

The Quest for Sustainable Catalysis through Transition Metal Doped Carbon-based Single-Atom Catalysts

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ABSTRACT

Single-atom catalysts have recently received much scientific attraction as sustainable catalysts due to their greater activity and selectivity arising from the uniform distribution, electronic properties, and quantum mechanical interactions at the nanoscale of single atoms coupled with interactions at the metal-support interfaces. Carbon-based materials are an excellent support material for single-atom catalysts owing to their inherent properties such as adjustable pore size, high surface area to volume ratio, and ease of surface functionalization. The interactions at the single atom-carbon support interfaces give rise to the extraordinary catalytic activity in carbon-based single metal catalysts thus opening doors for a wide range of sustainable applications. This review focuses on the evolution of carbon-based single-atom catalysis covering different types of carbon substrates, usage of different single atoms with special attention to transition metals, and its wide range of applications including photocatalysis, organic catalysis, and electrocatalysis followed by the future perspectives on carbon-based single-atom catalysts.

Keywords: Single-atom catalyst; Carbon-based single-atom catalysts; Transition metals; Graphene; Fullerene; Sustainable catalysis

1. Introduction

Energy has been a key factor governing all the industrial processes since the inception of the industrial revolution in the 18th century and up until today and beyond. As the energy demand continues to grow, the world is facing a major crisis to meet the requirements while maintaining sustainability. Achieving “affordable and clean energy” is also one of the goals of United Nations 2030 Sustainable Development which further emphasizes the need for moving towards sustainable energy/power pathways. Catalysis is an excellent way to reduce the energy consumption of industrial chemical processes making them much greener and more economical. In simple words, catalysts lower the activation energy

required for a chemical reaction to occur without being used during the reaction. Over the centuries catalysts have enabled the carrying out of chemical reactions at lower temperatures and pressures leading to energy-efficient and commercially viable industrial-scale production processes.

Catalysts could be divided mainly into two classes namely, homogeneous catalysts and heterogeneous catalysts. Of these two types, heterogeneous catalysts were found to be more efficient due to the synergistic effects that give rise to extraordinary properties at different interfaces present within the catalyst. One type of heterogeneous catalysts, Single-atom catalysts (SAC), consists of an isolated single atom on active sites of catalysts while minimizing the usage of precious metal with 100% atom-utilization efficiency [1]. Owing to this unique characteristic feature, SAC has resulted in

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improved catalytic reactivity with greater scientific attention in the field of catalysis. More importantly, the distinct micro atomic environment of SAC is responsible for the greater atomic efficiency, selectivity and stability for heterogeneous catalysis.

In the recent past, Zhang and co-workers have synthesized single atoms of platinum immobilized on iron oxide (Pt1/FeOx) for the first time. More interestingly, this Pt1/FeOx has shown a high catalytic activity for the oxidation of CO. When investigating the mechanism behind this increased catalytic activity, they found that an electron has transferred from the Pt atom to FeOx and it has led to modifications in the electronic structure with successive stabilization of the Pt atom in SAC. From there onwards, scientists have investigated different types of substrates such as alumina [2], zeolite [3], carbon [4], [5] and iron [6]. Among those substrates carbon-based SAC has grabbed a greater scientific interest due to sustainability, cost-effective precursors and ease of synthesis [7].

In recent years, utilization of carbon-based substrates in SAC has also found significant applications in most catalytic reactions by providing anchoring sites for the single metal atoms. In carbon-based SAC, strong interfacial interactions between metal atoms and nearby carbon atoms are also used to manipulate the charge density and electronic structure of single metal atoms [8]. Moreover, this carbon-based SAC consists of a higher electrical conductance due to the graphitic skeletons as well. The escalating catalytic performance due to the development of a great number of active sites is compensated for by these specific distinguishing features[9].

Although there is a variety of SAC, carbon-based SAC gives exceptional and extraordinary performance among different catalytic systems, and it has been reported in previous studies as well. Carbon-based SAC is composed of carbon, nitrogen, and oxygen, which are abundant elements in nature. In this regard, these SAC can be prepared straightforwardly with easy synthetic routes and inexpensive precursors. Therefore, carbon-based SAC is environmentally friendly and sustainable catalysts. Moreover, SAC supported on carbon-based materials has the advantage of contrast in characterization techniques such as Transmission Electron Microscopy, which is well-sufficient for proving their morphological nature in SAC. Among all the reported SAC, carbon-based SAC paves the way for the most promising and sustainable advanced catalysts employed for a wide range of catalytic applications.

In this review, we have narrated the different types of carbon substrates and their unique characteristic

properties to be used in SAC, synthetic routes, potential applications of carbon-based SAC in photocatalysis, electrocatalysis, and organic catalysis, and finally, a future perspective of SAC.

2. Different carbon substrates that are being used and their unique characteristic features to be used in SAC

Graphene is a two-dimensional carbon allotrope that possesses extraordinary physical and chemical properties while having the potential platform for constructing SAC [10],[11]. When atomically dispersed transition metal atoms are strongly anchored on the graphene surface resulting in a high surface area and excellent electronic properties, this is beneficial in catalysis [12]. Transition metal atoms can attach to graphene in three different ways (sites): top sites, where a metal atom is directly above a carbon atom, hollow sites, where the metal atom is directly above the hexagonal ring (center of the ring), and bridge sites. Metal atoms coordinate to the carbon-carbon link at these hollow places. (See **Fig. 1**). Depending on the oxidation state and electronic configuration of the transition metal atom, different binding sites are preferred by different transition metal atoms. Although the majority of transition metal atoms prefer to coordinate at hollow sites, platinum and palladium bind at graphene's C- C bridging sites. The atoms of copper (Cu), silver (Ag), and gold (Au) have a tendency to cluster towards the top [13]. Single adatoms titanium (Ti), iron (Fe), palladium (Pd), and gold (Au) were discovered on pristine graphene by Chan et al [14]. Covalent metal support interaction, which is characterized by orbital overlaps between the d orbitals of single atoms and the p orbitals of carbon atoms, is compatible with transition metals such as Pd, Ti, Fe, and Au, as well as carbon atoms in graphene. Ionic interactions on the graphene layer's lattice are thought to be minimal. However, covalent interactions cause the graphene layer to have substantial in-plane lattice distortions [15]. Further, transition metal single atoms on graphene support, are bound weakly due to the lack of possible valence sites at the anchoring sites of graphene [10].

Defective graphene with a single vacancy (SV) or double vacancy (DV) can improve the stability of a transition metal single atom [10]. These vacancies can be created by removing one or two carbon atoms from pristine graphene that is valence balanced. When considering SV, it undergoes a JahnTeller distortion which leads to the saturation of two of the three dangling bonds toward the missing atom. One dangling bond always remains owing to geometrical reasons [17]. This leads to the formation of a five-membered and a nine-

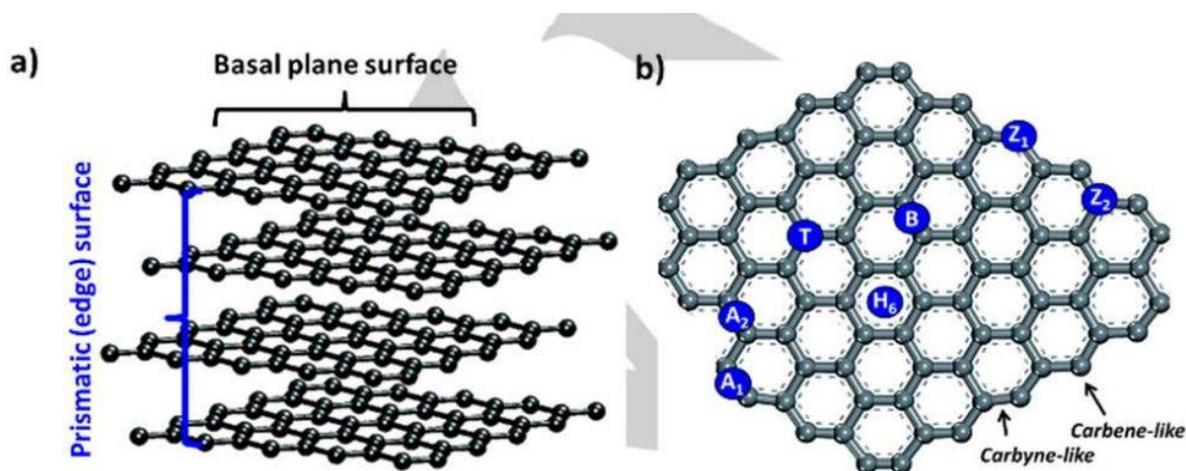


Fig. 1- a) basal plane and prismatic surfaces on sp^2 carbon materials; and b) adsorption sites on sp^2 carbon materials: hollow H₆, bridge B, top T, A₁ and A₂ high symmetry armchair sites, and Z₁ and Z₂ high symmetry zigzag sites. Adapted with permission from ref. [16]. Copyright 2018 John Wiley and Sons

