



Synthesis of Single-Atom Catalysts Through Top-Down Atomization Approaches

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Single-atom catalysts (SACs) have emerged as a hot research topic in recently years, and have been intensively investigated for energy storage and conversion applications. Significant advances in the synthesis of SACs have been achieved through enormous efforts in this area, however, their application is hindered by the low active site loading and poor long-term stability. In contrast with other methods, atomization, in which the SACs are synthesized from transformation of the nanoparticles to atomic sites, is a very attractive and innovative top-down approach to achieve high-density supported active sites with outstanding stability. However, limited attention has been paid to this area, despite the significant advances achieved in the past two years. In this short review, we discuss in detail the latest advances in atomization approaches for the synthesis of SACs and highlight the associated advantages and opportunities.

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INTRODUCTION

Nanomaterials are widely employed in environmental protection, energy storage/conversion, petrochemical engineering, and other fields (Amin et al., 2014; Abdalla et al., 2018; Hodges et al., 2018). In particular, they exhibit excellent properties and play a critical role in energy-related areas (Bevilacqua et al., 2015; Mao and Hatton, 2015; Cheng et al., 2016a; Cheng et al., 2018). The typical size of these materials is around 10 nm, which endows them with a larger specific surface area and exposed catalytic sites (Cheng et al., 2014; Cheng et al., 2015). Owing to the high cost and low abundance of precious metals, scientists and engineers are directing their efforts to increase the catalytic efficiency and utilization of the individual precious metal atoms by decreasing the nanoparticle (NP) size (Shao et al., 2011; Cargnello et al., 2013). Nevertheless, this reduced sizes cannot meet the demands of green chemistry applications, which require that most atoms of the nanomaterial participate in the catalytic reactions, in order to maximize their utilization (Yang et al., 2013). Noble metal reduction has attracted enormous attention, and approaches to reduce the NP size to clusters or even single atoms have been investigated (Shao et al., 2011; Reske et al., 2014; Cheng et al., 2016b). In contrast with supported NPs, which contain surface-active centers with different coordination environments, single-atom catalysts (SACs) consist of separated atoms, which endows these materials with very good uniformity (Zhang and Zheng, 2016; Kim et al., 2018). This reduces the complexity of the NPs and provides an effective approach to obtain homogenous catalysts.

SACs have attracted wide attention in recent years because of optimal atom utilization, controlled metal coordination environments, unique electronic properties, and homogeneous distribution of catalytic active site (Liu, 2017; Chen et al., 2018a; Cheng et al., 2018; Zhang et al., 2018). The

