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Promising approach for preparing metallic single-atom catalysts: electrochemical deposition

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Developing energy conversion technologies via electrochemistry will significantly facilitate the large-scale utilization of renewable energy, thus helping address issues regarding energy shortage and environmental deterioration. The application of electrochemical energy conversion reactions such as electricity generation and electrolysis is highly dependent on developing efficient electrocatalysts. Metallic electrocatalysts, including pure metals and alloys, possess superior intrinsic activities compared to other materials for various energy-conversion reactions, ascribed to the active *d*-electrons [1–3]. Traditionally, low-coordinated and unsaturated metal atoms have been the most important active sites for catalysis. Thus, over the past few decades, the most popular strategy to improve catalytic activity has been to reduce the particle size from bulk to nanoscale [4,5] as shown in Fig. 1. However, only a few atomic layers at the surface of nanoparticles contribute to these catalytic reactions, leading to lower metal utilization [6,7]. In addition, several active sites for side reactions exist, which further impede the improvement of selectivity and activity. For monolayer metallic electrocatalysts as a possible solution to achieve high utilization of metals, the choice of metallic atoms on the surface is limited by the compatibility of work functions between the core and shell metals [8]. Recently, single-atom catalysts (SACs) in which each atom can be exposed to catalytic reactions have garnered increasing attention as a promising pathway to increase metal utilization [9–12]. The active sites of SACs are isolated atoms surrounded by a coordinated environment of supports compared to the overall surface of nanoparticles. The catalytic atoms were well confined and highly dispersed on the support. Owing to the further optimized

electronic conditions, SACs possess desirable activity, selectivity, and stability and minimize metal loadings and maximize economic benefits [13,14].

Single atoms in SAC structures cannot survive and tend to agglomerate because of their high surface energy. Therefore, different strategies, including defect design, special confining, and coordination during SACs fabrication, have been proposed and employed to achieve stable anchoring of the central atoms [17], as shown in Fig. 2. In addition to the stability problem of the central atoms, other factors can also influence the performance of the central sites, such as the uniformity and population of metal sites, as well as their neighboring coordination conditions [18,19]. Overall, the biggest challenge in the fabrication of SACs is the difficulty in reconciling the high metal loading and high dispersion of single atomic sites. When the metal loading increases, agglomeration gradually arises to form clusters or even nanoparticles. The successful dispersion of central atoms with a high metal loading of SACs is generally related to the number of defect sites on the substrate, which requires complex pretreatment. Wet chemistry and pyrolysis methods are mostly used to prepare SACs [9, 20–22]. Following wet chemistry routes, capping agents such as oleylamine [23] and triphenylphosphine [24] are essential to protect single atoms from agglomeration. Unfortunately, these macromolecular organic species are difficult to remove and thus inevitably cover and inactivate the active sites. And the impurities can make the characterization of SACs less accurate. In addition, the trial-and-error process makes it difficult to understand the growth mechanism and guide top-down synthesis, because the duration is so short that it is difficult to capture the information through methods using nanoscale materials [25]. For the thermal pyrolysis method, selecting the appropriate temperature, precursors, pressure, and atmosphere requires numerous trials. The migration of metal atoms is inevitable at such high temperatures. Accordingly, appropriate substrates that can effectively stabilize isolated atoms are required [18,19,26,27]. In

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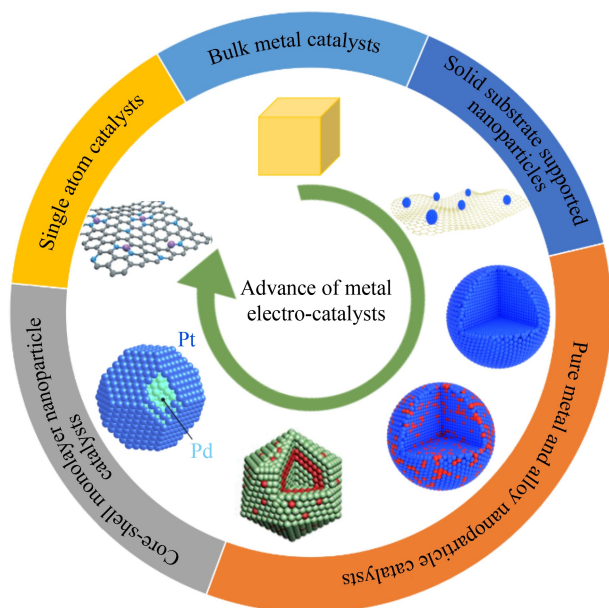


Fig. 1 Development of metallic electrocatalysts (adapted with permission from Refs. [11, 15, 16].

addition, the yield ratio of isolated single-atomic active sites can also be used to measure the efficiency of different synthetic approaches.