membered ring. DV can be created either by the coalescence of two SVs or by removing two neighboring atoms. More specifically, there is no dangling bond present in a fully reconstructed DV so that two pentagons and one octagon appear instead of four hexagons in perfect graphene. The atomic network remains coherent with minor perturbations in the bond lengths around the defect [18]. At the defect site, the remaining free valence of carbon atoms will boost the stability. Transition metal single atoms in SV-graphene can be seen to make three covalent connections with surrounding carbon atoms. Single transition metal atoms are frequently found above the graphene surface, however the distance between the graphene surface and the transition metal atoms is shorter on DV-graphene than on SV-graphene. (**Fig. 2**) Early transition metals have poorer binding to DV-graphene than SV-graphene, but late transition metals with larger atomic sizes, such as Cu, Zn, Pt, Ag, and Au, have stronger binding [19]. Furthermore, from pure graphene to defective graphene, metal atom migration barriers increase. As a result, structural flaws in graphene play a key role in inhibiting metal adatom diffusion and migration, which is crucial for creating metal graphene materials for catalysis.

Nonmetal-doped pristine graphene, nonmetal-doped defective graphene, and graphene oxide are the three types of graphene decoration variants (GO) [10]. The nonmetal dopants boron and nitrogen are the most sought after in graphene [20]. Furthermore, pure graphene doped with nonmetal components including phosphorus, oxygen, and sulfur has been shown to improve SAC stability [21]. The nonmetal dopants replace the boundary C atoms of the vacancy site in doped defective graphene [22]. Graphene oxide (GO) is

a kind of decorated graphene that has a lamellar structure and a nonstoichiometric material [23]. The physicochemical properties of GO are mostly determined by synthesis processes and post-modifications. Exfoliation of graphite with strong oxidants in acidic circumstances is a common way to make GO [24]. The creation of oxygen-containing functional groups such as alcohols, epoxides, oxo, hydroxides, carbonyls, and carboxylic acids occurs as a result of these highly exothermic processes. Transition metal atoms can use these abundant surface oxygen species of GO as anchoring sites. More crucially, strong ionic and covalent interactions hinder metal atom movement and aggregation [25].

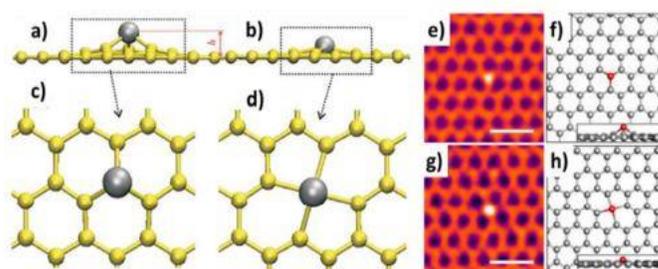


Fig. 2 - Typical atomic configurations of transition metal atoms adsorbed on SV and DV in a graphene sheet. Metal atom on a SV: Side view a), top view b). Note that the metal atom is above the surface, with an elevation h of up to 2 Å. Metal atoms on a DV: Side view c) and top view d). The grey balls are metal atoms, the yellow balls carbon atoms. e) - h) Single Fe atoms in graphene vacancies. (e) Smoothed ACTEM images of single Fe atoms in (a) monovacancy and (g) divacancy sites shown in false color. (f,g) DFT optimized atomic models corresponding to (e,f). Adapted with permission from ref.[16]. Copyright 2018 John Wiley and Sons

Graphyne and graphdiyne are two 2D carbon allotropes of graphene [26]. In graphyne, there are C6 rings and acetylene bridges while graphdiyne consists of C6 rings and butadiyne bridges [27]. Both allotropes have honeycomb structures connected to aromatic C6 rings. These compounds are used in SAC due to the presence of a large number of cavities that can host transition metal single atoms. As an example, transition metals (vanadium, chromium, cobalt, nickel, iron and manganese) have been doped into both graphyne and graphdiyne [28].

Graphitic carbon nitride (g-C₃N₄) is a nitrogen-doped carbon material that can be found in two-dimensional and three-dimensional configurations [29]. Because of the imperfections/defects on the sheets, which assist the trapping of various transition atoms in a well-defined environment, two-dimensional porous carbon nitride sheets have attracted greater scientific attention in SAC. Sp² hybridization occurs in both carbon and nitrogen atoms. The nitrogen atoms coupled to two carbon atoms are the most reactive atoms in this g-C₃N₄. Because the N6 or N9 cavities are larger, the transition metal bonds strongly to the nitrogen atoms nearest to it, while the remaining nitrogen atoms are positioned at a great distance from it [30]. The charges on the carbon substrate-bound metal atoms have been used to demonstrate charge transfer from transition metal d-states to the p* states of the g-C₃N₄. The occupied anti-bonding states are observed to be stabilized while changing to lower energies as a result of this charge transfer [31]. This finding explains why SAC behaves differently in transition metal nanoparticles where charge transfer happens from the carbon support to the metal [32].

Fullerenes are a type of carbon allotrope that can combine the characteristics of a homogeneous catalyst with those of carbon-based materials [5, 33]. Finally, it was discovered that the chemical characteristics of transition metals had synergistic effects on chemical transformations. Without disrupting the cage, transition metal atoms can be confined inside (endohedral metallofullerenes) [34] or bound outside (exohedral metallofullerenes) [35]. (See **Fig. 3**) When a transition metal atom is introduced into a fullerene cage, it immediately influences electrical characteristics by lowering the work function of the material compared to pure C60 [36]. SAC can be made by doping one carbon atom of fullerenes with transition metal atoms [37]. Rivera-Cárcamo et al. identified six distinct coordination modes for fullerenes, which are as follows [16]:

- η^1 hapticity with a possible sigma bond, when the metal atom is immediately bonded above any carbon atom;
- η^2 hapticity; two 6-membered rings (6,6) or one 6-membered ring and one 5-membered ring (6,5), the latter being uncommon;
- η^3 hapticity, the metal is connected to three carbon atoms on either a 6- or 5-membered ring, resulting in hapticity.;
- η^4 hapticity, it has four carbon atoms connected to the metal atom;
- η^5 hapticity, in which the metal is linked directly to a five-membered ring;
- η^6 hapticity, the metal is immediately linked to a six-membered ring in this method.

As an example, Marco-Martínez et al have synthesized metallo-pyrrolidino [60]-fullerenes (metallofulleropyrrolidines) 1Ir, 1Rh, and 1Ru and used hydrogen transfer reactions to evaluate their catalytic effect [38]. Further, researchers have used density functional theory calculations to study the adsorption of transition metals on C60 fullerene [39]. It has been revealed that scandium, titanium, cobalt, nickel, copper and zinc lead to a more stable structure with η^2 (6, 6) hapticity while η^6 hapticity was preferred for vanadium, chromium, manganese, and iron. The stronger adsorption energy was found for nickel (5.11 eV), followed by Co (3.40 eV), Cr (3.15 eV). For the other elements, the order is: titanium (3.12 eV) > vanadium (2.61 eV) > copper (2.52 eV) > manganese (2.34 eV) > scandium (2.15 eV) > iron (1.58 eV) > zinc (- 1.53 eV). In these structures, the positive charges on the transition metal atoms and the negative charges on the C atoms engaged in the transition metal-C bond ensure charge transfer from the transition metal to the C60 fullerene [16].

