A minireview on the synthesis of single atom catalysts

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Single atom catalysis is a prosperous and rapidly growing research field, owing to the remarkable advantages of single atom catalysts (SACs), such as maximized atom utilization efficiency, tailorable catalytic activities as well as supremely high catalytic selectivity. Synthesis approaches play crucial roles in determining the properties and performance of SACs. Over the past few years, versatile methods have been adopted to synthesize SACs. Herein, we give a thorough and up-to-date review on the progress of approaches for the synthesis of SACs, outline the general principles and list the advantages and disadvantages of each synthesis approach, with the aim to give the readers a clear picture and inspire more studies to exploit novel approaches to synthesize SACs effectively.

1. Introduction

Single atom catalysis describes a process in which a single atom on a catalyst surface drives a catalytic reaction.1–3 The catalyst with a single atom on its surface is called a single atom catalyst (SAC). The concept of SAC was raised up by Zhang et al. in 2011, based on a study that a catalyst with Pt atoms singly dispersed on FeOx (named as Pt1/FeOx) was much superior in CO oxidation reaction than its nanoparticle counterpart.4 The individually dispersed active sites on SACs can ① tune electronic states, which directly or indirectly regulates the catalytic activity, and ② minimize the number of binding configuration choices between reactants and SACs, which consequently leads to an extremely high selectivity towards the target product.4–9

Initiated by this seminal work, the nomenclature of SACs (M1/Support) has become widely accepted, which sparked researchers’ interest and boosted extensive studies.10–20 It has been proved that synthesis approaches play crucial roles in determining the properties of SACs, such as crystallinity, composition, morphology, pore structure and valence states, which eventually contributes to the performance of SACs.

Over the past few years, significant efforts have been devoted to the synthesis of SACs. To the best of our knowledge, tens of methods have been adopted to synthesize SACs. In this review, we summarize the scientific achievements of synthesis approaches.
approaches of SACs to the catalysis community, aiming at providing a clear picture and inspiring more studies to exploit novel and effective approaches to synthesize SACs.

2. Synthesis approaches of SACs

In this section, we divide the synthesis approaches into dry chemistry route and wet chemistry route (Scheme 1), review the general principles of the approaches to synthesize SACs and compare the advantages and disadvantages of each synthesis approach.

2.1 Dry chemistry routes

2.1.1 Atomic layer deposition (ALD) method. ALD method also referred as atomic layer epitaxy. It was originally proposed by Finnish scientists in 1970s and developed for the preparation of polycrystalline fluorescent materials ZnS : Mn$^{2+ - 28}$ and amorphous Al$_2$O$_3$ insulating film$^{29-31}$ and recently it has been successfully used for the preparation of SACs.

An ALD reactor is indispensable for the synthesis of SACs via ALD method. The schematic illustration of a typical ALD reactor is displayed in Fig. 1. Its core is a chamber consisting of a static or rotary bed of substrates. The precursor vapor is pulsed into the chamber, where it diffuses and permeates to reach and coat the substrate surfaces.

The most common mechanism for synthesizing SACs via ALD method is the ligand exchange reactions, in which the ligands or functional groups on the substrate react with the precursor. When ALD method is used to synthesize SACs, catalyst support is the substrate placed in the chamber, into which the pulse stream of precursor containing the atomically dispersed active component diffuses and reacts with the ligands or functional groups on support surface (the schematic illustration is displayed in Fig. 2)$^{33-40}$ The stream of precursor is stopped when the reaction between the precursor and the substrate completes. The residuals of the precursor vapor and byproducts are purged with an inert gas or evacuated at high vacuum. These two steps are called the first half-reaction. After the first half-reaction, one ALD cycle is finished. If multiple ALD cycles are needed, a second stream of precursor is pulsed into the chamber to regenerate the ligands or functional groups on support surface. After purging to remove the residuals and byproducts, it is ready for next ALD cycle (the second half-reaction in Fig. 2).

According to the mechanism for the synthesis of SACs via ALD method, ligands or functional groups on support are necessary. Carbon, especially graphene, has been proved as excellent candidate support for anchoring metal atoms separately due to its unique electronic and structural properties, which facilitate the bonding between the singly dispersed atoms and carbon support through Metal–C and Metal–O–C coordination.$^{41}$ Using the ALD method, a number of graphene supported SACs, such as Pt/graphene, Pd/graphene and Co/graphene, have been successfully prepared.$^{42-48}$

Here the synthesis of Co$_1$/SiO$_2$ is taken as an example.$^{49}$ Gorte et al. utilized tris (2,2,6,6-tetramethyl-3,5-heptanedionato) cobalt|III| as ALD precursor, 0.7 g SiO$_2$ were evacuated and exposed to 5 Torr of precursor vapor at 250 °C for 5 min, after removing the excessive precursors via evacuation and removing the ligands via oxidizing it in a muffle furnace at 500 °C for 7 min, one ALD cycle is finished and Co$_1$/SiO$_2$ is obtained. The number of singly dispersed atoms on SACs could be controlled by adjusting the number of ALD cycles. Gorte et al. further
investigated the effects of the number of ALD cycles on the properties of the as-prepared catalysts. They discovered that isolated Co catalyst could be obtained with only one ALD cycle. Co loadings increased linearly with the number of ALD cycles. After several cycles, the single dispersion state of Co remained. Further increasing the number of ALD cycles, Co gradually transformed from the single dispersion state to clusters and eventually to nanoparticles.

