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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.[1,2] 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 FeO_x (named as Pt_1/FeO_x) was much superior in CO oxidation reaction than its nanoparticle counterpart.[3] 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 (M_1/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

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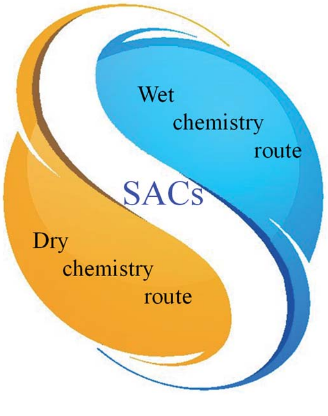

Scheme 1 Classification of the synthesis approaches of SACs.

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[21–28] and amorphous Al_2O_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_1/graphene, Pd_1/graphene and Co_1/graphene, have been successfully prepared.[42–48]

Here the synthesis of Co_1/SiO_2 is taken as an example.[36] 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

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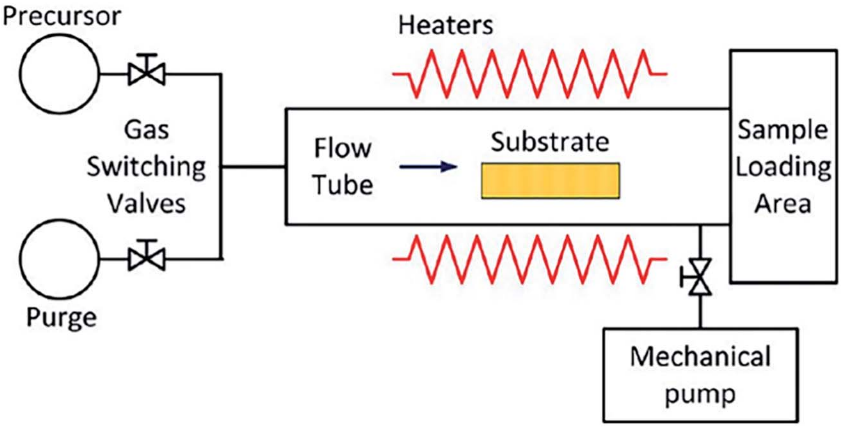

Fig. 1 Schematic illustration of an ALD reactor. This figure has been adapted/reproduced from ref. 32 with permission from American Chemical Society, copyright 2021.

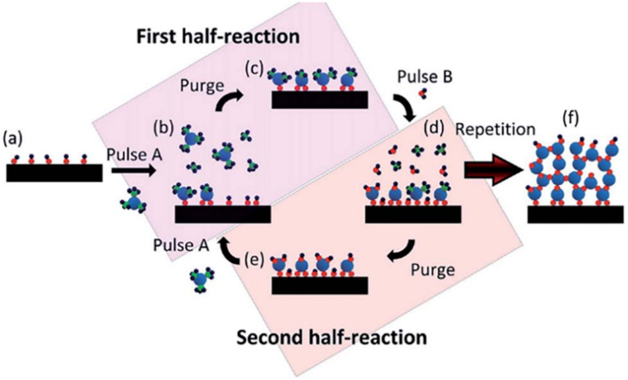

Fig. 2 Schematic illustration of the preparation of SACs by dosing two distinct precursors sequentially to the matrix. This figure has been adapted/reproduced from ref. 32 with permission from American Chemical Society, copyright 2021.

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.[36]

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.[31,49–54] 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 *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).

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 *via* this method in the past decade.[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 *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 *via* this method could be high up to 4 wt%.[77] Other metal–nitrogen–carbon SACs (M = W, Mo, Cu, Zn, Cr, Mn, Fe and Ni) could also be obtained *via* the pyrolysis synthesis method with bimetallic-organic frameworks as precursors.[78–83] (2) When Co phthalocyanine–silica colloid

Table 1 The metals used in the synthesis of SACs by ALD

Method	Singly dispersed metals
ALD	Pt, Pd, Co, Cu, Fe, Ni, Ti, Zn[32]

composite was used as precursor, singly dispersed Co catalyst Co–N$_x$/C could be prepared by the pyrolysis of the precursor and the subsequent removal of silica template and cobalt nanoparticles.[84] The as prepared Co–N$_x$/C SAC showed extremely high activity, chemoselectivity and stability toward the reduction of nitro compounds by H_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,[85] and this Co–N–C catalyst was reported to show high catalytic activity (turnover frequency, TOF, of 3.8 s^{-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_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.[86]

Taking the Co–N–C catalyst derived from the pyrolysis of cobalt–phenanthroline complexes on a mesoporous carbon support and Pd_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).[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_1/CeO_2 catalyst was successfully achieved by aging a mixture of Pt/Al_2O_3 and CeO_2 in air at 800 °C to promote the