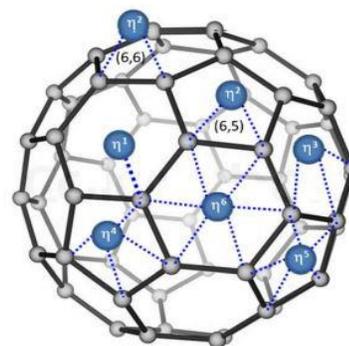


Fig. 3 - Most common adsorption sites on C60 fullerenes. Adapted with permission from ref.[16]. Copyright 2018 John Wiley and Sons

On the other hand, carbon quantum dots (CQD) have also been demonstrated to be an effective support for SAC due to their small size and numerous surface anchoring sites[40]. Conjugated microporous polymers (CMPs) are also used as carbon support in SAC since these polymers have predictable structures and functions for use in a broad range of contemporary catalytic applications. As an example, Fan and co-workers have synthesized cobalt-doped SAC with conjugated microporous polymers as an electrocatalytic sulfur host for enhancing cathode reaction kinetics[41]. Moreover, covalent triazine frameworks (CTFs) and CTFs hybridized with carbon nanoparticles have been used to load SAC [42].

3. Synthesis routes of transition metal doped carbon-based SAC

SAC should have certain spots on the catalytic surface that aid in the trapping of metallic atoms on the surface. The existence of defects in the catalytic surface, such as vacancies, increases the adsorption energy of metal adatoms substantially [43]. Because of the low manufacturing efficiency, high tech being involved, and particle generation, the creation of imperfections/defects is a vital phase and a more significant problem[7]. SAC can be made through physical or chemical processes, with isolated atoms anchoring around probable fault locations [44]. Several synthetic methods for making transition metal doped carbon-based SAC are explored in this section. (**Fig. 4**)

The wet chemistry pathway is one of the most common ways to make SAC. Under wet chemistry routes there are different kinds of pathways to synthesize transition metal doped carbon-based SAC. In the facile adsorption method, the singly dispersed active component is anchored onto the catalyst support *via* a simple adsorption mode [46]. This simple adsorption method makes use of interactions between the support and the active metal element to synthesize SAC. It is simple to use and could be completed in a typical chemistry lab. However, because metals are typically randomly absorbed on the surface of supports, the active metal component must interact properly with the catalyst support to correctly synthesis SAC. The dispersion state of the active metal components could also not be adequately regulated due to the heterogeneity of the support [46]. The strong electrostatic adsorption method is also significant among wet chemistry-based synthetic routes. Oxide materials frequently have a coating of hydroxyl groups on their surface. The point of zero charge is the pH at which the aqueous solution is neutral (pH_{PZC}). When the pH of an aqueous solution is below its isoelectric point, the oxides are positively charged,

and when the pH is above its isoelectric point, they are negatively charged. A monolayer of O, OH, or OH_2^+ could be created on the surface of oxides by altering pH levels. They can use a strong electrostatic contact to bind different metal ion complexes. One of the common preparation techniques for conventional heterogeneous catalysts is the wetness impregnation approach. In this method, the catalyst is impregnated with an aqueous or organic metal salt solution, and the metal salt then adheres to the support surface. To acquire the salt-impregnated catalyst, the remaining solvent is typically removed by evaporation. The ability of the support surface to adsorb organometallic complexes or inorganic salts is crucial to the impregnation process. As a result, the metal salt-support interaction is crucial and has a big impact on how much metal is loaded and how evenly it disperses on the support surface [46]. An overview of wet chemistry methods in synthesizing SAC is included in **Fig. 5**.

Vile and colleagues synthesized palladium (Pd)-SAC supported on mesoporous graphitic carbon nitride (C_3N_4) [48]. It was made by combining $PdCl_2$ and NaCl in a C_3N_4 dispersion, stirring and sonicating it, and then reducing it with $NaBH_4$. In this SAC, the strong coordination between the metal centers and the C_3N_4 N sites is noteworthy. Furthermore, by combining Pd SAC with K_2PdCl_4 , Xi et al have reported the production of Pd SAC supported on reduced graphene oxide/amorphous carbon [49]. Furthermore, strong non-covalent – stacking interactions between the pyrene moiety in the ligand and CNT [50] can graft nickel or cobalt complexes onto CNT surfaces, whereas Kim and co-workers have observed attaching platinum (Pt) single atoms onto thiolated CNT via covalent Pt-S bonds[51]. The key benefit of this wet synthesis process is that it makes it easier to construct a host-guest structure by encouraging covalent bonding and – stacking or electrostatic interactions between guest molecules and carbon-based host materials [52, 53].

Ball milling is one of the most sought after mechanochemical grinding methods which can be used to synthesize SAC [54]. As an example, Cheng et al have synthesized FeN_4 moieties in graphene matrices at high Iron (Fe) loadings (up to 4.0 wt%) by using ball milling [55]. Further, they have expanded their study to other transition metals such as manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), and copper (Cu) by simply using the corresponding metal phthalocyanine as the precursor in ball milling [56].

The Graphene Vacancy-Directed method is also used in the synthesis of SAC. In this synthetic route, the creation of graphene vacancies will be done through high-energy

atom/ion irradiation [57]. Moreover, the number of vacancies will be controlled by the energy density. After that, the graphene vacancies will be filled with selected transition metal atoms, such as Au, Pt, Fe, and Co by well-controlled sputtering or focused ion beams

[58][59][60]. The SAC obtained through this synthetic route has a well-defined and custom-tailored structure [61]. The sophisticated instrumentation, high-tech involvement, low yield and therefore scaling up are really difficult from a practical perspective [62].

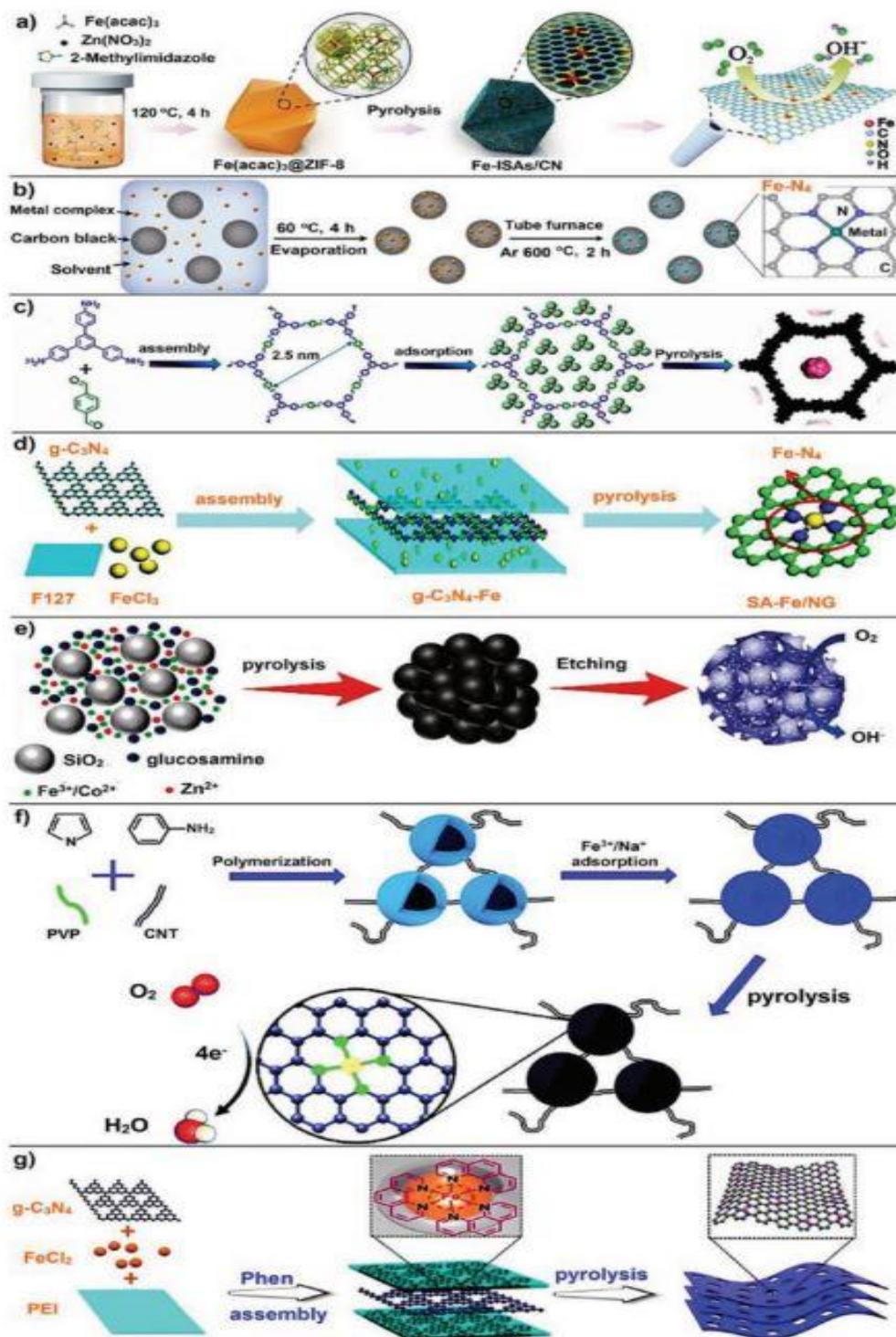


Fig. 4 - Various methods of preparation of SACs. a) Zeolitic imidazolate framework-based synthesis. b) Ligand mediated method for large scale synthesis. c) COF initiated the synthesis of SA catalyst. d) Using C_3N_4 as support. e) Using SiO_2 as a hard template. f) Polymerization process for SACs preparation on hollow carbon. g) Using C_3N_4 as support and PEI as N source. Adapted with permission from ref.[45] Copyright 2021 John Wiley and Sons