ALD possesses the following advantages, (1) the deposition parameters could be controlled precisely, (2) the desired thickness or size of the deposited precursor could be achieved by adjusting the number of cycles, (3) the deposition uniformity and reproducibility are excellent in spite that slight deviations from the ideal conditions are sometimes observed, and (4) different deposition materials can be controlled precisely at the atomic level to form composites with various morphologies.\textsuperscript{31-34} The advantages of ALD make it possible for providing ideal model catalysts for the basic studies of catalysis, which include exploring the effects of particle sizes, surface properties of catalyst supports and encapsulation (or surface coating) of metal or alloy nanoparticles, on the catalytic performance. In conclusion, ALD is an important approach to synthesize SACs and study the structure–activity relationship over SACs. The drawback is that, only materials with suitable ligands or functional groups could be chosen as support to disperse the metal atoms separately \textit{via} ALD method, meanwhile, this technology is not applicable for the commercial preparation of SACs currently, because of the stability and cost issues (Table 1).

\subsection*{2.1.2 Pyrolysis synthesis method.} Pyrolysis synthesis, as the name suggested, is a strategy to synthesize SACs by thermochemically decomposing the organic precursors of the catalysts at elevated temperatures under a specific atmosphere. A series of metal–nitrogen–carbon SACs have been successfully synthesized \textit{via} this method in the past decade.\textsuperscript{55-76}

At present, the precursors for the preparation of SACs by this method are mainly divided into metal–organic frameworks (MOFs), metal phthalocyanine–silica colloid composites, metal–phenanthroline complexes on carbon supports and amino-functionalized rigid molecules. Here, several examples are elaborated to illustrate the preparation procedures for SACs \textit{via} the pyrolysis of the several above-mentioned precursors. (1) For the preparation of stable Co–nitrogen–carbon SAC, bimetallic Zn/Co MOF is an excellent precursor. During the following pyrolysis process, Zn could be selectively evaporated away at high temperatures above 800 °C and Co could be reduced by the carbonization of the organic linker. The loading of singly dispersed Co atoms achieved \textit{via} this method could be high up to 4 wt\%\textsuperscript{.77} Other metal–nitrogen–carbon SACs [M = W, Mo, Cu, Zn, Cr, Mn, Fe and Ni] could also be obtained \textit{via} the pyrolysis synthesis method with bimetallic-organic frameworks as precursors.\textsuperscript{78-81} (2) When Co phthalocyanine–silica colloid

![Fig. 1](image1.png) Schematic illustration of an ALD reactor. This figure has been adapted/reproduced from ref. 32 with permission from American Chemical Society, copyright 2021.

![Fig. 2](image2.png) Schematic illustration of the preparation of SACs by dosing two distinct precursors sequentially to the matrix. This figure has been adapted/reproduced from ref. 32 with permission from American Chemical Society, copyright 2021.

| Method | Singly dispersed metals |
|--------|-------------------------|
| ALD    | Pt, Pd, Co, Cu, Fe, Ni, Ti, Zn |
composite was used as precursor, singly dispersed Co catalyst Co–N\textsubscript{x}/C could be prepared by the pyrolysis of the precursor and the subsequent removal of silica template and cobalt nanoparticles.\textsuperscript{84} The as prepared Co–N\textsubscript{x}/C SAC showed extremely high activity, chemoselectivity and stability toward the reduction of nitro compounds by H\textsubscript{2}. (3) The noble-metal-free Co–N–C catalyst could also be derived from the pyrolysis of cobalt-phenanthroline complexes on a mesoporous carbon support at high temperatures,\textsuperscript{85} and this Co–N–C catalyst was reported to show high catalytic activity (turnover frequency, TOF, of 3.8 s\textsuperscript{-1} based on Co single atoms) and good recyclability in the aerobic oxidation of over 28 examples of diverse substrates. (4) The preparation of Pd\textsubscript{1}/N-graphene from amino-functionalized rigid molecules is another example for pyrolysis synthesis method. In the preparation procedure, a precursor was firstly obtained by functionalizing the palladium phthalocyanines with four aminophenoxy groups at the periphery of the benzene ring of graphene, which was then pyrolyzed to anchor the isolated Pd atoms.\textsuperscript{86}

Taking the Co–N–C catalyst derived from the pyrolysis of cobalt-phenanthroline complexes on a mesoporous carbon support and Pd\textsubscript{1}/N-graphene prepared from amino-functionalized rigid molecules as typical examples, high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images clearly indicated that the precursors were successfully transformed into singly dispersed atoms (Fig. 3a–d).\textsuperscript{85,86}

The pyrolysis synthesis method is a straightforward route for the preparation of SACs. The singly dispersed atoms could be derived from precursors, in which there are suitable interactions between the metal precursor and support. Generally, the singly dispersed atoms are transitional metals, such as W, Mo, Cu, Zn, Cr, Mn, Fe and Ni, while the supports are originated from MOFs, silica colloids, carbon or amino-functionalized rigid molecules. Upon pyrolysis in a furnace under a specific atmosphere, the precursors gradually decompose, lead to the transformation of precursor to the desired support and single atoms. However, high pyrolysis temperatures are generally required, which makes it an energy intensive process. In addition, up to now, there have been no reports on the synthesis of non-metal-based SACs via this method (Table 2).