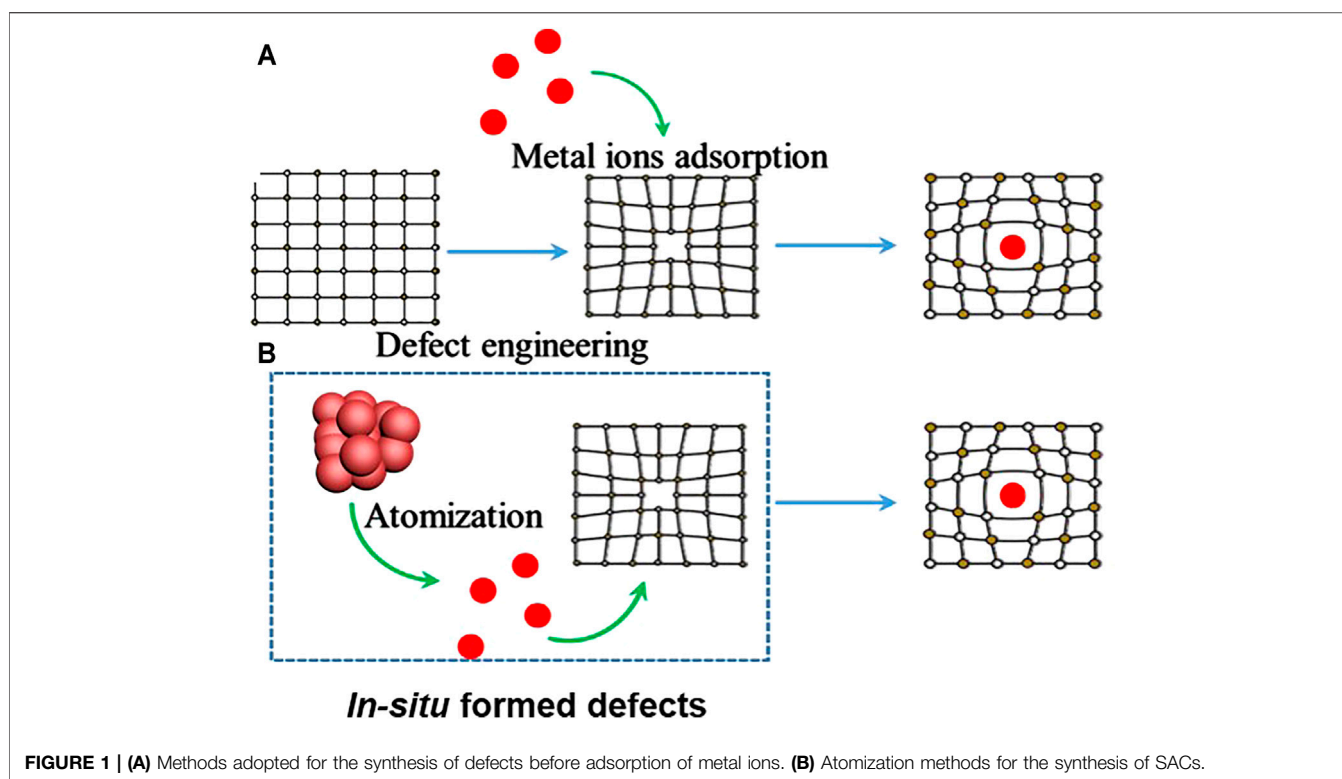


FIGURE 1 | (A) Methods adopted for the synthesis of defects before adsorption of metal ions. **(B)** Atomization methods for the synthesis of SACs.

electronic configurations of the highly dispersed atoms can be tuned by modifying the coordination environments, resulting in a class of materials with unique properties (Huang et al., 2012; Deng et al., 2015; Fei et al., 2015; Xiao et al., 2019; Lei et al., 2020). The distinctive properties of the SACs have attracted considerable interest, especially in the area of catalysis.

Owing to their high surface energy, SACs are loaded on supports and are normally referred to as supported SACs (Liu, 2017; Chen et al., 2018a; Cheng et al., 2018; Zhang et al., 2018). The use of SACs has been explored for various applications, such as oxygen reduction/evolution reactions (Zhang et al., 2017; Pan et al., 2018; Yang et al., 2018), carbon dioxide reduction (Cheng et al., 2019b; Cheng et al., 2019c), nitrogen reduction (Zhang R. et al., 2019), and organic synthesis (Zhang et al., 2016). In the past several years, substantial efforts have been dedicated to develop new SACs for a variety of applications, and novel methods have been employed for their synthesis (Szuromi, 2016; Liu, 2017; Cheng et al., 2019b). Recent studies found that SACs can be synthesized by atomization of NPs; this novel strategy provides a route to synthesize SACs with high loading and superior stability. In this review, we first summarize the synthesis methods for SACs and the chemical interaction between the single atoms and their supports. Then, we describe atomization approaches for SAC synthesis and discuss the associated opportunities.

THE ROAD TO ATOMIZATION APPROACHES

The synthesis of SACs remains a hot topic, a large number of methods have been developed. These include wet-chemistry,

pyrolysis, atomic layer deposition, special confinement (Yang et al., 2013; Wang et al., 2018a; Zhang et al., 2018). The key challenge in SAC synthesis is to avoid the aggregation of the metal atoms resulting from the high surface energy of the atomically dispersed metal atoms. The atomic sites are stabilized through strong metal–support interactions on supports such as metals, metal oxides, chalcogenides, and carbon materials (Huang et al., 2012; Wang et al., 2018c; Xiao et al., 2019; Lei et al., 2020). A strong interaction between metal atoms and support is required to stabilize the dispersed metal atoms (Cheng et al., 2019b). Moreover, a strong coordination environment is the prerequisite to obtain stable SACs. The strong interaction between metal atoms and support will unavoidably affect the properties of both components (Yang et al., 2013; Cheng et al., 2019b), thus offering great opportunities for designing catalysts with controlled characteristics (Yang et al., 2013; Cheng et al., 2019b).

The key step in SAC synthesis is to control the metal–support interactions (Liu, 2017). This interaction is highly dependent on the anchoring sites, such as defects or functionalities introduced to immobilize the metal atoms (Liu, 2016). The ultimate goal in the synthesis process is to create anchoring sites for the metal atoms (Lee et al., 2008). These sites can be created before supporting the metal atoms, or formed *in situ* at high temperature, simultaneously with the single-metal atomic sites (Figure 1A). In the case of the initial preparation of anchoring sites for stabilizing the metal atoms, a number of methods have been developed since the advent of SACs. They include wet chemistry (Chen et al., 2018a; Liu et al., 2020), atomic layer deposition (Cheng and Sun, 2017), and photochemical reduction

(Wei et al., 2017) strategies. In these methods, the supports are initially treated by etching or functionalization to provide defect sites able to stabilize the isolated metal atoms (Zhang Y. et al., 2019). The introduction of defects or ligands of complexes on the support surface facilitates the chemical combination between single atoms and substrate. Therefore, regardless of the wet chemistry, atomic layer deposition, or photochemical reduction approach employed, the success of the synthesis does not depend on how the precursor is introduced, e.g., *via* solvent or vapor, but relies on the anchoring sites provided. In order to stabilize the atomically dispersed metal atoms, the SACs should normally be annealed at high temperature to create a coordination strong enough to stabilize the atoms during the catalytic process; however, the annealing process unavoidably leads to aggregation of the metal atoms. More importantly, surface defect engineering normally provides a limited amount of surface anchoring sites and leads to weak binding before annealing; this inevitably results in aggregation of metal atoms and low loading of single atoms, which limits the application of this approach in catalysis.