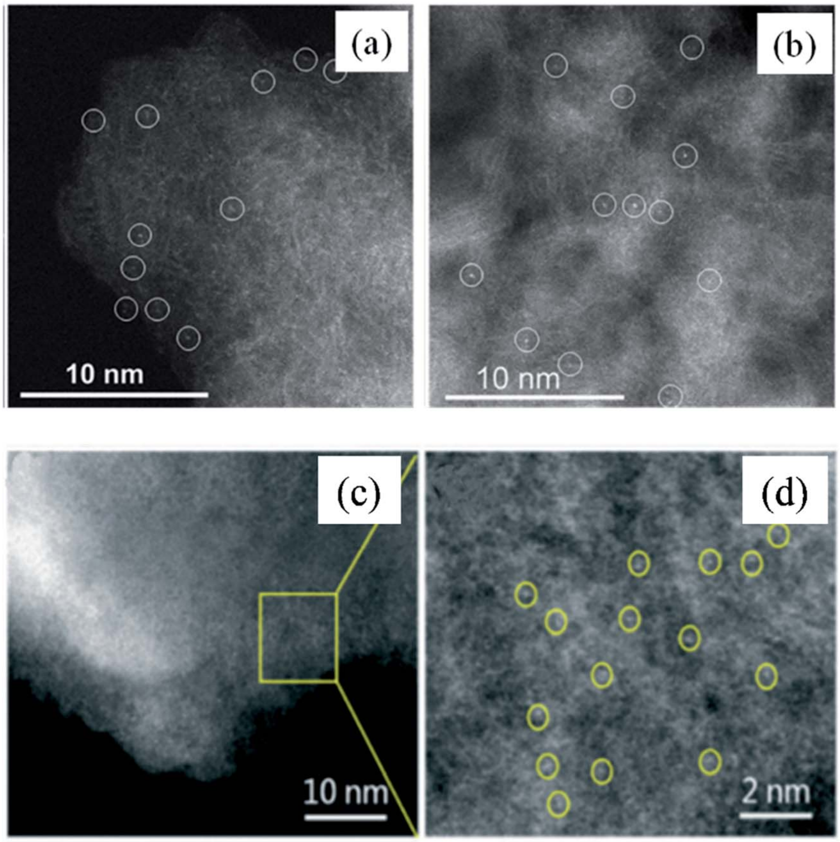

Fig. 3 HAADF-STEM image of Co–N–C catalyst prepared by the pyrolysis synthesis method (a and b) and Pd_1/N-graphene catalyst prepared by the pyrolysis synthesis method (c and d). These figures have been adapted/reproduced from ref. 85 and 86 with permission from American Chemical Society and Royal Society of Chemistry, copyright 2015 and 2022.

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[77]	W, Mo, Cu, Zn, Cr, Mn, Fe, Ni[78–83]

transfer of Pt from Al_2O_3 to CeO_2, where it was strongly anchored as single site (Fig. 4).[87] CeO_2 nanorods were more effective than CeO_2 cubes at trapping the Pt atoms. Aging at high temperatures ensured that only the most stable binding sites on CeO_2 were occupied, and thus yielded a sintering-resistant atomically dispersed catalyst.[87] 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).[88]

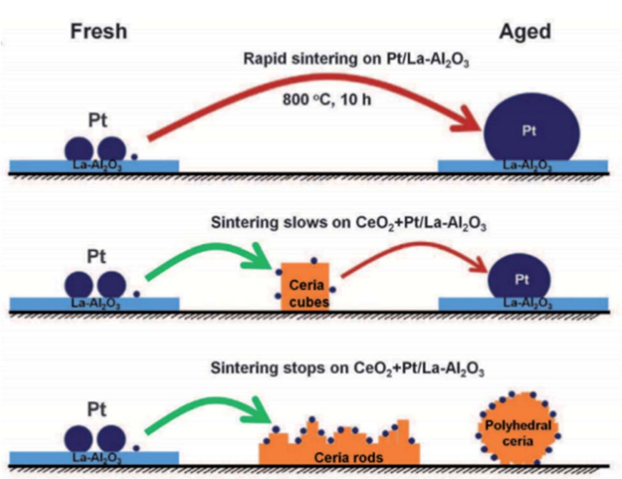

Fig. 4 Illustration of the synthesis of Pt_1/CeO_2 SAC *via* the trapping of mobile Pt by CeO_2 due to the migration of Pt at high temperatures. This figure has been adapted/reproduced from ref. 87 with permission from American Association for the Advancement of Science, copyright 2016.

The atom trapping method is applicable to synthesize a series of SACs, including Pd,[88] Au,[88] Cu[89] and Ni[90] 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.[88]

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).