2.1.3 Atom trapping method. Atom trapping method is a promising approach to synthesize singly dispersed catalysts by utilizing the migration property of metal atoms at elevated temperatures. It was initially adopted for the synthesis of SACs in 2016 by Jones et al., who reported that a thermally stable single atom Pt\textsubscript{1}/CeO\textsubscript{2} catalyst was successfully achieved by aging a mixture of Pt/Al\textsubscript{2}O\textsubscript{3} and CeO\textsubscript{2} in air at 800 °C to promote the

Fig. 3 HAADF-STEM image of Co–N–C catalyst prepared by the pyrolysis synthesis method (a and b) and Pd\textsubscript{1}/N-graphene catalyst prepared by the pyrolysis synthesis method (c and d). These figures have been adapted/reproduced from ref. 85 and 86 with permission from American Chemical Society and Royal Society of Chemistry, copyright 2015 and 2022.
transfer of Pt from Al₂O₃ to CeO₂, where it was strongly anchored as single site (Fig. 4). CeO₂ nanorods were more effective than CeO₂ cubes at trapping the Pt atoms. Aging at high temperatures ensured that only the most stable binding sites on CeO₂ were occupied, and thus yielded a sintering-resistant atomically dispersed catalyst. The transformation of nanoparticles to stable single atoms could be directly observed via HAADF-STEM. Fig. 5a–d displayed the evolution of Pd nanoparticles on zinc 2-methylimidazole metal organic framework (ZIF-8) to single atoms. Fig. 5a was the HAADF-STEM image of ZIF-8. During the first stage of heating, the crystalline Pd nanoparticles became larger and the size distribution became inhomogeneous (Intermediate I, Fig. 5b). Upon heating the second stage, the number of nanoparticles was significantly reduced, and the crystalline Pd nanoparticles were transformed into an amorphous state (Intermediate II, Fig. 5c). With the further extension of heating time, the remaining nanoparticles were fully digested within the substrate. At the same time, ZIF-8 was decomposed and converted into SACs (Fig. 5d).

The atom trapping method is applicable to synthesize a series of SACs, including Pd, Au, Cu and Ni SACs. These SACs could be synthesized by transforming the relevant nanoparticles in an inert atmosphere above 900 °C, when nitrogen-doped carbon is used as support to capture the mobile atoms.

The atom trapping method is a simple approach for synthesizing SACs. Nevertheless, the approach requires a supply of mobile atoms and a support that can trap the mobile species. Additionally, the very high synthesis temperatures are not favorable from an energy perspective. However, if the catalyst preparation process is applied to high-speed moving automobile exhaust, its temperature can be easily reached under operation, which makes this method very practical (Table 3).

### Table 2

**Summary of precursors and metals for pyrolysis synthesis of SACs**

| Method          | Precursors                              | Single-atom metals |
|-----------------|-----------------------------------------|--------------------|
| Pyrolysis synthesis | MOFs, Silica colloids, Carbon or amino-functionalized rigid molecules | W, Mo, Cu, Zn, Cr, Mn, Fe, Ni⁷⁶–⁸³ |

### Table 3

**Summary of metals used in the synthesis of SACs by atomic trapping**

| Method            | Synthesis of single-atom metals |
|-------------------|---------------------------------|
| Atom trapping     | Pt⁷⁷, Ru⁷⁷, Co⁷⁷, Pd⁸⁸, Au⁸⁸, Cu⁹⁰, Ni⁹⁰ |
Two-step doping method takes advantages of the easy creation of vacancies on support and the high binding energies between the dopant and the vacancies. To the best of our knowledge, the support of SACs prepared by the two-step doping method is strictly limited to graphene, while the non-dependence on the type of dopants endows wider applications. The catalysts prepared by this method are highly stable due to the high binding energy between the dopant metal and the vacancy; however, high energy atom/ion generator is required to create vacancies if SACs are synthesized through this method (Table 4).

### 2.1.5 Ball-milling method

As a mechanochemical technique, ball milling method takes advantages of mechanical interactions to convert reactants into products during the reaction process. It plays an important role in synthetic organic chemistry. For example, Gan et al. used a simple, green and scalable ball milling method to synthesize a cobalt alloy Pt SAC (Pt$_{1}$/Co) in a kilogram-scale. It was reported that, over Au$_{1}$/FeO$_{x}$ catalyst, Au single atoms were separately dispersed on iron oxide crystallites, and the Au atoms were positively charged and anchored covalently to FeO$_{x}$. The as-prepared Au$_{1}$/FeO$_{x}$ catalyst exhibited ultrahigh stability and remarkable catalytic performance for CO oxidation at a wide temperature range.

The facile adsorption method is an approach to synthesis SACs utilizing the interactions between the active metal element and the support. It is easy and simple to operate, and could be achieved in a common chemistry lab. However, the metals are generally randomly absorbed on the surface of support, therefore, appropriate interaction between the active metal component and catalyst support is required to synthesize SACs successfully. In addition, due to the heterogeneity of support, the dispersion state of the active metal elements could not be well controlled.

### 2.2 Wet chemistry routes

#### 2.2.1 Methods taking advantages of the adsorption between single atom precursor and support

##### 2.2.1.1 Facile adsorption method

Facile adsorption method, as the name indicates, the singly dispersed active component is anchored onto the catalyst support via a simple adsorption mode. Zhang et al. used the facile adsorption method to synthesize Au$_{1}$/FeO$_{x}$ catalyst. It was reported that, over Au$_{1}$/FeO$_{x}$ catalyst, Au single atoms were separately dispersed on iron oxide crystallites, and the Au atoms were positively charged and anchored covalently to FeO$_{x}$. The as-prepared Au$_{1}$/FeO$_{x}$ catalyst exhibited ultrahigh stability and remarkable catalytic performance for CO oxidation at a wide temperature range.