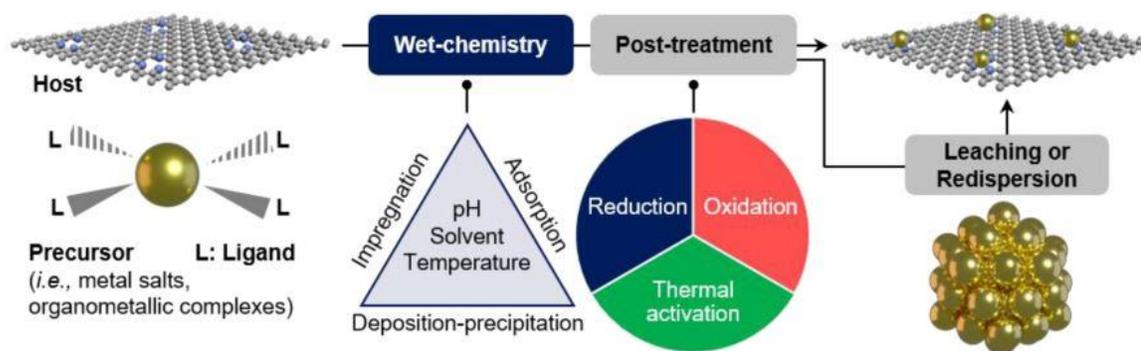


Fig. 5 - Overview of wet-chemistry approaches to synthesize SAC. Adapted with permission from ref. [47]. Copyright 2020 American Chemical Society

MOFs (metallic organic frameworks) or ZIFs (zeolitic imidazolate frameworks) have been attracting extensive scientific interest because of the well-defined tunable porous structure and highly ordered arrangement of organic linkers and metal nodes [63]. The significance of using these MOFs and ZIFs in the synthesis of SAC is that it avoids metal atom aggregation by forming nanoparticles during high-temperature pyrolysis [64][65]. Further, various transition metals can be easily and uniformly introduced in the metal nodes, ligands, or pores of the respective precursors of MOFs/ZIFs [66]. Furthermore, large amounts of nitrogen-containing ligands in precursors provide an added advantage by providing a strong stabilization of SAC.

The single sites in SAC may include one or more atoms, but they are all structurally distinct, spatially separated, and interact with reactants at the same energetic level as every other single site, just like the single sites in homogeneous molecular catalysts. As single-site catalysts are always well-defined structurally and are made up of one or more identically acting atoms (each site interacts with the reactant with the same energy as any other single site)[67]. Metal Organic Frameworks (MOFs) are crystalline porous materials made up of a multidentate organic molecule-supported three-dimensional (3D) network of metal ions [68].

There are three ways to achieve the metal stabilizing effect in MOFs: Functional organic linkers provide abundant coordination sites for the decoration of desired metal atoms, coordinately unsaturated metal clusters offer coordination sites that can be supplied by other metal atoms, and pore space is home to a variety of guest species that can incorporate metal atoms, including carbon-based materials, inorganic oxides, metal complexes, and polyoxometalates (POMs). MOFs are the perfect substrate for the creation of SAC because of the significant functionalization potential in organic linkers, metal nodes, and pore spaces [67].

Organic linkers in Co-containing MOFs, for example, can be transformed into N-doped porous carbon during the pyrolysis process, according to Yin and coworkers [70].(Fig. 6 (a)) Cobalt was reduced by carbon, and aggregation ensued, resulting in a hybrid made up of Co nanoparticles embedded in N-doped carbon [70]. (Fig. 6 (b)) Furthermore, Zn/Co bimetallic MOFs with a uniform distribution of Zn and Co have been produced. Under a nitrogen environment, Zn atoms can be evaporated during pyrolysis at 800 °C. During pyrolysis, the departing Zn^{2+} provides free N sites, which aid in the stability of Co single atoms. Wu and colleagues have also discovered a similar approach for producing Co-graphitic carbon nitride SAC by immersing CoN_4 in a graphitic carbon matrix. By trapping Ni^{2+} and Fe^{3+} within the ZIF-8 pores, Ni and Fe doped SAC has been created [71]. $FeCl_3$ can still be contained in the cavities when ZIF-8 is substituted with Co-containing bimetallic MOFs, resulting in (Co,Fe)-NC SAC [72]. The pyrolysis of MOF/ZIF has been used as a generic technique for the synthesis of SAC in a carbon matrix, as evidenced by these instances.

A template can be used to modulate the textural features of catalysts. The template-sacrificial strategy involves the insertion of a textural agent or "template" that provides more surface and porosity, which is then removed using acids or bases in an etching process [73]. Some of the template materials employed in the synthesis of f Co1@N-C and Fe1@N-C SAC include 60 SiO_2 particles, ordered mesoporous silica, and montmorillonite clay. Vitamin B12 (VB12) and polyaniline-Fe (PANI-Fe) were chosen as cobalt and iron precursors, respectively, in this SAC synthesis [74]. Because of the high nitrogen/carbon atomic ratios of the aforementioned precursors, N doped carbon compounds with high nitrogen content can be produced. Furthermore, oleic acid ligands stabilized iron oxide nanocubes that self-assembled in cubic superlattices and were employed as sacrificial templates. The

superlattices were created using a drying-mediated assembly of Fe_3O_4 nanocubes, and N-doping was achieved via a 900 °C heat treatment with ammonia.

Other strategies for the synthesis of SAC include atomic layer deposition (ALD) and chemical vapor deposition (CVD) [75]. ALD is a gas-phase deposition technology that allows the user to control the number of materials deposited, from nanoparticles to nanoclusters to single atoms. Sun and Botton, for example, used the ALD cycle numbers to manufacture Pt-SAC supported on graphene using (methylcyclopentadienyl)-trimethylplatinum as the Pt supply [76].

This method, in particular, has allowed the number of ALD cycles in this synthesis to be controlled, and it is

the fundamental element driving this synthesis. Yan and colleagues also created Pd SAC on graphene by anchoring palladium hexafluoroacetylacetylate ($\text{Pd}(\text{hfac})_2$) onto the oxygen functional groups of the material. At the end of the process, ALD conditions were used to remove the hfac ligands. Huang et al. also controlled the exposure period of the $\text{Pd}(\text{hfac})_2$ precursors to create various Pd- C_3N_4 composites, including Pd-SAC supported on C_3N_4 [77]. (Fig. 7) It is worth noting that the SAC produced via ALD synthesis is often irregular in size and shape, making it difficult to examine and comprehend the relationship between material structures and catalytic performance.