2.1.4 Two-step doping method.

Two-step process is effective for doping metal elements atomically into graphene. It is carried out *via* two-steps. Firstly, vacancies are created *via* high energy atom/ion bombardment; then, the vacancies are filled with desired dopants (Fig. 6). Several different elements (including Pt, Co, and In) have been introduced as dopants in the single atom form into graphene *via* the two-step doping method.[91,92]

Table 3 Summary of metals used in the synthesis of SACs by atomic trapping

Method	Synthesis of single-atom metals
Atom trapping	Pt,[87] Ru,[87] Co,[87] Pd,[88] Au,[88] Cu,[89] Ni[90]

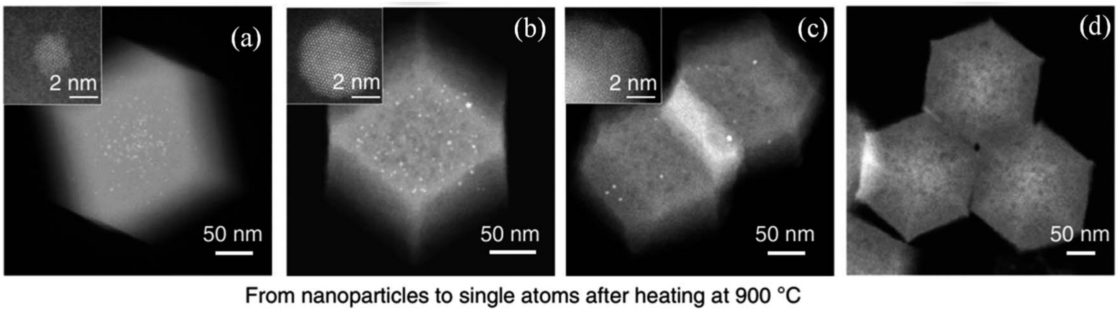

Fig. 5 Evolution of Pd nanoparticles on ZIF-8 to single atoms *via* HAADF-STEM. (a) Pd nanoparticles on ZIF-8, (b) intermediate I, (c) intermediate II and (d) Pd single atoms. This figure has been adapted/reproduced from ref. 88 with permission from Nature Publishing Group, copyright 2018.

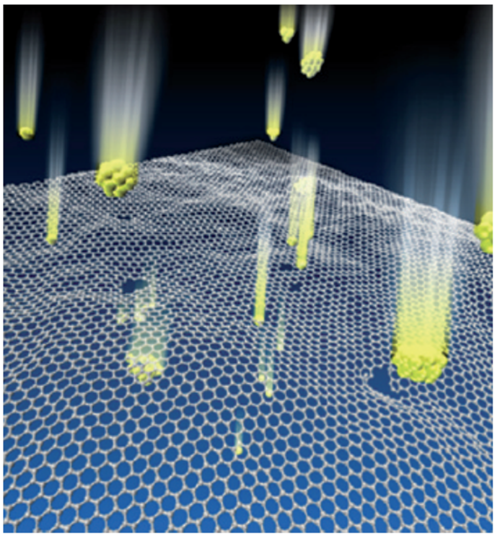

Fig. 6 Schematic illustration of the high-energy particle bombardment process. This figure has been adapted/reproduced from ref. 91 and 92 with permission from American Chemical Society, copyright 2012 and 2015.

Table 4 Summary of metals used in the synthesis of SACs by two-step doping

Method	Synthesis of single-atom metals
Two-step doping	Pt, Co, In,[91,92] Fe,[93] Cu,[93] Ni[93]

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 is reported that the as-prepared Pt_1/Co catalyst gave excellent performance in the hydrodeoxygenation of 5-hydroxymethylfurfural.[94] The HAADF-STEM image clearly revealed that the platinum atoms in the Pt_1/Co catalyst were finely dispersed on the Co sup5port without obvious Pt aggregation (Fig. 7a), indicating that the ball milling method can realize the scale-up production of SACs.

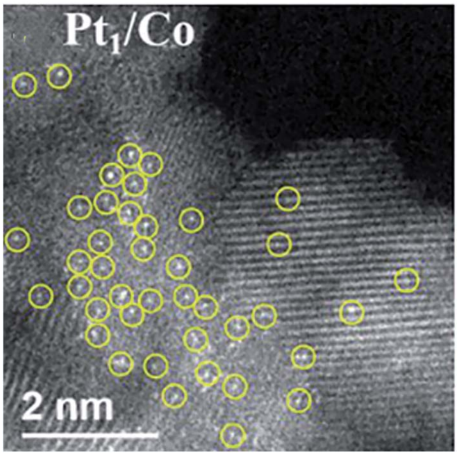

Fig. 7 HAADF-STEM image of Pt_1/Co. This figure has been adapted/reproduced from ref. 94 with permission from American Chemical Society, copyright 2020.