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##### 2.2.1.2 Strong electrostatic adsorption method

The surface of oxide materials is often covered with a layer of hydroxyl groups. The pH at which the aqueous solution is neutral is termed the point of zero charge (PZC). The oxides are positively charged in aqueous solutions when pH values are below its isoelectric point and negatively charged at the cases when pH values are above its isoelectric point. By adjusting pH values, a monolayer of O$^-$, OH or OH$_2^-$ could be formed on the surface of oxides. They are capable of anchoring various metal ion complexes via strong electrostatic interaction. Taking Pt salt as an example,
the metal ion complexes are \([\text{[NH}_3\text{]}_4\text{Pt}]^{2+}\), \([\text{H}]^+\) or \([\text{PtCl}_6]^{2-}\) (Fig. 8). SACs could be obtained after carefully removing the ligands of the complexes via post-treatment.97

It is expected that pH, ionic strength as well as the properties of the metal ion complexes play critical roles on the properties of catalysts prepared by the strong electrostatic adsorption method.98-100 Morales-Garcia et al. computationally investigated the interaction between the singly dispersed Pd atoms and silicalite-1 as well as that between the Pd clusters and silicalite-1.101 The interaction between a single Pd atom and silicalite-1 was strong with dominant contribution coming from the electrostatic effects, which resulted in a preferable binding of the isolated Pd atoms to the silanol groups on the external surface of silicalite-1.99 On the other hand, the interaction between Pd clusters and silicalite-1 was mainly dispersion interactions, with only a small contribution from electrostatic adsorption, which made Pd clusters preferably located inside the channels of silicalite-1. Pillay et al. adopted density functional theory (DFT) study to simulate the grafting of sulfur single atom onto Pt(111) and Pt,Ni(111) surfaces via the strong electrostatic adsorption method.102,103 From both the experimental and theoretical reports, it was found that the potential energy surfaces, appropriate functionalization of the support surface and the utilization of metal ion complexes with strong electrostatic interaction to the support, are key factors for the successful preparation of stable SACs.102,103

The strong electrostatic adsorption method is discovered to be effective for preparing high quality SACs, particularly for the preparation of singly dispersed noble metal catalysts. However, the adsorption behavior of metal complexes is influenced greatly by the heterogeneity of functional groups and the presence of various defects on the surface of the oxide matrix. In addition, the pH values of the aqueous solution change with the prolonging of the adsorption time, which might further affect the quality of the resulting SACs.

2.2.1.3 Wetness impregnation method. The wetness impregnation method is one of the typical preparation methods for traditional heterogeneous catalysts. In this approach, an aqueous or organic metal salt solution impregnates the catalyst, with the metal salt adsorbing on support surface. The residual solvent is removed, commonly by evaporation, to obtain the salt impregnated catalyst. The impregnation process relies greatly on the adsorption capacity of the surface of the support towards the organometallic complexes or inorganic salts.104-106 Therefore, the metal salt-support interaction is critical, and significantly influences the amount of metal loading and the dispersion of the metal anchored on the support surface.

When an oxide is employed as the catalyst support and impregnated with an aqueous solution, polarization occurs similarly to that for the strong electrostatic method. In an acidic solution, the surface adsorption sites on the support (M-OH) are positively charged and attract anions. In the alkaline solution, the surface adsorption sites (M-OH) are negatively charged and attract cations. According to the Brunelle adsorption model, the key parameters for controlling the metal dispersion include (1) the type and concentration of the metal salt, (2) the pH value of the aqueous solution, and (3) the type of catalyst support and the functional groups on its surface.

The Al atom in \(\gamma\text{-Al}_2\text{O}_3\) is hexa-coordinated and exhibits a penta-coordinated structure after calcination at high temperatures, resulting from the dehydration and removal of hydroxyl groups on the surface of \(\gamma\text{-Al}_2\text{O}_3\) and leading to the generation of unsaturated Al sites.107 By utilizing these unsaturated Al sites on \(\gamma\text{-Al}_2\text{O}_3\), which possess the capacity to stabilize single Pt atoms, Kwak et al. successfully prepared a single atom Pt/\(\gamma\text{-Al}_2\text{O}_3\) catalyst by impregnating \(\gamma\text{-Al}_2\text{O}_3\) with an aqueous solution of Pt salt.108 After introducing the singly dispersed Pt atoms on \(\gamma\text{-Al}_2\text{O}_3\) by the impregnation method, the number of penta-coordinated Al atoms was significantly reduced. With the increase of Pt loading, the penta-coordinated Al atom sites were not sufficient to stabilize all Pt single atoms, thus resulting in the formation of larger Pt particles.109 The HAADF-STEM images of 1 wt% Pt/\(\gamma\text{-Al}_2\text{O}_3\) revealed that most of the Pt species were atomically dispersed and the HAADF-STEM images of 10 wt% Pt/\(\gamma\text{-Al}_2\text{O}_3\) demonstrated the existence of both atomically dispersed Pt and Pt cluster/nanoparticles (Fig. 9).105

The wetness impregnation method is simple to operate, but it is difficult to ensure uniform dispersion of the metal atoms on the surface of the support and it is not suitable for the preparation of SACs with high metal loadings.108,109

2.2.2 Methods taking advantages of the photochemical and electrochemical properties of single atom precursors/support

2.2.2.1 Photoreduction method. Photoreduction is a method to prepare SACs by reducing the metal salts into their metallic states with light as the driving force. Zheng et al.’s work in Science is one of the presentative studies on adopting the photoreduction method to synthesize SACs.110 The authors used photochemical reduction assisted wet chemical method to prepare Pd/\(\text{TiO}_2\). The surface of the \(\text{TiO}_2\) film was positively charged and attracted a large amount of \([\text{PdCl}_4]^{2-}\) anions, which enriched on the surface of the \(\text{TiO}_2\) sheet by carefully controlling the pH of the solution. Extended X-ray absorption fine structure (EXAFS) analysis (Fig. 10a) and HAADF-STEM image (Fig. 10b) suggested that a single atom Pd catalyst with a loading high up to 1.5 wt% could be obtained by UV light irradiation. Pd/\(\text{TiO}_2\) could activate hydrogen via a pathway...
different from those over traditional heterogeneous catalysts, and exhibited a good activity for the hydrogenation of C=C and C=O bonds (Fig. 10c and d).