In contrast, it is promising to employ electrochemical deposition methods to prepare SACs under precise regulation of the growth of deposits, and this has significant potential to easily obtain nucleation and growth information through measurable parameters such as current densities and applied potentials [28–30]. In addition, the deposition process can be adjusted by

changing the concentration of precursors and adding substances that may affect complexation or reaction pathways [31,32]. Moreover, electrochemical methods are more tolerant of a wider range of metal elements and substrates.

The electrodeposition mechanism of single atoms is significantly different from that of nanoparticles. First, the generally accepted mechanism for nanoparticles, including nucleation and subsequent growth processes, might be inapplicable to SACs because the electrochemical deposits comprise a single atom instead of aggregated atoms. Second, the classical electrodeposition theory might be inapplicable to deposition using ultralow ion concentrations. Third, multisite deposition of isolated single atoms might be produced from adsorbed ions on the substrates. Thus, clarifying the mechanism of electrochemical deposition of single atoms is critical to flexibly control the synthesis of SACs.

Current electrochemical approaches for the preparation of SACs include over-potential electrodeposition (OPD), under-potential deposition (UPD), potential cycling deposition, and multi-step potential deposition [33]. OPD is driven by the electrochemical potential of the reduction reaction. Zeng et al. proposed an electrochemical potential-scanning deposition route to synthesize Ir/Co(OH)₂ [34]. It is believed that a relatively low precursor concentration (no more than 10⁻⁴ mol/L), proper scanning cycles, and scanning rate jointly ensure isolated single atoms by maintaining minimum supersaturation. Its generality was well evidenced for a wide range of SACs, including (Ir, Ru, Pt, Pd, Rh, and

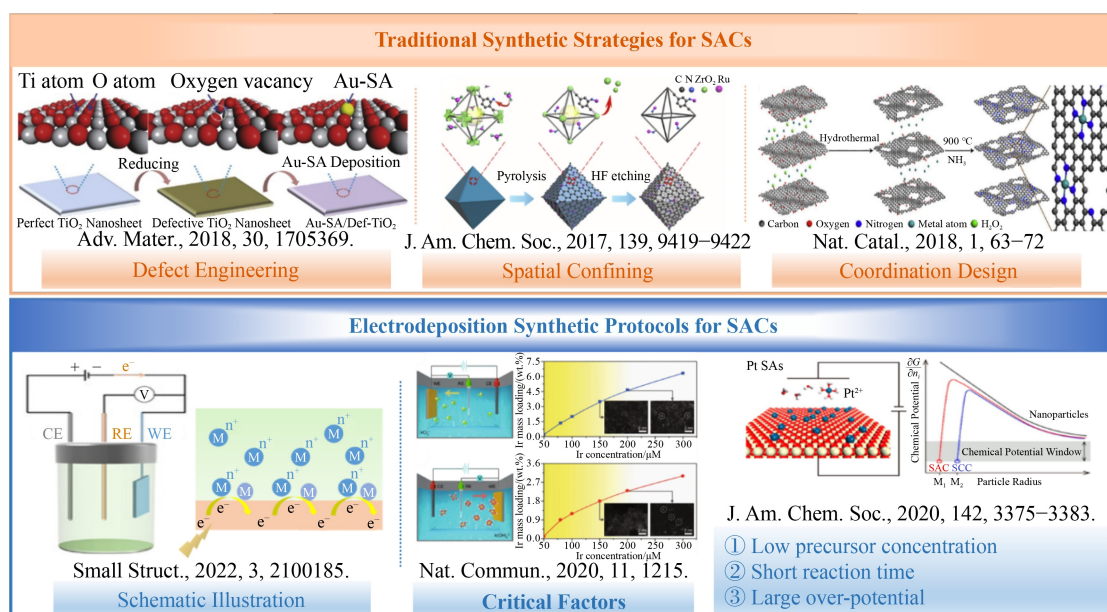


Fig. 2 Comparison of traditional preparation methods and electrochemical methods for SACs (adapted with permission from Refs. [34, 38, 40, 42–44]).