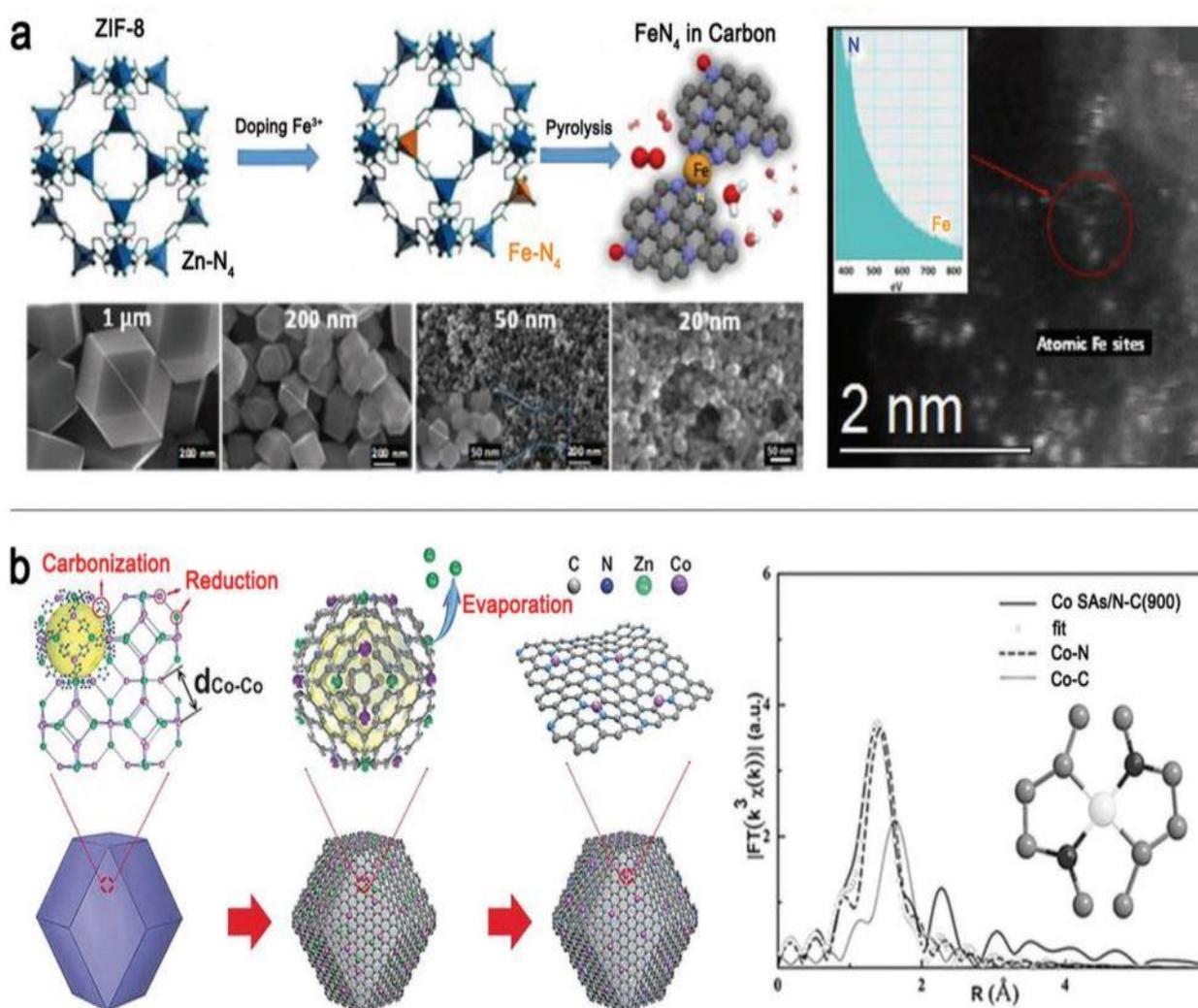


Fig. 6. Construction of MOF-derived SACs by the mixed-metal strategy. a) Synthesis illustration of the Fe single-atom catalysts derived from different sizes of Fe-doped ZIFs and the inset shows the EELS results. b) The synthesis process and calculated structure of Co SAs/N-C fabricated by the carbonization of Co-doped ZIF-8. Adapted with permission from ref. [69]. Copyright 2021 John Wiley and Sons

pyrolysis by allowing the synthesis of Fe-N-C hybrid structures. Furthermore, by pyrolysis of dual nitrogen-precursors of polyaniline (PANI) and cyanamide, Zelenay and co-workers have produced SAC with FeN₄ complex embedded in a graphitic carbon matrix [85].

Photoreduction is also one of the methods to prepare transition metal doped SAC by reducing the metal salts into their metallic states with light as the driving force[11]. Furthermore, the process called galvanic replacement makes use of the variations in reduction potential between metal in a template and metal ions in a solution[62]. The metal atoms in the template would be oxidized and dissolved into the solution, while the metal ions in the solution would be reduced and plated on the surface of the metal template if the potential differences were right. This would result in the spontaneous occurrence of the galvanic replacement reactions. Cyclic voltammetry (CV) method is also an approach to synthesizing SAC in an electrochemical working station equipped with a counter electrode (CE), reference electrode (RE) and a working electrode (WE)[86]. A technique for carefully introducing a foreign precursor from an aqueous solution onto the support is the ion exchange method. All procedures in which ionic species from aqueous solutions exchange with the charged sites on the support are referred to as ion exchanges[87]. This method has just recently been employed for the synthesis of SAC, but it has been widely used for the creation of catalysts with readily exchangeable ions on supports, such as those found in zeolites, heteropoly acids, or MOFs.

The one-pot synthesis method is a strategy to improve the efficiency of the synthesis approach whereby the catalyst precursors are subjected to successive chemical reactions within one single reactor[88]. The one-pot wet chemistry method is more favorable for large-scale production because it fails to call for specialized experimental equipment or multistep reaction conditions. Additionally, with this method, significant loading densities of separated metals are possible. Due to potential solubility restrictions of the numerous precursors in the necessary reaction solvents as well as the influence of impurities and by-products formed in each step, the one-pot synthesis approach is currently difficult to use for the synthesis of SAC. The standard supported metal catalysts are typically submerged in a dilute aqueous NaCN solution before being rinsed at room temperature with a high pH NaOH solution in the presence of O₂. The metal cations are not damaged during this process; only the metal nanoparticles are eluted. Due to the potential for environmental degradation during the catalyst production process, the metal leaching method is only suited for a limited

number of specific metals and supports and is not practical for the large-scale preparation of SAC in the near future[89]. Flame spray pyrolysis is an efficient technique for synthesizing metal catalysts with uniform size and has significant advantages in the preparation of supported metal catalysts[90]. The flame spray pyrolysis process can produce supported metal catalysts with some advantages[90]. It could atomically combine every precursor. The catalysts' form and size can be successfully adjusted by altering the synthesis conditions. Large-scale, very effective production of the catalysts might be accomplished in a single step. However, there are few instances of high-temperature catalytic applications for the synthesis of SAC by flame spray pyrolysis, thus it is impossible to tell from the literature currently in existence whether this approach is actually a viable one for high-temperature SAC.

4. Structural characterization of SAC

Single transition metal atoms are dispersed on carbon support in transition metal-doped SAC. Another significant obstacle to the advancement of SAC is the characterization of useful single-atom species. Subangstrom-resolution aberration-corrected scanning transmission electron microscopy (AC-STEM), one of the most recent developments in atomic resolution characterization techniques, can precisely locate the individual metal atoms in such SAC, providing immediate local structural information about the metal species on supports. In addition, more thorough characterizations of the structures of SAC are starting to become a possible perfect combination of cutting-edge experimental techniques like X-ray absorption spectroscopy with sophisticated modeling and simulation techniques in computational chemistry. For instance, by combining a number of spectral tests and density functional theory (DFT) modeling, it is possible to determine the precise surface structure of SAC. In this regard, the physico-chemical/structural characterizations of transition metal doped SAC should preferably be combined with computational modeling studies[91]. When it comes to modeling studies, reducing the number of transition metal atoms is recommended because it takes less time and is simpler than using metallic nanoparticles.

On the other hand, developing SAC requires experimental evidence/confirmation of solely isolated single transition metal atoms on corresponding carbon supports, as well as the characterization of their chemical environment and spatial distribution of single metal atoms. Directly visualizing the SAC immobilized on supports is the simplest and most basic technique for this. Scanning tunneling electron microscopy (STEM)

and aberration-corrected high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) in combination with single-atom X-ray spectroscopy (atomic-resolution energy dispersive X-Ray spectroscopy (EDX) mapping) provide a direct and simple method for locating isolated transition metal atoms in SAC. Furthermore, HR-TEM images and XPS surface characterization techniques help to investigate SAC structural features before and after transition metal doping. Probe molecule infrared (IR) spectroscopy is also a potent site-specific characterization approach for supported metals [92]. It can reveal information about the local structure, oxidation state, and coordination environment. Because adsorbed molecules establish bonds, their adsorption sites on supported metals become sensitive to local geometric and electrical environments. Probing molecules can be used to adsorb onto various types of supported metal sites, causing changes in the vibrational frequency and bandwidth of the adsorbed molecules' IR spectra.