In practice, a good catalyst should have a high turnover frequency and a large number of accessible active sites, as well as good stability (Won-Jun et al., 2018). Normally, the turnover frequency is strongly dependent on the type of active sites, the coordination environment, and the support, which can affect the electronic structure of the active sites. Enormous efforts have been dedicated to develop new catalysts able to achieve a high turnover frequency through control of the coordination environments (Munnik et al., 2015; Gao et al., 2019; Li et al., 2020a). Because the high temperature can normally create more dynamic defects, the *in situ* formation of defects during the annealing process is attracting increasing attention (Hiroshi, 2014). Taking carbon-supported SACs as an example, non-metal dopants such as N, P, and S could form defects able to stabilize the single metal atoms and avoid their aggregation or migration during the annealing process (Zhang Y. et al., 2019). During the pyrolysis process, metal atoms can be anchored by the *in situ*-formed defects, providing a strategy to achieve high-density atomic sites. As a further route to avoid aggregation, spatial confinement strategies can be employed to further prevent the migration of single atoms, especially when large amounts of metal precursor are introduced (Li Z. et al., 2020). The materials employed for spatial confinement are porous systems such as metal-organic frameworks (MOFs), covalent organic frameworks (COFs), carbon nitrides, lamellar materials, graphdiyne, porous carbon, and zeolites (Li Z. et al., 2020). Unfortunately, these strategies normally leads to encapsulation of the active sites inside the structure rather than on the surface, which results in low utilization of metal atoms (Hou et al., 2020).

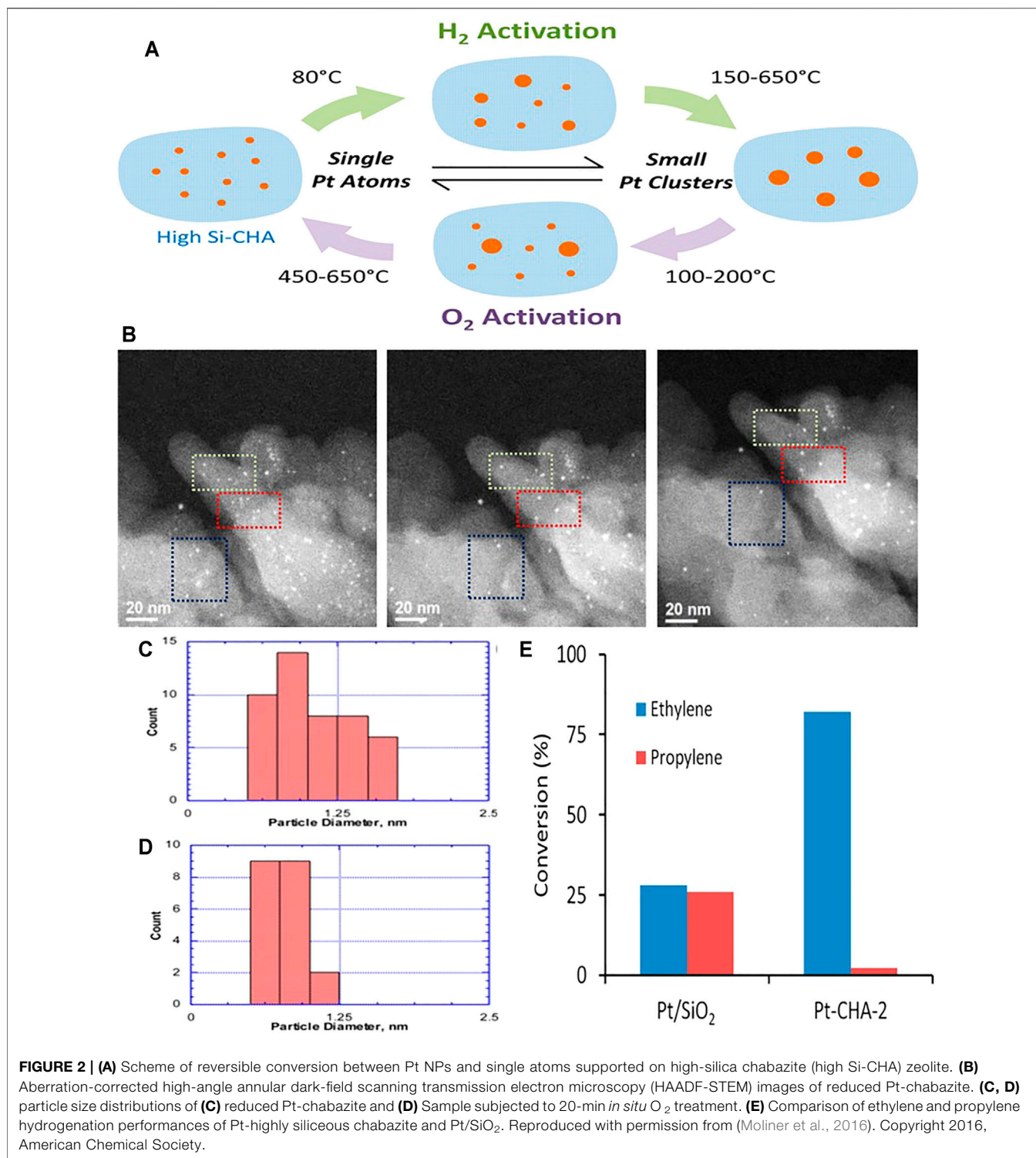
Although the development of SACs with a high density of surface-active sites is critically important, this is not an easy task. One of the important strategies to achieve a high weight content of single atoms over carbon is to simultaneously create defects for trapping single atoms (Wang J. et al., 2018). In this process, the *in situ*-created defects will be stabilized and thus increase the metal loading, because high-temperature annealing can create a huge number of dynamic defects. The latter can trap the metal atoms to form a stable

coordination environment, leading to a high loading of surface-supported single atoms with high stability.