On one hand, no special equipment is needed for the photoreduction method, so it is easy and can be achieved in conventional chemical laboratories. On the other hand, the
catalytic active sites of the catalysts prepared by this method generally are not uniform, because of the co-existing of singly dispersed sites and continuously packed sites (Table 5).

2.2.2.2 **Galvanic replacement method.** Galvanic replacement is a technique which takes the advantage of the reduction potential differences between a metal in a template and metal ions in a solution. Given proper potential differences, the galvanic replacement reactions could occur spontaneously, with the metal atoms in the template being oxidized and dissolved into the solution while the metal ions in the solution being reduced and plated on the surface of the metal template (Fig. 11). The galvanic replacement method has been successfully adopted in the synthesis of atomic layer deposited PtRu,114,115 PdCu,116–118 PdAu119–121 PtPd,122–124 and Hg(1−x)Cd_xTe.125

In occasional cases, to protect the intact structure of the template metal, a ternary metal might be introduced as sacrificial metal template for the galvanic replacement method. For example, to deposit atomic monolayer Pt on polycrystalline Au, a layer of Ni could be pre-electrodeposited on Au, which serves as the sacrificial metal template in the following galvanic replacement reaction. After exposing the resultant Ni-rich surface to Pt solution, Pt atomic monolayer is controllably grown on Au by galvanically replacing Ni by Pt.127 The utilization of sacrificial metal template offers an environmentally friendly and cost-effective approach for adopting the galvanic replacement method in atomic layer metal synthesis.

This galvanic replacement method is simple, versatile and could be used to synthesize SACs with a wide variety of metal templates and metal ions in the solution. At the same time, it is limited by the requirement of an appropriate difference in electrochemical potentials between the two metals (Table 6).

2.2.2.3 **Cyclic voltammetry (CV) method.** CV method is an approach to synthesize SACs in an electrochemical working station equipped with counter electrode (CE), reference electrode (RE) and a working electrode (WE). In case that CE is a Pt foil, upon potential cycling operation, trace amount of Pt on CE dissolves and is atomically deposited on RE. By assuming RE as a support, singly dispersed Pt catalyst is achieved (Schematic illustration is shown in Fig. 12). Luo et al.’s work is a typical example. They used a saturated calomel electrode as RE, a Ni foam (NF) with CoP-based nanorod/nanosheet arrays on its surface as WE and phosphate as butter solution, and successfully synthesized Pt1/CoP/NF catalyst via CV method.129 Pd1−N8/CNT, a N8/C0 Lewis base catalyst, was synthesized via a similar procedure, where Pd foil is used as CE.130

In CV method, less additives are demanded and no interfering products are generated, which make it easily scalable. However, an electrochemical station is needed, indicating the operation cost is high.

2.2.3 **Other wet chemistry routes to synthesize SACs**

2.2.3.1 **Ion exchange method.** The ion exchange method is an approach for introducing a foreign precursor from aqueous solution onto the support in a controlled way. The term ion exchange has been adopted to describe all processes where ionic species from aqueous solution exchange with the charged sites on the support.131 This approach has been commonly used for the preparation of catalysts with easily exchangeable ions on supports, such as those in zeolites, heteropoly acids, or MOF, but has only recently been applied for the synthesis of SACs.132,133

A representative example of SACs prepared by the ion exchange method was demonstrated by Zhang et al., who utilized ion exchange followed by NaBH₄ reduction method to synthesize ion exchange resin supported AuPd alloy SAC.134

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**Table 5** Summary of metals used in the synthesis of SACs by photoreduction

| Method       | Synthesis of single-atom metals |
|--------------|---------------------------------|
| Photoreduction | Pt, Pd, Au, Co, Ni¹¹¹ |

**Table 6** Summary of metals used in the synthesis of SACs by galvanic replacement method

| Method                  | Synthesis of single-atom metals |
|-------------------------|---------------------------------|
| Galvanic replacement    | Pt, Ru,¹¹⁴,¹¹⁵ Pd, Cu, Au,¹¹⁶,¹²¹ Ag¹²⁸ |

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Fig. 11 Schematic illustration of the galvanic replacement process (here the galvanic replacement of Ag by Au is shown as an example). This figure has been adapted/reproduced from ref. 126 with permission from Wiley-Blackwell, copyright 2013.
With the increase of Au/Pd molar ratio, the continuous Pd ensembles on the ion exchange resin surface were gradually separated and eventually isolated by Au atoms, forming the Au alloyed Pd SAC (evidenced by the appearance of CO adsorption peaks on diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) spectra shown in Fig. 13). This catalyst was active without leaching for the Ullmann reaction of aryl halides under mild conditions in aqueous media, particularly effective for the activation of less reactive aryl chlorides.\(^{134}\)

The ion exchange method is effective in producing high loadings of single atoms on the surface of a support; however, only limited types of SACs can be synthesized via this method.

### 2.2.3.2 Templated hydrothermal method

The templated hydrothermal method was first adopted to synthesize SACs by the Thomas group. The authors used AlPO-18, a framework-substituted aluminophosphate, which could be hydrothermally treated with various divalent ions, such as Mn, Co and Zn,\(^{135-139}\) as a precursor for the synthesis of SACs.