Synchrotron radiation has become a helpful technique in the research of deposited, size-selected clusters and even single atoms due to the high flux of X-rays available and the variety of beam lines. Furthermore, synchrotron radiation allows for the analysis of bulk materials, as well as the clarification of the overall structure of single metal atoms, rather than only local

and surface information, when used in conjunction with the aforementioned electron microscopy techniques. The absence of metal–metal interactions in synchrotron radiation investigations is a clear indication of the absence of particles in which single supported atoms are oxidized in general, and if metal–metal interactions are not observed after the reduction of samples at high temperatures, rafts can be ruled out. Another significant benefit of synchrotron analysis is its capacity to reveal the chemical makeup and stabilization structure of single atoms on supports.

For oxidative homocoupling of benzylamines, Zboril et al. reported a mixed-valence SAC (**Fig. 8 A**). Cu(II) ions have been coordinated to CN functionalized graphene to produce the mixed-valence SAC [93]. Graphene-induced charge transfer partially reduced Cu(II) ions coupled to CN functionalized graphene to Cu(I). The absence of any inorganic crystalline species, aggregations, or nanoparticles was confirmed by high-resolution TEM images (HR TEM, **Fig. 8 B**). Images before and after the catalytic reaction purporting to show the emergence of single copper metal atoms. Copper metal has long been known to be more effective at oxygen activation. The fabrication and successful application of 2D mixed valence SAC for amine oxidative coupling were examined in this regard.

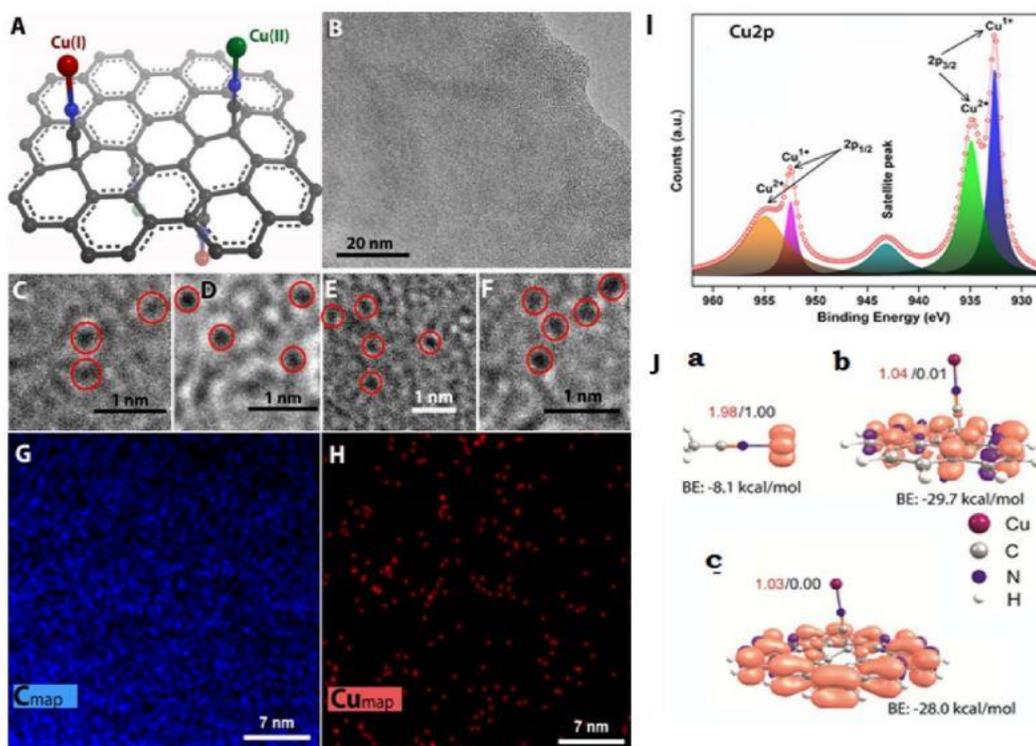


Fig. 8 - (A) Schematic model of G(CN)-Cu catalyst. (B) TEM image. (C,D) HRTEM images before catalytic reaction. (E,F) HRTEM image after the reaction. (G,H) Elemental maps. (I) Cu 2p HR-XPS showing two valence states of Cu. (J) Copper(II) coordination with calculated binding energies. Adapted with permission from ref [4] Copyright 2020 American Chemical Society

5. DFT Calculations on SAC

DFT calculations on SAC are critical for the development of SAC and a better understanding of the catalytic reaction mechanism of each metal atom. Zhang and coworkers, for example, have effectively synthesized single Pt atoms onto iron oxide, which has been employed in CO oxidation. For the oxidation of CO, at least one Pt-Pt bond is required, according to the Langmuir–Hinshelwood scheme. Zhang and colleagues have proposed a chemical mechanism for CO oxidation on Pt1/FeOx based on a modified L–H scheme and DFT simulations in this regard. In the active sites, Pt atoms are coupled with two/three oxygen atoms. They discovered that oxygen in iron oxide is actively involved in CO oxidation, making it easier to oxidize CO adsorbed on Pt atoms. Furthermore, due to the interaction with oxygen atoms of the iron oxide substrate, DFT studies revealed that single Pt atoms embedded onto iron oxide surfaces have a high oxidation state. As a result of this coordination, the rate-determining step of CO oxidation on single Pt atoms (0.79 eV) exhibits lower reaction activation barriers than Pt (111) (1 eV).

DFT calculations can be utilized to detect SAC in addition to clarifying catalytic reaction processes of supported single metal atoms. Ogitsu et al., for example, conducted DFT calculations for hydrogen catalysts including transition metal atoms buried within graphitic carbon [94]. These researchers identified ten compounds that showed promise as highly efficient HER catalysts, two of which were also promising for HOR, based on several characteristics such as stability, activity, and poisoning resistance. Furthermore, several of the proposed materials were fully made up of earth-abundant components, which provided significant synthesis and financial benefits. For example, a catalyst made up of Mo atoms embedded in graphene divacancy sites (4CMo) appears to be very promising for HOR catalysis as well as HER, making it an excellent candidate for use in proton exchange membrane fuel cell anodes.

Overall, more sophisticated and precise instruments to identify SAC structures and unravel reaction processes are needed to completely comprehend the improved catalytic activity of SAC. Furthermore, to determine the structure-function correlations of SAC in catalytic processes, in situ characterization methods must be developed.

Furthermore, advances in theoretical techniques may make it possible to simulate more complicated systems and predict SAC with high catalytic activity.

6. Applications of transition metal-doped carbon-based SAC

It is important to compare directly the catalytic performance of SAC from various classes of SAC in terms of activity, selectivity, and stability to evaluate, expand the use of, and find potential synergies among the various SAC classes. Here, we will provide different kinds of applications for carbon-based SAC are included, focusing on photocatalysis, electrocatalysis, and organic catalysis.

6.1 Photocatalysis

The creation of electrons and holes for initiating reduction and oxidation reactions through absorbing photons by catalysts is the process of photocatalysis. There are three key steps in a photocatalytic reaction: light-harvesting, charge generation and separation, and catalytic reaction [95]. SAC can establish a greater potential to increase the photocatalytic activity of a typical reaction by significantly affecting the aforementioned three key steps. SAC will enhance the interaction between transition metal single-atom and carbon support [96]. The embedding of single atoms into the carbon supports can enhance the energy band structure and electronic structure by increasing their light absorption ability and charge transfer dynamics. Further, the surface structures of single-atom photocatalysts can be easily adjusted through different transition metals–carbon support interactions for enhancing the adsorption and activation capability of the photocatalyst toward reactants [97]. Several new reduction processes have been reported to be catalyzed by single-atom photocatalysts recently. Utilizing experimental data and/or calculations based on density functional theory (DFT), the synthesis of fuels and/or value-added compounds, such as H₂O₂ and aniline, through single-atom photocatalysis has been studied [98]. Additionally, it has been reported that using single-atom photocatalysts allowed for the efficient activation of O₂ for aerobic organic conversion. Additionally, single-atom photocatalysts are used to dehalogenate organic halides, removing toxic organic halides and achieving detoxification. As an example, H₂O₂, a widely available chemical product, is used in a wide range of industrial and commercial processes, including as an oxidizing agent in the manufacturing chemicals, a disinfectant in healthcare settings, and a remover of pollutants and toxins from the environment. H₂O₂ is used as an accessible, ecologically friendly oxidant since it has a reasonably high oxidation potential ($E^0 = 1.763 \text{ V vs NHE at pH} = 0$), only releasing H₂O and O₂ after use. Liquid H₂O₂ has a significant potential for storing energy due to its high

energy density and can also be used in fuel cells. However, the traditional methods for manufacturing H_2O_2 on an industrial scale have high energy costs and/or harmful pollutants. Therefore, it is highly desirable to produce H_2O_2 at a cheap cost under ambient settings by utilizing a photocatalytic process that is favorable to the environment. Recently, two-dimensional (2D) carbon nitride (C_3N_4) loaded with anthraquinone (AQ) and cobalt (Co) single atoms were created to generate H_2O_2 from solar light[99]. Therefore, the transition metal doped SAC significantly improves the photocatalytic activity of respective reactions. (**Table 1**)