Intriguingly, recent research found that metal NPs can be dispersed into atoms at high temperatures (Hermenegildo, 2014). Conventionally, owing to the thermal migration of metal atoms, single metal atoms or ultrafine metal NPs with high surface free energy tend to aggregate into larger particles under high-temperature conditions, in a process called Ostwald ripening (Lochhead, 2017). Once these migrating atoms are effectively trapped by the dynamic defects at high temperature, atomically dispersed metal sites are formed. Therefore, anti-Ostwald ripening is an efficient way to obtain SACs, and the transformation of the support at high temperature can usually provide more dynamic spaces for anchoring metal atoms (Figure 1B), achieving a high surface density of single atoms. More importantly, the formation of single atom sites at high temperature can create a strong bond between the metal atoms and the substrate, thus endowing the materials with high stability and preventing the sintering of the dispersed atomic sites (Moliner et al., 2016). These advantages indicate an innovative route to achieve high-density single-atom active sites with outstanding stability.

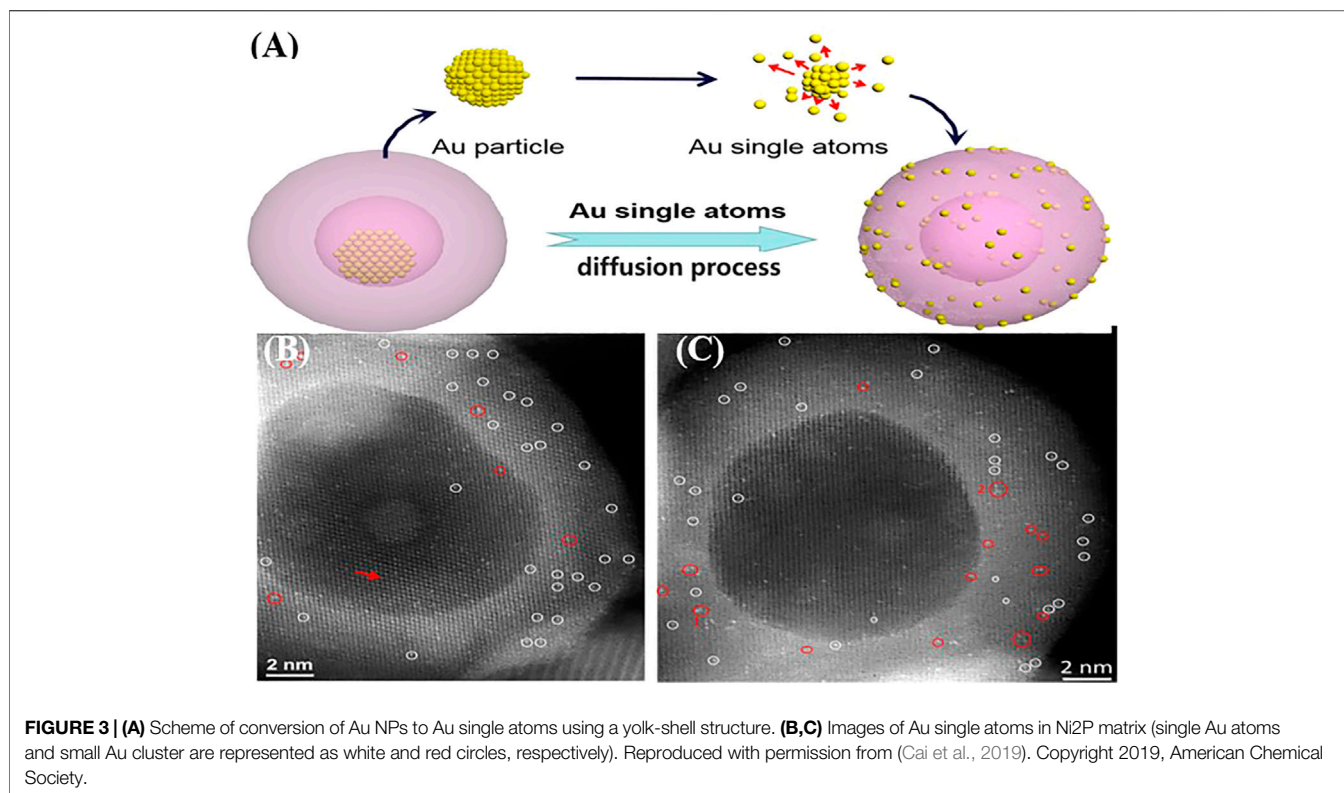
RECENT ADVANCES IN ATOMIZATION FOR SAC SYNTHESIS

At high temperature, the presence of the defects in metal oxides is more dynamic and the defect concentration is significantly higher than at room temperature; this opens up opportunities to obtain high-density single atoms with enhanced stability (Sasaki and Maier, 1999). Metal oxides are ideal supports that can provide defects or vacancies, especially at high temperature, creating dynamic sites able to immobilize the migrating atoms (Jones et al., 2016). SACs based on noble metals such as Pt, Pd, and Au have been synthesized by mixing the NP source with metal oxide supports (Yu-Yao and Kummer, 1987). Under high-temperature conditions, Pt can be released as volatile PtO₂ and transferred from the pristine metal nanoparticles to the metal oxide (Yu-Yao and Kummer, 1987; Bruix et al., 2014; Moliner et al., 2016). Ceria oxide has been shown to provide a type of “nanopocket” able to bind Pt²⁺ ions so strongly that they withstand sintering and bulk diffusion (Bruix et al., 2014). Neitzel et al. pointed out that the Pt cations remain stable on the surface of the substrate, instead of diffusing into the ceria bulk (Neitzel et al., 2016). Based on these findings, the Datye group found that aluminum oxide-supported Pt NPs can be converted into single Pt atoms and trapped on CeO₂ (100) surfaces. Compared with ceria cubes, it is easier to trap Pt species on polyhedral ceria and ceria nanorods to form atomically dispersed catalysts, suggesting that the support plays an important role (Jones et al., 2016). Moliner et al. (2016) found that Pt NPs can transform into single Pt atoms in O₂ atmosphere and high-temperature conditions. Reversible conversion of NPs and single atoms can be achieved efficiently in reducing and oxidizing atmospheres (Figure 2) (Moliner et al., 2016). Using N, N, N-trimethyl-1-adamantammonium and a Pt-mercapto complex as organic structure-directing agent and Pt precursor,



respectively, single Pt atoms were synthesized in O₂ atmosphere; these atoms were stable at 650°C. The Pt–O coordination number was found to be 2.71 after calcination at 500°C. Pt single atoms supported on highly siliceous chabazite could convert >80% of ethylene to ethane (Moliner et al., 2016).

Recently, Cai et al. (2019) reported an effective way to convert noble Au NPs to single atoms by annealing and used this approach to anchor Au single atoms on Ni₂P (**Figure 3**). First, nanoscale Au@Ni₂P yolk-shell structures were synthesized using chloroauric acid, oleylamine, octadecylene, and triphenylphosphine. Then, the Au@

