), which is associated with H₂-evolution activity. Compared with Pt nanoclusters modified g-C₃N₄, the g-C₃N₄ with Pt₁-N₄ active sites exhibited more efficient photocatalytic H₂ activity due to the optimized electronic structure of single-atom Pt.

The nature of single-atom metal active sites on the surface of g-C₃N₄ has also been explored by theoretical calculations [18, 42, 80–83]. Cao *et al.* [64] studied the energy profile and reaction pathway of photocatalytic H₂ generation on the Co₁-N₄ active sites of g-C₃N₄ by DFT calculation. As shown in Fig. 13(a), the 3H atoms co-adsorption models exhibited 0.11 eV energy barrier and a highly exothermic of 0.82 eV, while 2H atoms co-adsorption models were 0.63 and 0.49 eV, respectively. This result indicated that H₂ generation on 3H atoms co-adsorption models is both kinetically and thermodynamically easier than that on the 2H atoms co-adsorption models. Figure 13(b) exhibited the formation process of H₂ on Co₁-N₄ active sites. Three H atoms adsorb on Co atom and two neighboring N atoms. The H* on N atom can transfer to bond with the adjacent H* on Co atom, and form H–H bond to release H₂ molecule. The photogenerated electron transfer from coordinated N atoms to Co atoms increased the electron density of Co, and reduced the energy barrier of Co–H intermediate, which greatly accelerated H–H coupling to H₂ generation.

In addition to single-atom metals, nonmetal single-atom B anchored on g-C₃N₄ is also one of the potential pho-

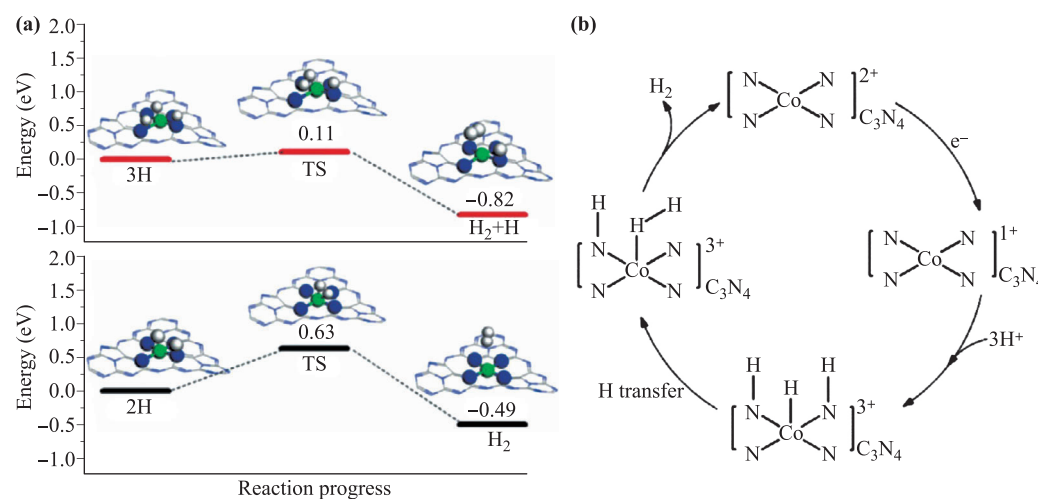


Fig. 13 (a) The calculated reaction barriers of 3H atoms and 2H co-adsorption models. (b) Proposed photocatalytic H₂ evolution process on single-site Co₁-N₄ (N blue, Co green, H white spheres) [64].