This work enables kilogram-scale production of Pt_1/Co without scale-up effects, with great potential for practical applications. It provides a facile and scalable method for the synthesis of single-atom alloy catalysts.[95]

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.[96] It was reported that, over Au_1/FeO_x catalyst, Au single atoms were separately dispersed on iron oxide crystallites,[96] and the Au atoms were positively charged and anchored covalently to FeO_x.[96] The as-prepared Au_1/FeO_x catalyst exhibited ultrahigh stability and remarkable catalytic performance for CO oxidation at a wide temperature range.[96]

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.

2.2.1.2 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,

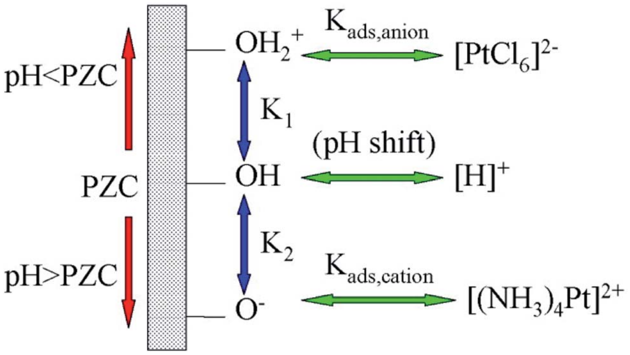

Fig. 8 Mechanism of strong electrostatic adsorption method in the preparation of SACs. This figure has been adapted/reproduced from ref. 98 with permission from American Chemical Society, copyright 2008.

the metal ion complexes are $[(NH_3)_4Pt]^{2+}$, $[H]^+$ or $[PtCl_6]^{2-}$ (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_n 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 $Pt_3Ni(111)$ 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 γ-Al_2O_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 γ-Al_2O_3 and leading to the generation of unsaturated Al sites.[106] By utilizing these unsaturated Al sites on γ-Al_2O_3, which possess the capacity to stabilize single Pt atoms, Kwak *et al.* successfully prepared a single atom Pt_1/γ-Al_2O_3 catalyst by impregnating γ-Al_2O_3 with an aqueous solution of Pt salt.[107] After introducing the singly dispersed Pt atoms on γ-Al_2O_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.[107] The HAADF-STEM images of 1 wt% Pt/γ-Al_2O_3 revealed that most of the Pt species were atomically dispersed and the HAADF-STEM images of 10 wt% Pt/γ-Al_2O_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_1/TiO_2. The surface of the TiO_2 film was positively charged and attracted a large amount of $[PdCl_4]^{2-}$ anions, which enriched on the surface of the 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_1/TiO_2 could activate hydrogen *via* a pathway

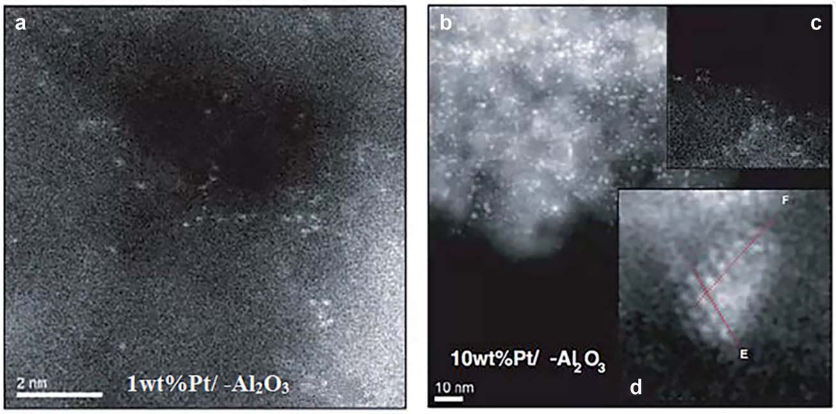

Fig. 9 HAADF-STEM images of (a) 1 wt% Pt/γ-Al_2O_3 and (b) 10 wt% Pt/γ-Al_2O_3. The insets in Fig. 8b showed the presence of (c) atomically dispersed Pt and (d) Pt cluster/nanoparticles. This figure has been adapted/reproduced from ref. 107 with permission from American Association for the Advancement of Science, copyright 2009.