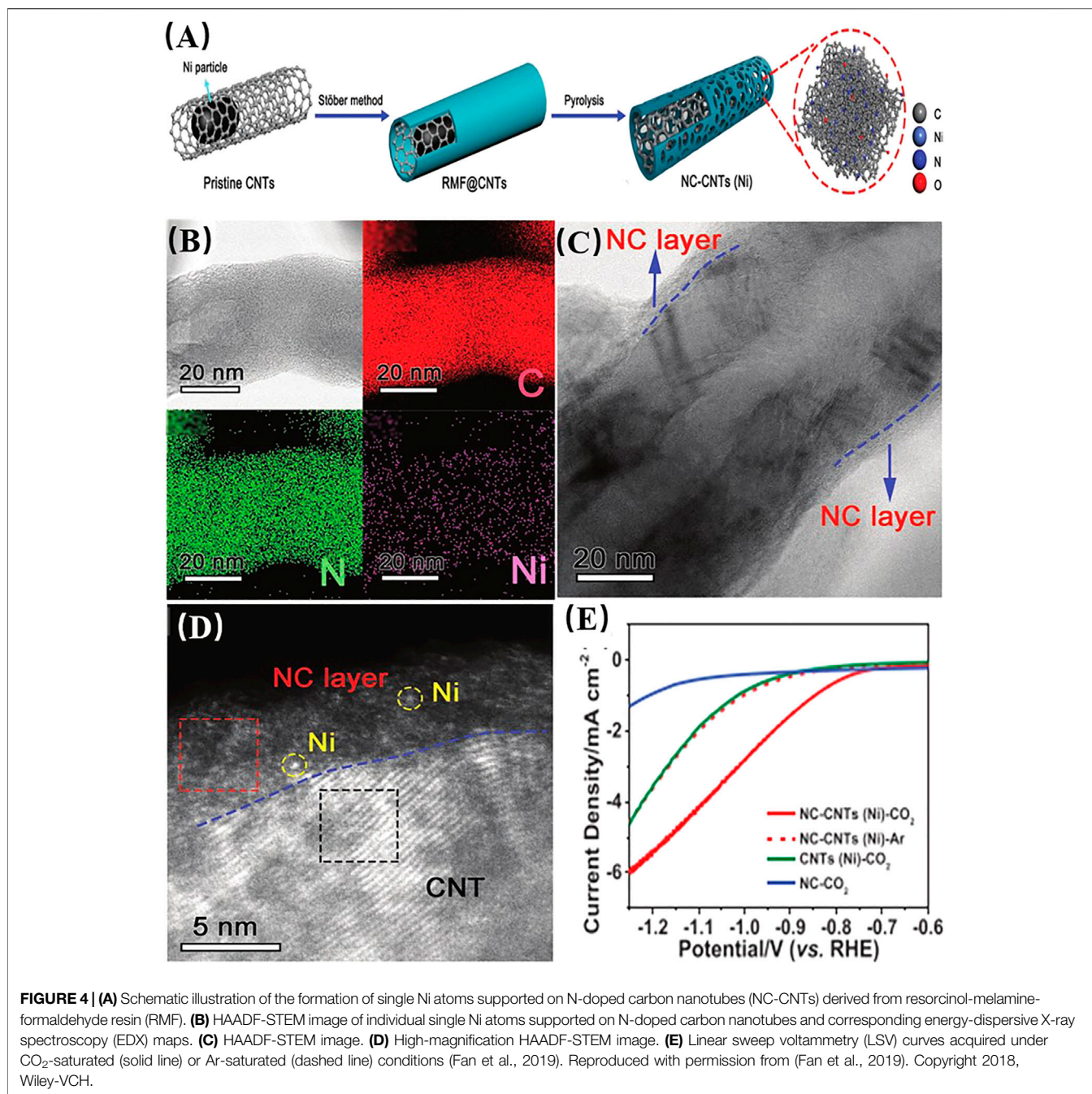


Ni₂P yolk-shell structure was heated to 350°C and kept at that temperature for 1 h. The annealing procedure can change the morphology and atomic structure of Au@Ni₂P nanoparticles, and the results of aberration-corrected *in situ* high-resolution STEM showed that single Au atoms could be well dispersed in the Ni₂P matrix by diffusing into the Ni₂P shell. At 1.47 V vs. RHE, the annealed sample exhibited a better oxygen evolution performance than fresh Au@Ni₂P, pure Ni₂P, and commercial IrO₂, with 12-, 40-, and 16-fold increases in the oxygen evolution reaction (OER) rate, respectively (Cai et al., 2019).

Huang et al. (2012) synthesized Ag single atoms supported on hollandite-type manganese oxide by *in situ* atomization of supported Ag NPs. Typically, the Ag NPs were supported onto hollandite-type manganese oxide upon annealing at 230 °C, as the Ag NPs fragmented into Ag atoms and migrated to the inside of the hollandite-type manganese oxide. This was followed by the formation of single Ag atom chains, resulting in the Ag atoms being anchored at hollandite-type manganese