6.2 Electrocatalysis

Recently, transition metal-doped SAC has grabbed striking attention in electrocatalysis. More significantly downsizing metal nanoparticles into single atoms can enhance the catalytic activity of electrochemical reactions. Moreover, it can enhance the selectivity toward electrochemical reactions as well. The increased number of dispersion of single transition metal atoms in carbon support in SAC facilitates high catalytic activity and specific selectivity toward a wide range of electrocatalytic reactions[112].

Furthermore, the increased atom utilization and reduced capital costs in industrial/large-scale applications are important in electrocatalysis[68]. On the other hand, the interactions between single atoms and carbon supports of SAC can improve electrocatalytic performance.

These kinds of interactions emerge in tunable electronic structures, by increasing the catalytic performance of SAC. Moreover, unsaturated coordination environments of atomically dispersed catalysts play a pivotal role in the adsorption of metal atoms and activation of reactants on catalytic sites. As a result of that, the energy barrier of electrochemical reactions will be lowered [113]. Furthermore, the recognition of active sites at the atomic scale will pave the way for discovering the structure-property/activity relationships on active sites in different kinds of electrocatalysis [114]. Here we have summarized the utilization of carbon-based transition metal-doped SAC for oxygen reduction reaction (ORR) [115], hydrogen evolution reaction (HER), oxygen evolution reaction (OER), hydrogen oxidation reaction (HOR), and nitrogen reduction reaction (NRR).

In sophisticated electrochemical energy conversion systems, the oxygen reduction reaction (ORR) is of vital significance. The slow kinetics of ORR frequently necessitates substantial precious metal loading amounts on catalysts, which prevents its commercialization. Many SAC with excellent catalytic efficiency have, however, recently been produced. As an example, Li and co-workers synthesized a catalyst with Co atoms anchored on N-doped carbon (Co SAs/N-C), forming an active site of Co-N₄[70]. Furthermore, a comparison of a series of SAC synthesized at different temperatures was carried out to assess the difference in structure and catalytic efficiency among them.

Table 1 - Transition metal doped carbon-based SAC and their applications in photocatalysis

| Carbon Substrate | Transition Metal Atom | Reaction | Ref |
|---------------------------------|---------------------------------|---|--------------|
| Graphene | Cobalt (Co) | Photocatalytic hydrogen generation from in visible light irradiation | [100] |
| porphyrinic MOF | Platinum (Pt) | Hydrogen generation under visible light irradiation | [101] |
| Carbon nitride | Cobalt (Co) | photocatalytic CO ₂ reduction | [102] |
| Porous graphitic Carbon nitride | Copper (Cu) | Photocatalytic dinitrogen fixation | [103] |
| Porous graphitic Carbon nitride | (Mo) | Photocatalytic dinitrogen fixation | [104] |
| Carbon nitride | Platinum (Pt) | Hydrogen evolution reaction | [105] |
| Graphitic Carbon nitride | Silver (Ag) | Photocatalytic degradation of sulfamethazine | [106] |
| Nanoporous graphene | Nickel (Ni) | Hydrogen evolution reaction | [21] |
| N-doped carbon dots | Platinum (Pt) | Hydrogen evolution reaction under visible light | [107], [108] |
| Graphitic carbon nitride | Platinum (Pt) Palladium (Pd) | Photocatalytic reduction of CO ₂ toward HCOOH and CH ₄ | [109] |
| Graphitic carbon nitride | Silver (Ag) | Naproxen photocatalytic degradation | [110] |
| Graphitic carbon nitride | Iron (Fe) | Photodegradation of bisphenol A Phenol production from benzene oxidation under visible light | [111] |

The hydrogen evolution reaction (HER), which can significantly reduce the quantity of noble metal loading and save power through high atomic usage and activity, is thus given a new opportunity by SAC. Sun et al. further studied the Pt single atom and cluster anchored on nitrogen-doped graphene nanosheets (NGNs) for the efficient HER[116]. Further, a nickel atom anchored on the graphitized carbon, denoted as the activated-Ni-carbon (Ni-C), was synthesized by Yao *et. al.* [117]. The optimal activity of Ni-C can be attributed to the strong interaction between graphitized carbon and Ni single atoms, permitting highly efficient electrical communication among the metal center, the reactant and the underlying electrode substrate.

The oxygen evolution reaction (OER), which makes up the second half of the water splitting reaction, holds great promise for extensive usage of electricity. OER differs from HER in that it moves at a much slower rate and has a more complicated process overall. Electrocatalysis has garnered a lot of interest in the nitrogen reduction process (NRR). The electrocatalysis still has a lot of room for improvement compared to the Haber-Bosch method, though. As a result, it would be advantageous to design electrocatalysts that are highly active and selective for NRR. Some of the examples for transition metal doped SAC in electrocatalysis are mentioned in **Table 2**.

6.3 Organic catalysis

Carbon-based transition metal doped SAC has been widely used in various organic reactions such as oxidation, reduction, hydrogenation, and coupling reactions. (**Fig. 9** and **Table 3**)

7. Concluding remarks and future prospects

Transition metal doped carbon-based SAC is providing a promising era to develop robust, cost-effective and

high-efficient catalysts which could be used in a variety of chemical catalytic reactions[137]. The synthesis routes and the carbon substrates which are being most widely used in SAC have been discussed in detail in this review with examples of a wide variety of chemical reactions including electrocatalysis, organic catalysis, and photocatalysis. Reduction of transition metal

loading into carbon-based catalysts without affecting the catalytic activity is one of the main objectives of developing these carbon-based SAC. Therefore, stabilizing SAC on carbon supports can be achieved through the development of potential defective sites on the carbon support, where the transition metal atoms can be trapped via strong interactions. Carbon-based supports such as graphenes, graphene oxide, graphyne, graphdiyne, graphitic carbon nitride (g-C₃N₄) and carbon-containing MOF/ZIF are more significant in the synthesis of SAC since a well-established environment will be provided for SAC. Further, these carbon supports enable modulation of electronic interactions through doping of carbon support with transition metals as discussed. Another important aspect is the synergistic effect of these transition metal doped SAC. This synergistic effect arises due to the interactions between the carbon support and the doped transition metals and metal-metal/metal-oxygen-metal (bimetallic SAC) escalates the catalytic performance[138].