The Co cations mainly existed in the following two states when they were incorporated into AlPO-18 with a high loading (about 10 at%): a substantial amount of Co\(^{3+}\) replacing the Al\(^{3+}\) sites in AlPO-18 and the other portion of Co\(^{3+}\) ions located at the opposite ends of each AlPO-18 cage.\(^{139}\) The existing states of Co\(^{3+}\) were detected via EXAFS, which suggested that they were singly dispersed. Similar arguments pertaining to an ionic active site were also obtained for a Fe-AlPO-31 catalyst, which behaved multi-functionally for the selective oxidation of cyclohexane to adipic acid in O\(_2\).\(^{135,139}\) In both of the cases, Co\(^{2+/3+}\) and Fe\(^{2+/3+}\) functioned predominantly as ionic oxidation catalysts. It has been shown that a combination of coordinative unsaturation at the ionic site and its ability to exhibit redox behaviour are essential requirements for its role as a catalytically active centre.

For the catalysts prepared by templated hydrothermal method, again, there is little doubt that in each case a single atom does act as a catalytically active site for reactions such as the selective oxidation of hydrocarbons.\(^{135-140}\) At the same time, unfortunately, only limited types of SACs could be synthesized via the templated hydrothermal method (Table 7).

### Table 7: Summary of precursors and metals for templated hydrothermal synthesis of SACs

| Method          | Precursor              | Synthesis of single-atom metals |
|-----------------|------------------------|---------------------------------|
| Templated hydrothermal | Mn\(^{2+}\), Co\(^{2+}\), Zn\(^{2+}\) (ref. 135–139) | Pt, Pd\(^{141}\), Rh, Ru, Au, Ir\(^{412}\) |
Fig. 14  (a) HAADF-STEM image and (b) EXAFS analysis of Pt₁/FeOₓ catalyst; (c)–(i) HAADF-STEM, XANES, EXAFS and corresponding EDX mapping of Pd SAC. This figure has been adapted/reproduced from ref. 3 and 147 with permission from Nature Publishing Group and Springer Nature, copyright 2011 and 2020.
2.2.3.3 Co-precipitation method. The co-precipitation method is another typical catalyst preparation approach, in which a soluble mixture of precursors for the active component, support and even promoter are co-precipitated by a suitable precipitant. SACs can be obtained by drying or calcining the resulting sediments.

The adoption of the co-precipitation method to synthesize SACs was initiated by Zhang et al.\(^3\)\(^{143}\) In their work, the mixture solution of chloroplatinic acid and ferric nitrate was co-precipitated in an alkaline environment, and the resulting precipitate was filtered, washed and calcined to obtain Pt\(_x\)/FeO\(_x\) catalyst as shown in Fig. 14a (Sample A: Pt loading was 0.17 wt% and Pt/Fe atomic ratio was 1/1430. Sample B: Pt loading was 2.5 wt% and Pt/Fe atomic ratio was 1/95). Pt\(_x\)/FeO\(_x\) exhibited remarkably high catalytic performance in CO oxidation and nitroarene hydrogenation reactions.\(^3\)\(^{143}\) Following the successful preparation of Pt\(_x\)/FeO\(_x\), the co-precipitation method was extended to synthesize other metallic catalysts, such as atomically dispersed Ir\(^{144}\)\(^{-146}\) and Pd\(^{147}\) (the existence of Pd single atoms was confirmed via HAADF-STEM, X-ray absorption near edge structure (XANES), EXAFS and corresponding energy dispersive X-ray spectroscopy (EDX) mapping, as shown in Fig. 14c–i).

Table 8 Summary of metals used in the synthesis of SACs by co-precipitation method

| Method         | Synthesis of single-atom metals |
|--------------|---------------------------------|
| Co-precipitation | Pt\(^{143}\), Ir\(^{144}\)\(^{-146}\), Pd\(^{147}\) |

The co-precipitation method is important for preparing composite oxides containing two or more uniformly dispersed metal elements.\(^3\)\(^{143}\) However, the metal loading is low. Moreover, many of the parameters in the catalyst preparation process including the solution addition speed, droplet size, stirring degree, reaction temperature, pH value and reaction time, have considerable influence on the properties and performance of the catalyst and need to be strictly controlled. In addition, some of the active metal atoms of catalysts prepared by the co-precipitation method are not exposed and cannot participate in the reaction, which reduces the overall performance of SACs (Table 8).

2.2.3.4 One-pot wet chemistry method. 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.\(^149\)\(^{-151}\) The one-pot wet chemistry method can be used to synthesize atomically dispersed Ru on ultrathin Pd nanoribbons via a two-step process, in which Pd nanoribbons are firstly obtained by heating a mixture of Pd(acac)\(_2\), polyvinylpyrrolidone, dimethylformamide and water in a CO atmosphere. Subsequently, a Ru salt is injected into the suspension of Pd nanoribbons to allow Ru to be singly dispersed onto the ultrathin Pd nanoribbons.\(^152\) Through this method, the content of singly dispersed Ru sites on Pd nanoribbons could be as high as 5.9%. The ultrathin Ru\(_x\)/Pd nanoribbons exhibited good catalytic selectivity for the hydrogenation of C=C bonds due to the remarkable inhibition of the hydrogenolysis pathway.\(^152\)