oxide tunnel openings. The conversion of Ag NPs to single Ag atom chains by annealing was demonstrated by X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), and Fourier-transform extended X-ray absorption fine structure (EXAFS) characterizations. The single Ag atom catalyst exhibited superior ability in the activation of lattice oxygen atoms and molecular oxygen, which promote the oxidation of formaldehyde (Huang et al., 2012). Lang et al. (2019) used covalent metal-support interactions to trap vaporized Pt atoms on the surface of Fe₂O₃ and synthesize a high-loading Pt SAC. As the temperature increased from 300 to 700°C, the Pt

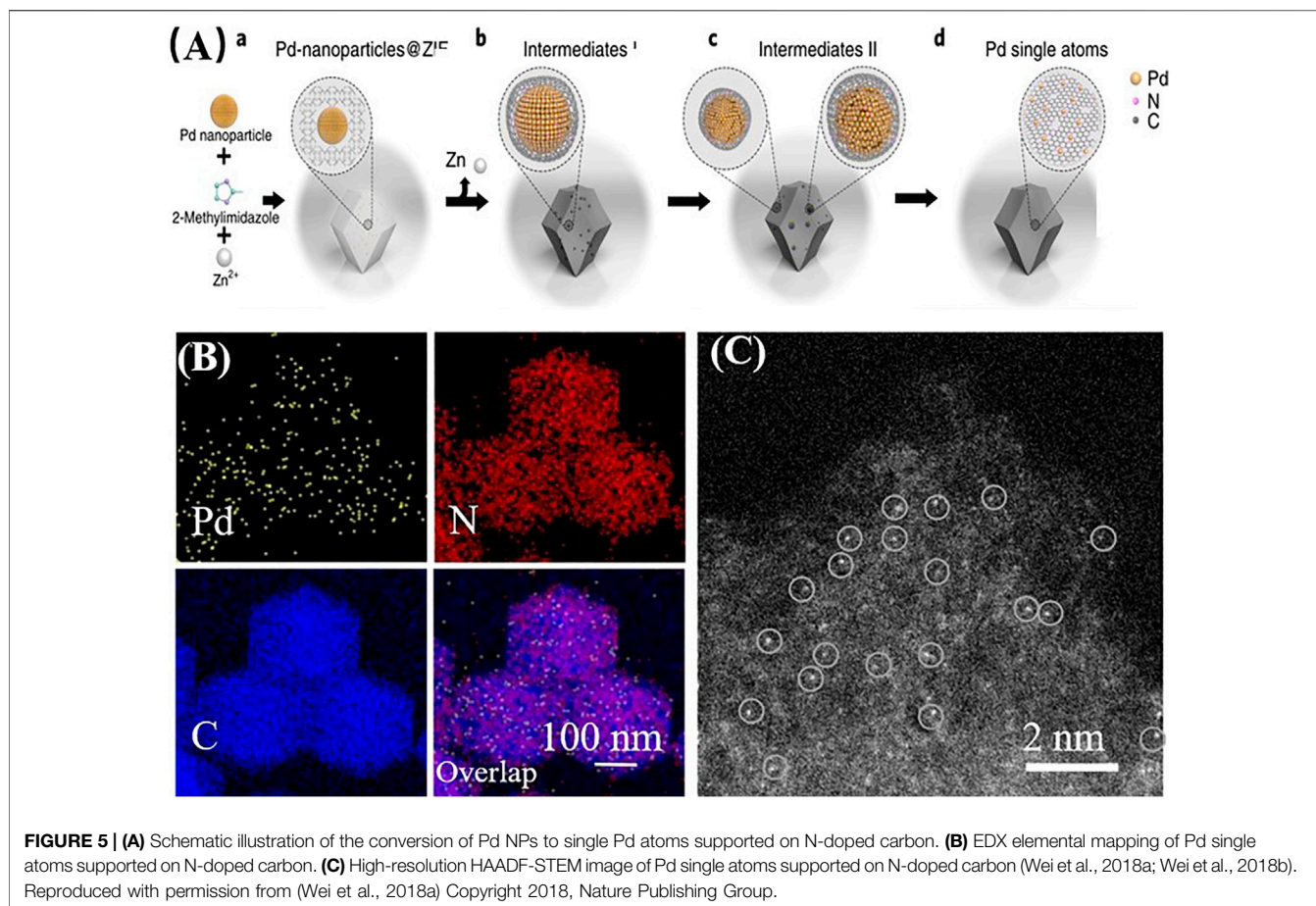
NPs were converted to Pt single atoms on Fe₂O₃ (Lang et al., 2019). The Pt NPs eventually disappeared and a high density of single Pt atoms was obtained by calcination at 800°C for 5 h. Calculation results showed that the formed Pt atoms coordinated four surface oxygen atoms, with an average Pt–O length of 1.94 Å. And the obtained catalyst methane combustion exhibited outstanding activity to promote methane combustion. (Lang et al., 2019).