The coordination environment or orientation of the active site geometry of SAC should be studied because it has a significant impact on the catalyst's overall performance. Different transition metal atom doping (heteroatom doping) can be used to modify the coordination environments around the transition metal atom, allowing different nearby transition metal atoms to be used in different combinations. Homogenization of active sites during catalyst synthesis is difficult, and as a result, produced catalysts always feature a variety of active sites. The different molecular faulty sites have

Table 2 - Transition metal-doped carbon-based SAC and their applications in electrocatalysis

| Carbon Substrate | Transition Metal Atom | Reaction | Ref |
|--|-----------------------|---|--------------|
| N-graphene | Cobalt (Co) | Hydrogen evolution reaction | [77], [118] |
| N-porous carbon | Cobalt (Co) | Oxygen reduction reaction | [119] |
| Graphitic Carbon Nitride | Cobalt (Co) | Oxygen reduction reaction and oxygen evolution reaction | [70] |
| N-graphene | Iron (Fe) | Oxygen reduction reaction | [120] |
| Onion-like carbon shell | Niobium (Nb) | Oxygen reduction reaction | [121] |
| Graphitic layers | Tungsten (W) | Oxygen reduction reaction | [122] |
| N doped carbon | Ruthenium (Ru) | Nitrogen reduction reaction | [123] |
| Hierarchically ordered porous N-doped carbon | Cobalt (Co) | Oxygen reduction reaction and hydrogen evolution reaction | [124], [125] |
| | Iron (Fe) | | |
| | Nickel (Ni) | | |

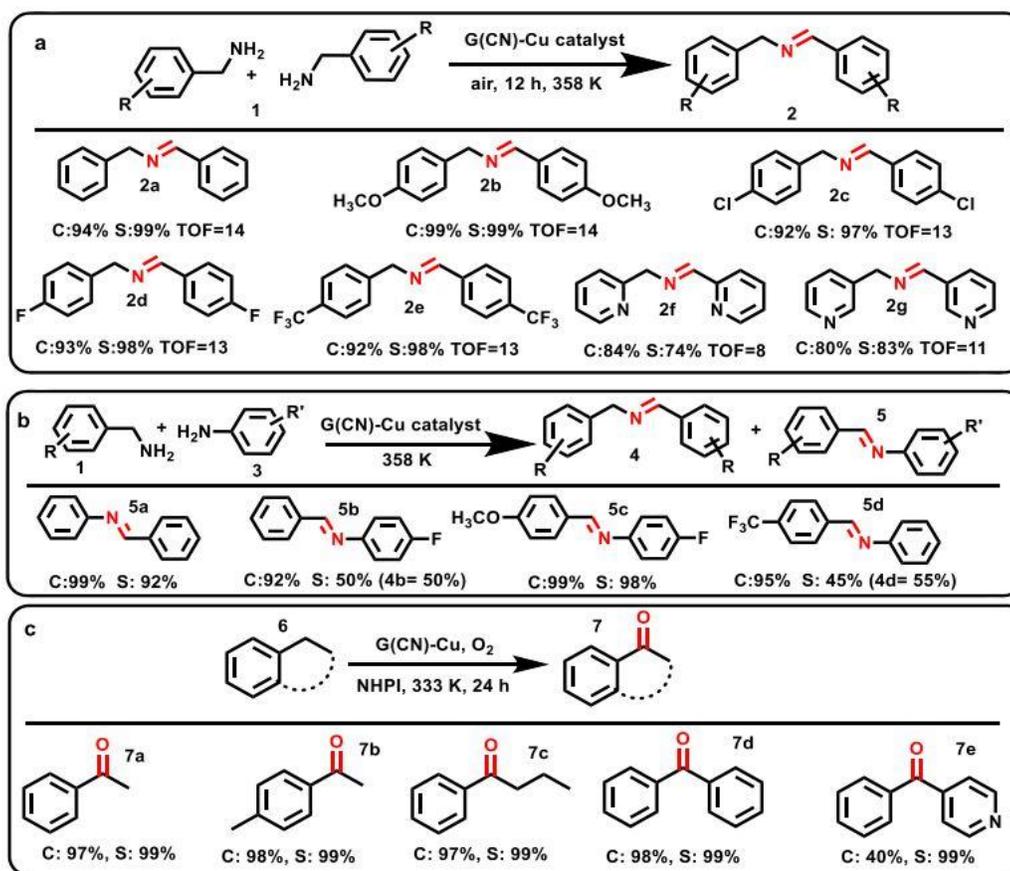


Fig. 9 - (a) Oxidative homocoupling of substituted benzylamines. (b) Oxidative cross-coupling reaction. (c) Oxidation reactions of benzylic C–H bonds with G-CN catalyst. Adapted with permission from ref [4] Copyright 2020 American Chemical Society

varying levels of activity and selectivity for the same reactions, which is difficult to predict at the atomic level. Furthermore, transition metal atom interactions have a significant impact on catalytic characteristics, as well as assisting in the stabilization of some intermediates, facilitating catalytic cycles. Surface sensitivity characterization techniques including XPS, AFM, and DFT modeling could be useful in the development of various types of SAC.

The utilization of SAC at higher temperatures is encouraged but it is essential to keep them isolated during the operation. Therefore, the operational temperature is normally kept below 300 °C. The strong contact between the transition metal and the carbon support can increase the thermal stability of SAC. The programmable high-temperature shockwave approach, atom trapping, and entropy-driven methods were employed to stabilize transition metal single atoms. The development of thermodynamically beneficial strong metal-carbon bonds was aided by periodic on-off heating for a brief duration, such as 55 ms.

Further, the loading of transition metals into carbon-supported SAC is very low hence the production yield

is not at all sufficient for practical applications. Therefore, increment of metal loading has inherited issues of moving and agglomeration of transition metal atoms to form nanoparticles. In this regard, a proper way should be established between metal loading into SAC and catalytic performance. There is an optimistic way to do the development of a high amount of metal loading into SAC through theoretical modeling and simulations.

In that way, SAC with high metal loading and uniform coordinated structures could be developed. Vehicles with selective catalytic converters (SCR) employ a sophisticated emission control device that injects a liquid-reductant agent into the exhaust stream to reduce NO_x levels. While these catalysts are made of Rh, Pt, and Pd, they will convert NO_x to N₂ and O₂. The catalytic activity can be increased even more with the creation of transition metal doped SAC solid electrolyte cells. Normally, heterogeneous catalysis is employed to dechlorinate water and air, however, SAC electrolyte cells can improve this process. On the other hand, given the growing demand for energy and the widespread use of electric vehicles, SAC for metal-air batteries have a greater potential to meet the battery's needs.

Table 3 - Transition metal-doped carbon-based SAC and their applications in organic catalysis

| Carbon Substrate | Transition Metal Atom | Reaction | Ref |
|---|-----------------------|---|-------|
| Graphene | Platinum (Pt) | Methanol oxidation | [76] |
| Graphene | Palladium (Pd) | Selective hydrogenation of 1,3-butadiene | [76] |
| N-graphitic layers | Cobalt (Co) | Hydrogenative coupling of nitroarenes | [70] |
| N-graphene | Iron (Fe) | Oxidation of benzene | [126] |
| Fullerene | Iridium (Ir) | Reduction of ketones by hydrogen transfer from isopropanol | [127] |
| N doped carbon nanotubes | Nickel (Ni) | Wet air oxidation of acetic acid | [128] |
| Phosphomolybdic acid (PMA)-modified active carbon | Platinum (Pt) | hydrogenation of cyclohexanone and nitrobenzene | [129] |
| Mesoporous graphitic carbon nitride | Palladium (Pd) | hydrogenation of alkynes and nitroarenes | [79] |
| Mesoporous graphitic carbon nitride | Palladium (Pd) | Hydrogenation of alkene | [130] |
| Exfoliated graphitic carbon nitride | Palladium (Pd) | Suzuki couplings | [130] |
| Mesoporous N doped carbon | Cobalt (Co) | Selective hydrogenation of challenging nitroarene substrates under benign conditions | [71] |
| Multi-walled carbon nanotubes | Palladium (Pd) | Reduction of CO ₂ | [131] |
| N doped graphene | Cobalt (Co) | Selective oxidation of numerous alcohols including 4-chlorobenzyl alcohol, 4-methylbenzyl alcohol, and 4-methoxy-benzyl alcohol | [132] |
| MOF | Ionic Copper | Oxidation of ethers to esters under ambient conditions | [133] |
| Graphitic carbon nitride | Gold (Au) | Silane oxidation | [134] |
| MOF | Lanthanide (La) | Epoxidation of olefins | [135] |
| Graphene | Uranium-and thorium | Oxygen and hydrogen peroxide reduction | [136] |

Future research studies will pave the pathway to the synthesis of SAC with more different active single atom sites. As an example, Chen and co-workers have reported a combination of double (DAC)/triple single-atom catalysts (TAC) which can be used in environmental and catalytic applications[61]. In this example, the main aim is to prepare a single atom of DAC and TAC on a carbon support. Then the investigation of its synergistic effect with the mechanism for specific catalytic activity such as organic catalytic, electrocatalytic and photocatalytic applications is also very significant in future research studies. In this regard, SAC, DAC, and TAC will establish a potential application in catalytic reactions with high efficacy. Therefore, the field of transition metal doped carbon-based SAC has already started a greater contribution to heterogeneous catalysis with novel reactivity concepts with a probability of diverse applications.

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