In addition, a series of gold pseudo-atom supported MOF catalysts (PSAC-Au/MOFs) could be prepared via the one-pot wet
| Classification          | Synthesis method            | Advantages                                                                 | Disadvantages                                                                                     |
|-------------------------|----------------------------|----------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------|
| Dry chemistry routes    | Atomic layer deposition    | (1) Precise control of parameters                                          | (1) Only materials with suitable ligands or functional groups could be chosen as support         |
|                         |                            | (2) Excellent deposition uniformity and reproducibility                    | (2) Not applicable for the commercial preparation                                                |
|                         |                            | (3) The loading of the singly dispersed atoms could be adjusted via regulating the number of cycles |                                                                                                  |
|                         | Pyrolysis synthesis        | Straightforward for the preparation of SACs                                | Requires high pyrolysis temperature                                                               |
|                         | Atom trapping              | The operation is simple                                                     | (1) Need to provide mobile atoms and support that could capture mobile species                    |
|                         |                            | (2) High temperature synthesis                                             | (2) High temperature synthesis Requires high energy atom/ion generator                             |
|                         |                            |                                                                             |                                                                                                  |
|                         | Ball-milling               | Simple, green, scalable production                                          | The catalysts are prone to agglomeration                                                           |
| Wet chemistry routes    | Facile adsorption          | Simple and easy to operate                                                  | Proper interaction between active metal components and catalyst support is required                |
|                         | Strong electrostatic       | Applicable for the preparation of high-quality precious metal SACs         | Adsorption behavior is affected by many factors                                                   |
|                         | adsorption                 |                                                                             |                                                                                                  |
|                         | Wetness impregnation       | Simple to operate                                                           | Generally metal atoms are not uniformly dispersed on the surface of support                        |
|                         | Photo reduction            | No special equipment is required, easy to implement                        | Catalytic active center generally is not uniform                                                  |
|                         | Galvanic replacement       | Simple, versatile                                                           | Limited by the requirement of an appropriate difference in electrochemical potentials between the two metals |
|                         | Cyclic voltammetry         | Less additives are demanded and no interfering products are generated      | An electrochemical station is needed and the operation cost is high                               |
|                         | Ion exchange               | It could produce highly loaded single atoms on the surface of the support  | Only applicable for the synthesis of limited types of SACs                                         |
|                         | Templated hydrothermal     | Simple, easy to operate                                                     |                                                                                                  |
|                         | Co-precipitation           | Applicable for preparing composite oxides containing two or more uniformly dispersed metal elements |
|                         | One-pot wet chemistry      | (1) No special experimental setup and multi-step reaction conditions are required, which is beneficial for large-scale production | (1) Preparation parameters have a great impact on performance                                     |
|                         | Metal leaching             | Preparation of monodispersed catalysts by a two-step method                 | (2) Some active atoms are not exposed and cannot participate in the reaction                      |
|                         | Flame spray pyrolysis      | (1) It could mix all precursors at the atomic level                          | (1) Limited by the solubility of various precursors                                               |
|                         |                            | (2) The shape and particle size of the catalysts can be effectively controlled | (2) Impurities and by-products of individual steps have an impact                                |
|                         |                            | (3) Large-scale production                                                  | (1) Suitable for a small number of certain metals and supports                                    |
|                         |                            |                                                                             | (2) Environmental pollution during the preparation process                                          |
|                         |                            |                                                                             | Few application examples                                                                        |
chemistry method on a large scale. The as prepared PSAC-Au/MOFs exhibited excellent catalytic activity in the hydrogenation of p-nitrophenol.\textsuperscript{153}

The one-pot wet chemistry method does not require special experimental setup and multistep reaction conditions; thus, it favours for large scale production. Moreover, high loading density of isolated metal is achievable via this approach. However, the one-pot synthesis approach is still challenging for the preparation of SACs due to the potential solubility limitations of the various precursors in the required reaction solvents and the influence of impurities and by-products generated in each separate step.

2.2.3.5 Metal leaching method. The metal leaching method is generally carried out by immersing the conventional supported metal catalysts in a dilute aqueous NaCN solution and then rinsing at a high pH NaOH solution at room temperature in the presence of O\textsubscript{2}. In this process, the metal nanoparticles are selectively eluted, with the metal cations remaining intact. This method was firstly adopted for extracting Au from gold mine\textsuperscript{154,155} and further developed to prepare metal oxides supported metal cation catalysts.\textsuperscript{156,157}

Via the leaching method, a series of singly dispersed Au catalysts could be prepared via a two-step process (deposition–precipitation followed by leaching approach), including Au/CeO\textsubscript{2},\textsuperscript{158–160} Au/Al\textsubscript{2}O\textsubscript{3},\textsuperscript{167} Au/Fe\textsubscript{2}O\textsubscript{3},\textsuperscript{165} AuLaCeO\textsubscript{x},\textsuperscript{161} Au/La\textsubscript{2}O\textsubscript{3},\textsuperscript{158} Au/La\textsubscript{2}O\textsubscript{2}SO\textsubscript{4} (ref. 168) and Au(OH)\textsubscript{3}/TiO\textsubscript{2}.\textsuperscript{158} Not only limited to Au, the leaching method has successfully extended its application to the synthesis of several other SACs, with singly dispersed Pt/CeO\textsubscript{2} catalyst as a typical example.\textsuperscript{156,156}

The metal leaching method is only applicable to a few certain metals and supports, and it is not suitable for the large-scale preparation of SACs in the foreseeable future due to the possible environmental pollution during the catalyst preparation process.

2.2.3.6 Flame spray pyrolysis method. 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. For instance, Muravev et al. used two methods, the traditional impregnation and flame spray pyrolysis, to synthesize Pd\textsubscript{1}/CeO\textsubscript{2} catalysts.\textsuperscript{169} For both of the two Pd\textsubscript{1}/CeO\textsubscript{2} catalysts, there were no Pd or PdO clusters on the surface of CeO\textsubscript{2} (as evidenced by HAADF-STEM, Fig. 15). However, during its evaluation in CO oxidation reaction, the Pd atoms in Pd\textsubscript{1}/CeO\textsubscript{2} catalyst prepared by the traditional impregnation method aggregated into metal clusters and deactivated rapidly. As for Pd\textsubscript{1}/CeO\textsubscript{2} catalyst prepared by flame spray pyrolysis method, Pd\textsuperscript{2+} penetrated into the lattice of CeO\textsubscript{2} (as shown in Fig. 15b). The surface Pd single atoms exhibited high sintering resistance under CO oxidation conditions.