Ag)/(Co(OH)₂, MnO₂, MoS₂, N-C, and Co_{0.8}Fe_{0.2}Se₂). Various metal species and metallic site-substrate interactions determine the intrinsic catalytic properties. It has been found that the anodically prepared electrocatalysts are more active in the oxygen evolution reaction. Whereas, those cathodically deposited are highly active for the hydrogen evolution reaction (HER) [35].

Li et al. proposed a facile strategy for electrochemically anchored non-noble metal SACs, Ni and Fe, which exhibited remarkably enhanced activity and stability toward the HER compared to most bulk catalysts [36]. They also synthesized graphdiyne-supported Pd⁰ SACs by an *in situ* electrochemical reduction method [37]. This reliable catalyst exhibits lower overpotential, higher mass activity, and turnover frequency toward the HER at a relatively low Pd loading of 0.2% (mass fraction). The interaction between Pd and graphdiyne also contributes to the superior durability of the HER. Yan et al. indicated that the principle of metal atom–substrate interaction during the electrodeposition of SACs is similar to UPD [38]. However, the UPD method is highly dependent on the surface of the target substrate and the difference in work functions between the active sites and substrate. In addition, it is difficult to distinguish the potential range of UPD for isolated atoms from that of OPD.

In recent years, advanced characterization has facilitated the study of electrodeposited preparation of SACs [39]. Single metal atoms can be detected using scanning transmission electron microscopy. Synchrotron radiation techniques, such as extended X-ray absorption fine structure spectroscopy, can be used to study the coordination environments of the central active sites in SACs [40]. X-ray photoelectron spectroscopy and diffuse reflectance infrared Fourier transform spectroscopy can reveal the bonding features of SACs [39]. Computational techniques can also help understand electrochemical methods [41]. According to density functional theory [42], a potential-related adjustable strategy was discovered for single-atom preparation, in which there is a potential leap when clusters transfer to a single atom. It can be concluded that there are significant differences in the chemical potentials that could be related to the electrochemical potential or overpotential for preparing nanoparticles, clusters, and isolated atomic catalysts. Consequently, it is suggested that the number of metal atoms can be flexibly adjusted by manipulating the potential, which has been experimentally proven by preparing N-doped graphene-supported Pt, Pd, and Ni SACs in this study.

Notably, the critical factors of electrodeposition preparation of SACs include ultralow metal precursor concentration, short deposition time, and appropriate potential value (located at a large overpotential value or current density). A low metal ion concentration and short deposition time help maintain slow mass transfer, and a

large overpotential provides sufficient power for the high density of isolated metal atoms on the supports. The ligands of the metal ions also affect the reduction process. The electrochemically deposited SACs indicate a comparable loading of single metal sites to those prepared by traditional methods, as summarized in Table 1. However, there is greater tolerance to the selection of substrates. Measurable parameters in electrodeposition approaches help uncover the mechanisms of growth.

Table 1 Comparisons of metal loading of SACs prepared by traditional and electrodeposition methods

Samples	Methods	Atomic mass loading (mass fraction, %)	Ref.
Pt ₁ -N/BP	Pyrolysis	0.4	[31]
Pt/FeO _x	Thermal reduction	0.08	[45]
Pt-SA/TiO ₂	Thermal reduction	2.02	[46]
Ir/Co(OH) ₂	Electrochemical deposition	>2.0	[34]
Fe/GD	Electrochemical deposition	0.68	[36]
Ni/GD	Electrochemical deposition	0.278	[36]
Ir ₁ /TiO ₂ -CoOOH	Electrochemical deposition	1.2	[35]
Ir ₁ /VO-CoOOH	Electrochemical deposition	1.3	[35]

To satisfy the large-scale preparation of SACs, more stringent control of the synthetic process is required, which could also be proposed by understanding the deep insights into the deposition mechanism of SACs. The conflict between the requirement for high metal loading and uniform metal sites should be resolved. In addition, the synthetic strategy should be universally applicable to more metal elements and substrates to promise more possibilities for higher catalytic performance. Accordingly, electrochemical deposition protocols exhibit unique advantages in eliminating pollutant effects and avoiding agglomeration. It has been proven that isolated atom density, metal loading, and suitability between metal species and substrates can be achieved by regulating the metal precursor concentration or complexation in the electrolyte and deposition parameters (such as potential and duration time). The electrodeposition strategy is well known to be more controllable and more compatible between substrates and precursors, and has moderate and wide applications in large-scale manufacturing.

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