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

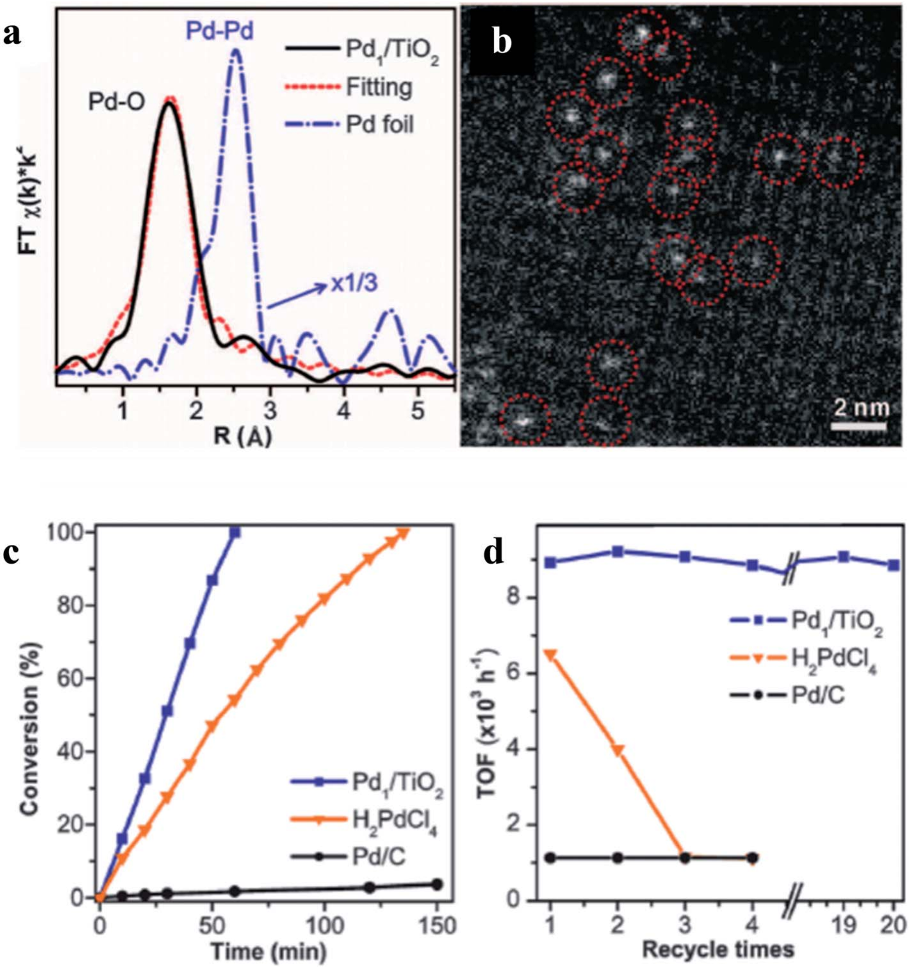

Fig. 10 (a) EXAFS analysis, (b) HAADF-STEM image as well as (c and d) catalytic performance of 1.5 wt%Pd/TiO_2 catalyst in styrene hydrogenation reaction. This figure has been adapted/reproduced from ref. 110 with permission from American Association for the Advancement of Science, copyright 2016.

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

Method	Synthesis of single-atom metals
Photoreduction	Pt, Pd, Au, Co, Ni[111]

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.[112,113] 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] PdAu,[119–121] 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).

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] Ag[128]

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 Pt_1/CoP/NF catalyst *via* CV method.[129] Pd_1–N_8/CNT, a N_8^- 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 $NaBH_4$ reduction method to synthesize ion exchange resin supported AuPd alloy SAC.[134]

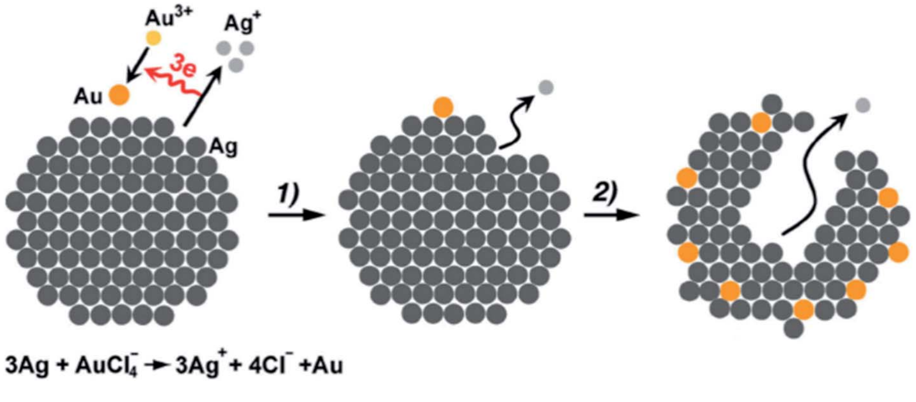

Fig. 11 Schematic illustration of the galvanic replacement process (here the galvanic replacement of Ag by Au is shown as an example). This figure has been adapted/reproduced from ref. 126 with permission from Wiley-Blackwell, copyright 2013.