Flame spray pyrolysis method has some advantages in the preparation of supported metal catalysts.\textsuperscript{170} (1) It could mix all precursors at the atomic level. (2) By changing the synthesis conditions, the shape and particle size of the catalysts can be effectively controlled. (3) The catalysts could be produced on a large scale, with a single step and high efficiency. However, so far, there are few examples of high-temperature catalytic applications for the synthesis of SACs by flame spray pyrolysis, and it is impossible to infer from the existing literature whether flame spray pyrolysis is indeed a feasible method for high-temperature SACs.

2.2.3.7 Other wet chemistry strategies for the synthesis of SACs. In addition to the above methods, several other wet chemistry strategies have also been predicted or proved capable of synthesizing SACs, such as metal–ligand self-assembly method, electrochemical potential window strategy and so on. For example, electrochemical potential window strategy is proposed to be effective in producing high-loading and high-purity SACs, such as Pt\textsubscript{1}/N-graphene, Pd\textsubscript{1}/N-graphene, Ni\textsubscript{1}/N-graphene, Pt\textsubscript{1}/Fe\textsubscript{2}O\textsubscript{3}, Pd\textsubscript{1}/Fe\textsubscript{2}O\textsubscript{4} and Ni\textsubscript{1}/Fe\textsubscript{2}O\textsubscript{4} \textsuperscript{71} Spatial sites separation strategy could be used to fabricate carbon-supported atomically isolated Ni catalyst, which is highly active in electrochemical CO\textsubscript{2} reduction reaction.\textsuperscript{72} Post-synthesis method, including spatial confining, freeze-drying and reducing steps, has been verified efficient for the construction of Pd\textsubscript{1}/silicoaluminophosphate-31 (Pd\textsubscript{1}/SAPO-31) catalyst.\textsuperscript{73}

3. Summary and outlooks

SACs are an important category of catalysts. To date, significant efforts have been devoted to develop SACs and tens of methods have been adopted for the synthesis of different types of catalysts at an atomic scale. Based on the above discussions, a summary of the advantages and disadvantages of wet and dry chemical routes is listed in Table 9.

In spite of the advantages and the rapid progress, challenges and tasks remain.

3.1 It is challenging to exclude the co-existence of continuously packed sites

Due to the un-uniformity nature of heterogeneous catalysts, over most of the as-prepared SACs, continuously packed sites...
coexist with singly dispersed sites (Fig. 16). It is challenging to obtain SACs with uniform-structured active sites. Therefore, there are great significance and challenges to develop novel approaches to synthesize SACs effectively.

3.2 Technologies for the characterization of SACs need innovation

The most important thing in the study of SACs is to determine the existence and spatial distribution of isolated single atoms. The intuitive method is to directly image the single atoms on the surface of the support via electron microscopy, such as HAADF-STEM. However, only a limited portion of the catalysts is observed, which could not fully reflect the properties of SACs. EXAFS and XANES techniques have been widely used to obtain information on the structural details of SACs, nevertheless, the operation is quite complicated and the analysis of EXAFS and XANES data are complex, which pose obstacles to the reproducibility of the final results. In addition, DRIFT could also be used to assess the presence of individual metal atoms using suitable probe molecules such as CO, NH₃, pyridine, etc. Especially, CO FTIR/DRIFT spectroscopy is very useful for detecting noble metals, whereas its application is limited by the interactions between the probe molecules and SACs. Raman spectrum is susceptible to errors caused by external influences, but it could be used to identify M–O–Ce [M = Pt, Rh, Ru] linkages. In conclusion, there is no such a technique that could directly and fully tell the structure of SACs. It is necessary to combine multiple techniques to characterize SACs accurately and effectively. Moreover, the development of new characterization techniques is of great significance for the development of SACs.

3.3 The singly dispersed sites over SACs might undergo transformation under the realistic reaction atmosphere

Over SACs, the singly dispersed atoms are regarded as the active sites to drive reactions. Some catalysts might undergo transformations under the realistic reaction atmosphere; therefore, it is necessary to confirm and determine the singly dispersed sites over SACs via in situ/operando techniques. Although several in situ/operando techniques have been used for the characterization of SACs, including HAADF-STEM, EXAFS, XANES, DRIFT, atmospheric pressure X-ray photoelectron spectroscopy, and high energy resolution fluorescence detected XANES, each technique has strengths and limitations. There is still lack of techniques which can readily provide information on the structure of each singly dispersed atoms on SACs. Therefore, the combination of these advanced techniques is highly desired to characterize SACs readily and precisely.

3.4 Application areas and development prospects of SACs

The applications of SACs span from traditional thermal-driven catalysis, photocatalysis as well as electrochemical catalysis, including CO oxidation, hydrogenation, CO₂ reduction, NO₂ reduction, hydrogen evolution reaction, oxygen reduction reaction and so on. The common characteristics of these reactions is that even a singly dispersed atom could drive its occurrence. With the development of SACs, it is prospected that the applications of SACs in more other reactions would be explored and the performance of SACs could be further enhanced.

In conclusion, SACs are a promising research area. Even though the research on SACs has made great progress, there is lack of techniques which could readily provide information on the nature of SACs under operation conditions and the synthesis of SACs with unified structures remains challenging. Therefore, more efforts are still needed and there is enough space to advance this research further.

Conflicts of interest

There are no conflicts to declare.

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