photocatalysts [84]. Ling *et al.* [10] investigated single-atom B decorated on g-C₃N₄ for photocatalytic N₂ fixation by first-principles calculations. As shown in Fig. 14(a), transition metals centers (TM Center) can act as active sites for nitrogen fixation is due to the coexistence of empty and occupied d orbitals. The empty d orbitals can accommodate the lone electron pair of N atom in N₂ molecule. The occupied d orbitals can provide electron to the anti-bonding orbital N₂ molecule, thus activating N≡N bonds and enhancing nitrogen fixation performance. Nonmetal B atom with sp³ hybridization [Figs. 14(b) and (c)] contains both empty and occupied orbitals, which is potential in N₂ fixation [Fig. 14(d)]. Theoretical calculation showed that B/g-C₃N₄ can effectively reduce N₂ into NH₃ through the enzymatic mechanism at a very low initial potential (0.20 V). Moreover, single-atom B modification can significantly enhance the visible light absorption of g-C₃N₄, so it is expected to realize the solar-driven nitrogen fixation reaction.

5 Conclusion and perspectives

To date, g-C₃N₄-based single-atom photocatalysts have been widely applied in various photocatalytic applications.

The advanced preparation method and characterizations are the key to develop efficient single-atom photocatalyst. Low metal precursor loading, abundant anchor sites and strong interaction between the g-C₃N₄ supports and single atoms are necessary conditions for obtaining stable single-atom g-C₃N₄ photocatalysts. The identification and action of active sites in photocatalysts are the decisive step in understanding the photocatalytic mechanism. In this review, the main preparation method and characterizations are summarized, providing some general guidelines for further development and characterization of single-atom photocatalysts. The main roles of single atoms in photocatalytic reactions, including the interactions with g-C₃N₄ supports, are also reviewed in detail. The intrinsic band structure of g-C₃N₄ support can be tuned by single-atom loading, improving the light efficiency and separation efficiency of photogenerated charge carriers. The strong interaction between single-atom metals and g-C₃N₄ support can greatly improve the intrinsic catalytic activity of the metal active sites. Although many single-atom g-C₃N₄ photocatalysts have been reported and characterized, the mechanism of high catalytic activity is still in their infancy. There are still plenty of challenges to be resolved in this area. Some typical issues are listed below:

- (1) The anchoring process of single atom on g-C₃N₄

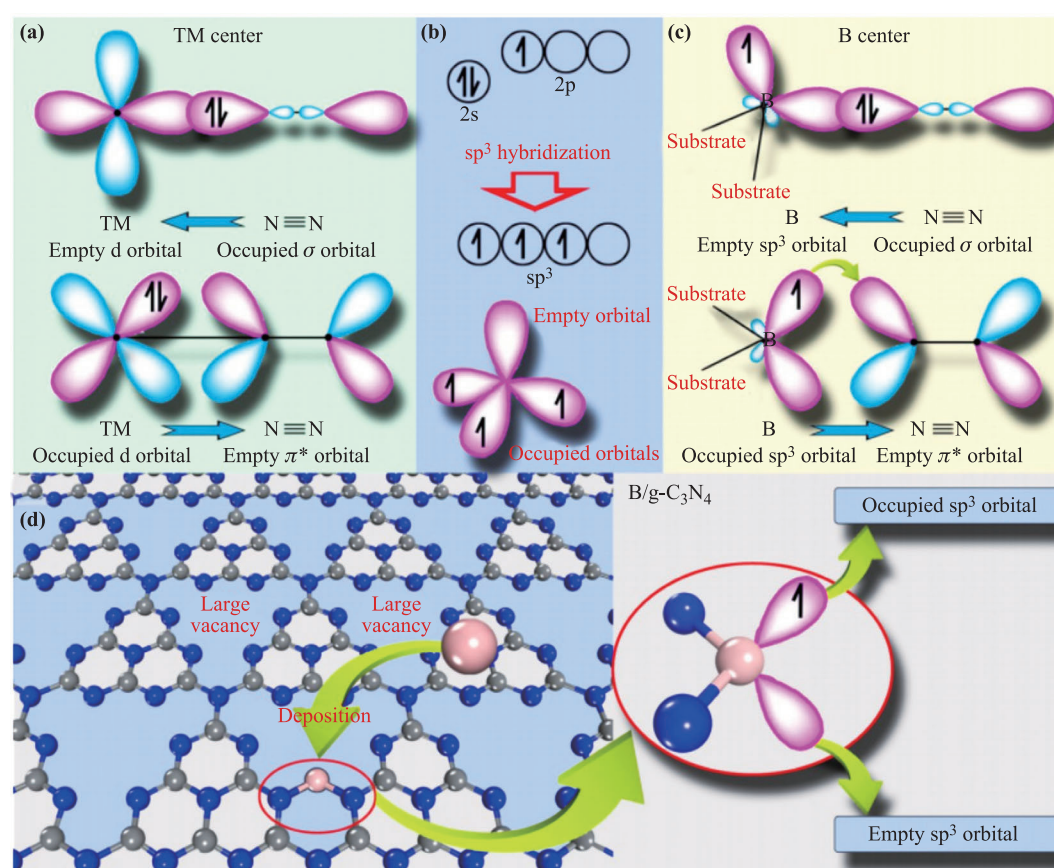
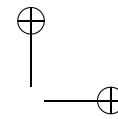
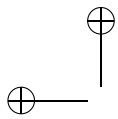