Carbon materials are effective supports for achieving high loadings of single atoms, owing to their high surface area and tunable structure. The introduction of heteroatoms (e.g., N, B, and P) in carbon nanomaterials can alter their electronic structure, providing inhomogeneous anchoring sites for metal atoms that could break the inert C₆ symmetry (Nistor et al., 2011; Dai et al., 2015). Owing to the ultrahigh doping levels that could be introduced, carbon supports provide an ideal pathway to achieve high loadings of single atoms (Cheng et al., 2018; Yan et al., 2018; Chang et al., 2019; Cheng et al., 2019a). Conventionally, the efficient way to synthesize carbon-supported SACs is to mix metal salt precursors with carbon and heteroatom precursors (Cheng et al., 2019b). During this process, metal atoms (M) coordinate nitrogen, phosphorus, sulfur, and/or carbon atoms, forming M–N/S/P/C-based single atoms (Chen et al., 2018b; Li et al., 2018). A recent study showed that using metal NPs annealed with carbon and nitrogen sources could be used to synthesize SACs. Yang et al. (Jian et al., 2018) prepared Ni atoms supported on the surface of carbon nanotubes (CNTs) and applied them to catalyze the electroreduction of CO₂. Owing to thermal diffusion, Ni NPs trapped on the carbon



nanotubes can be converted to single Ni atoms on the surface (Figure 4). The Ni NPs contribute to break C–C bonds on the carbon nanotube surface; then, the fragmented Ni atoms can be anchored by the N defects on the surface of the carbon matrix, after which the Ni NPs are gradually transformed into Ni single atoms. The conversion process was demonstrated by *in situ* environmental TEM. Quantitative EXAFS fitting results showed that the Ni atoms had a coordination number of 4.3 and a mean bond length of 1.89 Å, in contrast to the 12 and 2.48 Å values measured for Ni NPs, respectively. The Ni SACs showed a

higher electrocatalytic current than N-doped carbon and carbon nanotubes for electrochemical reduction of carbon dioxide. Similarly, Fan et al. (2020) synthesized Ni single atoms on the surface of N-doped carbon nanotubes through conversion of Ni NPs to Ni SAs at high temperature, using a polymeric layer of resorcinol, melamine and formaldehyde. Thermal migration on the CNT surface facilitated migration of Ni NPs into N-doped carbon nanotubes to form the Ni–N coordination shell. The atomic dispersed Ni atoms provided highly efficient electrocatalytic carbon dioxide reduction at low overpotentials



to produce CO, showing a CO faradaic efficiency over 90%, turnover frequency up to $12,000 \text{ h}^{-1}$, outperforming current state-of-the-art single atom catalysts.

Rong et al. synthesized a Bi SAC on N-doped carbon using *in situ* pyrolysis of a Bi-based metal-organic framework and dicyandiamide. The decomposition of dicyandiamide released NH_3 , which facilitated the atomization of Bi NPs. And the single-atom Bi-N₄ site was demonstrated the dominating active sites for carbon dioxide activation. Similarly, N-doped carbon was used to stabilize Ni SACs by enhancing the surface area and porosity (Zhang E. et al., 2019). Wei et al. (2018) prevented the sintering effects in SACs and successfully transformed noble metal NPs (Pd, Pt, Au) into highly active SACs. Using the thermal pyrolysis of a metal-organic framework (zeolite imidazolate framework-8, ZIF-8) to prepare an N-doped carbon matrix, the noble metal atoms were anchored on N-doped carbon at 900°C (Figure 5). *In situ* environmental TEM results showed that the sintering effects could still be observed in SACs at high temperatures. However, the increasing size of the NPs resulted in a higher collision probability between enlarged Pd NPs and nanoclusters; thus, the Pd NPs became gradually smaller and finally transformed into Pd single atoms. The thermal migration of large Pd particles within carbon nitride had a significant effect on the size reduction of sintered Pd NPs (Wei

et al., 2018). The thermally stable Pd single atoms exhibited even better activity and selectivity than nanoparticles (Pd-NPs) for semi-hydrogenation of acetylene.