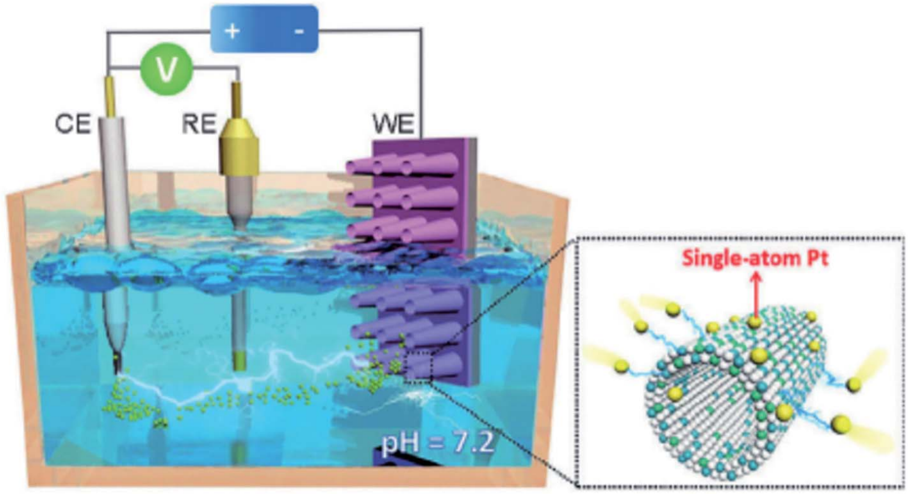

Fig. 12 Schematic illustration for the synthesis of Pt SAC *via* CV method. This figure has been adapted/reproduced from ref. 129 with permission from John Wiley and Sons Ltd, copyright 2017.

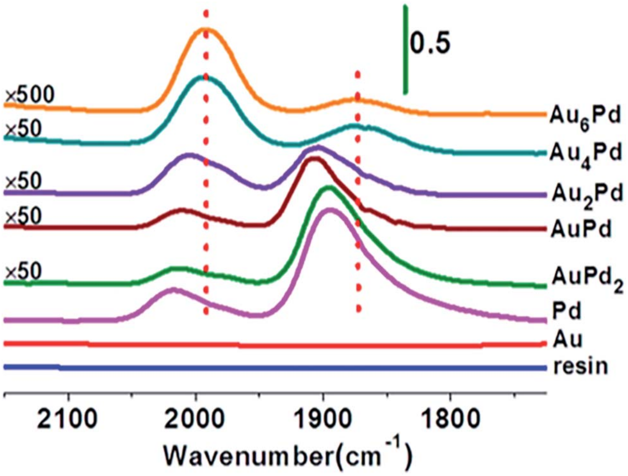

Fig. 13 DRIFT spectra of CO adsorption on Au–Pd/resin catalysts with different Au/Pd atomic ratios. This figure has been adapted/reproduced from ref. 134 with permission from American Chemical Society, copyright 2014.

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+}/Co^{3+} and Fe^{2+}/Fe^{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[142]