Fig. 14 (a) N₂ bonding to transition metals. (b) Electronic configuration of pure B atom and B atom with sp³ hybridization. (c) N₂ binding to B atoms. (d) Schematic diagram of single-atom on g-C₃N₄ for photocatalytic N₂ fixation [10].



support should be thoroughly analysed. Characterizations have proved that various preparation methods are able to obtain single atoms on g-C₃N₄. However, simple and efficient strategy to prepare high-loading single atoms on g-C₃N₄ is still lacking. Understanding the whole anchoring process is using for developing and optimising the preparation methods of single atom on g-C₃N₄ support.

(2) Actual active sites of single-atom g-C₃N₄-based photocatalysts should be identify. The g-C₃N₄ support is a star photocatalyst. Many studies have shown that the two-coordinated N atoms is the main active sites for photocatalytic reactions. Single-atom metals are generally anchored by N atoms in g-C₃N₄ supports, and M-N_x (M = single-atom metals) moiety can be formed. They are the actual active sites during photocatalytic reactions, the M-N_x, or surrounding N atoms or the single metal atom. Generally, during the process of photocatalytic CO₂ reduction, C₂ products need multi-site synergism. Single-atom sites are usually single active site, it is difficult to obtain C₂ product. At present, many reported single-atom photocatalysts can only produce C₁ products in photocatalytic CO₂ reduction, such as CO, CH₄, HCOOH, and CH₃OH. The high activity of single-atom sites is a great advantage of single-atom photocatalysts. However, the single-site is difficult to achieve complex multi-site reactions. Different types of single atoms have characteristic selectivity for different reactions. It is one of the potential strategies to implement complex multi-site tandem reactions by loading two or more different kinds of single-atom sites.

(3) The interactions between single-atom metals and g-C₃N₄ support should be highlighted, which is an important indicator for stable single-atom metal on support. More importantly, the strong interactions can well regulate the electronic structure of the metal, affecting the d-band centre through electron transfer between the metal and support. The shift of d-band centre further adjusts the adsorption properties of reactants and intermediates, and finally affect the catalytic activity of metal active sites [85].

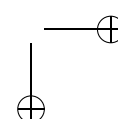
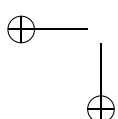
(4) More advanced in-situ characterization techniques should be developed to better study and understand the photocatalytic mechanisms. For example, in-site STM can directly observe the morphology and structure changes of photocatalysts during the reactions; in-site XAFS can study the real-time chemical environment change around the particularly interested atoms; in-site FTIR spectra can investigate the conversion of different intermediate products in catalytic process.

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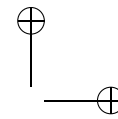
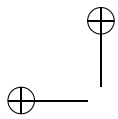
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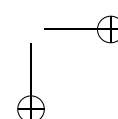
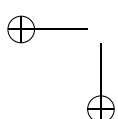




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