Despite the great progress made in this area, the atomization of NPs still faces several challenges at this stage, which include: a) operation conditions involving high temperatures; b) lack of a universal and simple approach; and c) a degree of atomization not high enough to achieve a high loading, due to the Ostwald ripening limitations. In order to achieve rapid atomization and suitable synthesis conditions, new agents have been introduced to promote the atomization process under mild conditions. Guo et al (Zhou et al., 2019) demonstrated that PH_3 could promote the effective conversion of noble metal NPs (M-NPs, M = Ru, Rh, Pd) at 400°C to M-P single atoms with good thermal stability on g-C₃N₄ nanosheets. Experimental and theoretical results revealed that single Pd atoms loaded on g-C₃N₄ nanosheets exist in the form of Pd-P₂.

Qu et al. developed a novel gas migration strategy to directly obtain SACs through conversion of bulk nanomaterials, resulting a material active for oxygen reduction reaction. During the gas migration process, ZIF-8 was pyrolyzed in Ar atmosphere at a high temperature (1,173 K) to obtain empty zinc nodes and abundant defects. At the same time, ammonia molecules combined with the Cu atoms from the Cu foam surface and formed volatile $\text{Cu}(\text{NH}_3)_x$ species in NH_3 atmosphere. Finally,

the $\text{Cu}(\text{NH}_3)_x$ species were trapped by the defects of the N-doped carbon support, generating Cu SACs. EXAFS and XPS results revealed that the Cu single atoms were coordinated to 4 N atoms. Furthermore, Qu et al. showed that this gas migration strategy can be applied to synthesize other Co. or Ni SACs (Qu et al., 2018).

Feng et al. reported the transformation of Ru, Rh, Pd, Ag, Ir, and Pt NPs into single atoms supported on carbon with high dispersion (5 wt%), assisted by a mixture of CH_3I and CO. Taking Rh as an example, the I^\bullet radicals and CO molecules could promote the breaking of Rh–Rh bonds to form mononuclear complexes. The isolated Rh mononuclear complexes were stabilized by the oxygen-containing functional groups. This method provides a general strategy for the development of single-site catalysts, also for other metals (Feng et al., 2019).

DISCUSSION

The preparation of SACs requires a high surface density of active sites and stable coordination. Atomization provides an efficient way to obtain stable supported SACs with high-density surface-active sites. The volatile metal species and defects are critical for the transformation of NPs into single atoms. The atomization of the metal nanoparticles is closely related with the atmosphere that applied to synthesis SACs, thus control the atomization environment is the key to achieve efficient atomization. Noticeably, some metal nanoparticles are stable and not easy to form atomic moieties, this limits the general applicability of this strategy for SAC synthesis, because the breaking of metal–metal bonds to form volatile species is an energy-demanding process (Rodriguez and Goodman, 1992; Berry and Lu, 2017), and the required energy varies significantly from metal to metal. For example, the Fe–Fe bond energy is 418 kJ mol^{-1} , which is 3.2 times that of Zn–Zn bonds (131 kJ mol^{-1}). This makes it particularly hard to develop general methods for atomization, and these universal approaches are urgently required. The introduction of new agents can enhance the mobilization or vaporization of metal atoms, providing new routes for the atomization process. However, high-temperature annealing is still required. Thus, the identification of new agents to assist the atomization process is a task of great significance.

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Furthermore, loading metal NPs on the supports followed by atomization at high temperature in the presence of agents normally requires a multistep process. However, simple methods for this purpose are lacking, and further investigations are required. The Li group developed a new approach involving the use of bulk copper as precursor to provide volatile Cu species in the presence of NH_3 ; this simple approach offers great opportunities for bulk synthesis (Qu et al., 2018). More importantly, the atomization process and mechanism need to be further explored in order to guide the development of novel strategies.

CONCLUSION

In summary, SACs are attracting enormous interest, and significant advances have been achieved in the development of new strategies to obtain highly active SACs. Compared with conventional approaches such as wet chemistry, atomic layer deposition, and photochemical reduction methods, the atomization of metal NPs provides a more effective route to achieve highly dispersed and stable SACs. Interestingly, the atomization of supported metal NPs normally takes place on the surface of the supports, thus providing an effective way to achieve a high surface density of active sites with superior stability. More importantly, this atomization method are easy scale up, thus offer opportunities to promote the practical application of SACs. This unconventional approach offers new opportunities for the synthesis of highly efficient SACs.

AUTHOR CONTRIBUTIONS

AZ drafted the manuscript. SJ revised the manuscript. All authors discussed the manuscript and approved the final version.

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Conflict of Interest: Authors AZ, MZ, SL, MC, and SJ was employed by State Power Investment Corporation Hydrogen Energy Company, Ltd. Co., Beijing, P.R.China.

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