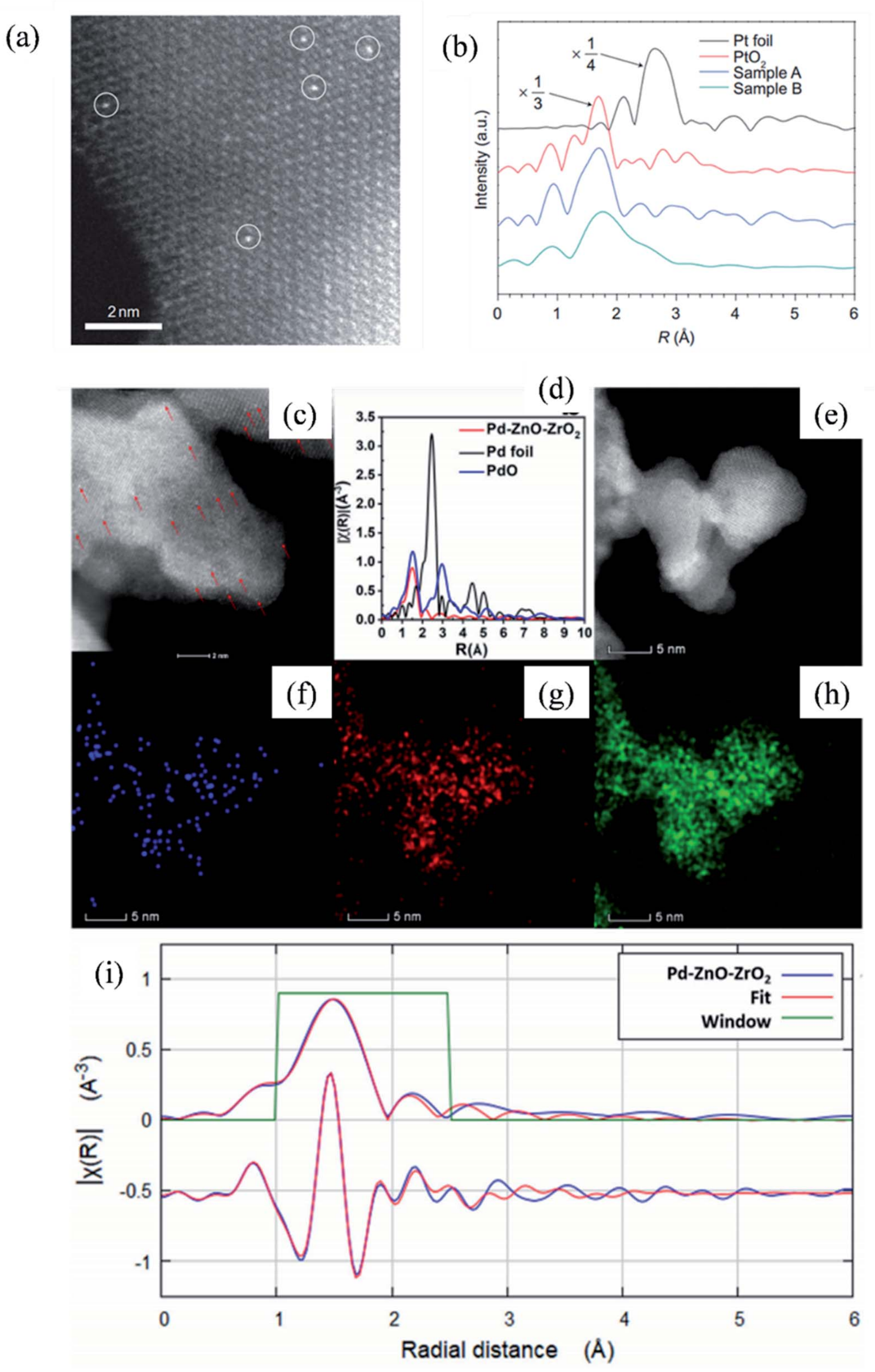

Fig. 14 (a) HAADF-STEM image and (b) EXAFS analysis of Pt_1/FeO_x catalyst; (c)–(i) HAADF-STEM, XANES, EXAFS and corresponding EDX mapping of Pd SAC. This figure has been adapted/reproduced from ref. 3 and 147 with permission from Nature Publishing Group and Springer Nature, copyright 2011 and 2020.

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_1/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_1/FeO_x exhibited remarkably high catalytic performance in CO oxidation and nitroarene hydrogenation reactions.[3,143] Following the successful preparation of Pt_1/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.[148] 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_1/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

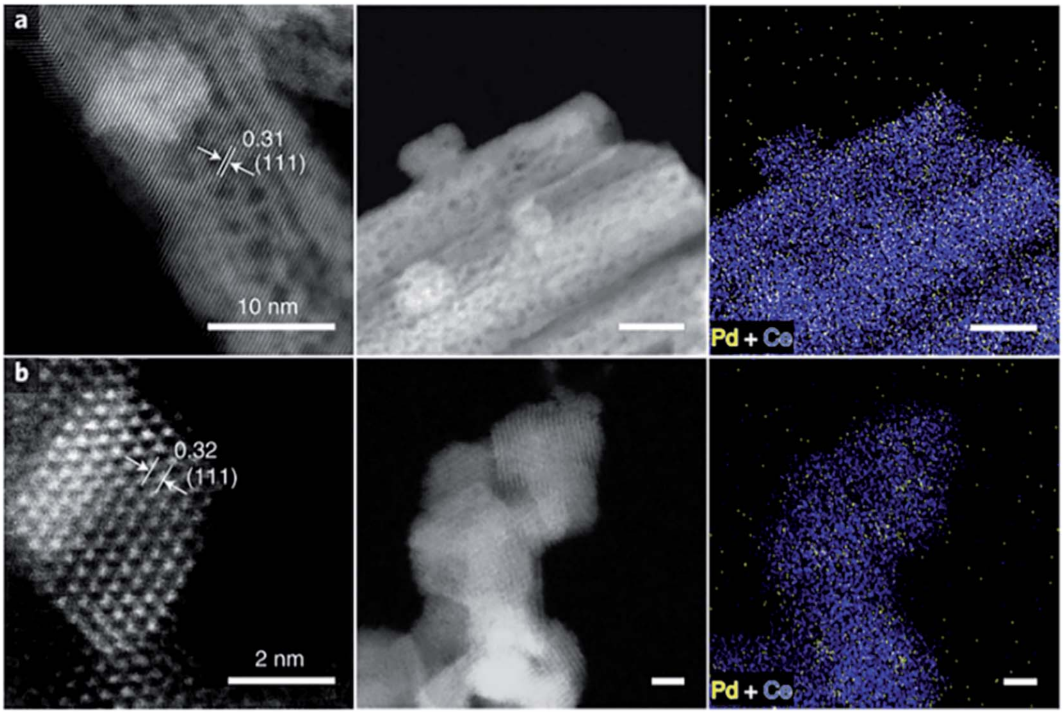

Fig. 15 Structure HAADF-STEM image of Pd_1/CeO_2 catalyst. (a) By impregnation method and (b) by flame spray pyrolysis. This figure has been adapted/reproduced from ref. 169 with permission from Nature Publishing Group, copyright 2021.

Table 9 Summary of the advantages and disadvantages of wet and dry chemical routes

Classification	Synthesis method	Advantages	Disadvantages
Dry chemistry routes	Atomic layer deposition	(1) Precise control of parameters (2) Excellent deposition uniformity and reproducibility (3) The loading of the singly dispersed atoms could be adjusted *via* regulating the number of cycles	(1) Only materials with suitable ligands or functional groups could be chosen as support (2) Not applicable for the commercial preparation
	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
	Two-step doping	High stability	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 adsorption	Applicable for the preparation of high-quality precious metal SACs	Adsorption behavior is affected by many factors
	Wetness impregnation	Simple to operate	Generally metal atoms are not uniformly dispersed on the surface of support
	Photoreduction	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	Only applicable for the synthesis of limited types of SACs
	Co-precipitation	Applicable for preparing composite oxides containing two or more uniformly dispersed metal elements	(1) Preparation parameters have a great impact on performance (2) Some active atoms are not exposed and cannot participate in the reaction
	One-pot wet chemistry	(1) No special experimental setup and multi-step reaction conditions are required, which is beneficial for large-scale production (2) High loading of isolated metals can be achieved	(1) Limited by the solubility of various precursors (2) Impurities and by-products of individual steps have an impact
	Metal leaching	Preparation of monodispersed catalysts by a two-step method	(1) Suitable for a small number of certain metals and supports (2) Environmental pollution during the preparation process
	Flame spray pyrolysis	(1) It could mix all precursors at the atomic level (2) The shape and particle size of the catalysts can be effectively controlled (3) Large-scale production	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.[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 diluted aqueous NaCN solution and then rinsing at a high pH NaOH solution at room temperature in the presence of O_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[154,155] and further developed to prepare metal oxides supported metal cation catalysts.[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_2,[158–166] Au/Al_2O_3,[167] Au/Fe_2O_3,[165] AuLaCeO_x,[161] Au/La_2O_3,[168] Au/$La_2O_2SO_4$ (ref. 168) and Au$(OH)_x$/TiO_2.[156] 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_2 catalyst as a typical example.[160,166]

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_1/CeO_2 catalysts.[169] For both of the two Pd_1/CeO_2 catalysts, there were no Pd or PdO clusters on the surface of CeO_2 (as evidenced by HAADF-STEM, Fig. 15). However, during its evaluation in CO oxidation reaction, the Pd atoms in Pd_1/CeO_2 catalyst prepared by the traditional impregnation method aggregated into metal clusters and deactivated rapidly. As for Pd_1/CeO_2 catalyst prepared by flame spray pyrolysis method, Pd^{2+} penetrated into the lattice of CeO_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.[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.

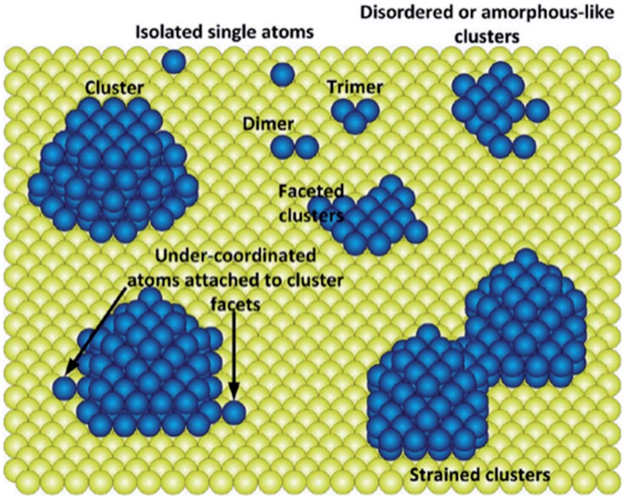

Fig. 16 Schematic illustration showing the co-existence of singly dispersed sites and continuously packed sites. This figure has been adapted/reproduced from ref. 32 with permission from American Chemical Society, copyright 2021.

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_1/N-graphene, Pd_1/N-graphene, Ni_1/N-graphene, Pt_1/Fe_3O_4, Pd_1/Fe_3O_4 and Ni_1/Fe_3O_4;[171] Spatial sites separation strategy could be used to fabricate carbon-supported atomically isolated Ni catalyst, which is highly active in electrochemical CO_2 reduction reaction;[172] Post-synthesis method, including spatial confining, freeze-drying and reducing steps, has been verified efficient for the construction of Pd_1/silicoaluminophosphate-31 (Pd_1/SAPO-31) catalyst.[173]

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, NH_3, 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,[174] hydrogenation,[175,176] CO_2 reduction,[177,178] NO_x reduction,[179] hydrogen evolution reaction,[180,181] oxygen reduction reaction[182,183] 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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