Recent advances of single-atom electrocatalysts for hydrogen evolution reaction

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Abstract

Sustainable, renewable and scalable production of highly pure hydrogen gas through hydrogen evolution reaction (HER) in electrochemical water splitting requires efficient and stable electrocatalysts. Single atom catalysts (SACs) with significant merits such as the maximum atom-utilization efficiency, unique electronic structure and fascinating properties, are considered as promising candidates electrocatalysts for HER. Based on this, recent developments of effective synthetic methodology toward SACs are summarized. Subsequently, the synergistic coupling interaction between the catalytic activity and SACs including the perspective of coordination environment, local structural identification and metal-support interaction are highlighted. Finally, the current challenges and future opportunities are briefly addressed to improve the performance of single-atom electrocatalysts for HER, which might offer some insights for applications in hydrogen production.

1. Introduction

In view of the ever-increasing global consumption of fossil fuels and the relative environmental issues, the researchers are committed to the exploration and development of sustainable and renewable energy sources [1, 2]. Renewable energy resources such as wind energy, solar energy, and ground thermal energy etc are alternative energy resources to address energy demands [3]. However, these intermittent and the utilization of renewable power are limited by spatial mismatch between supply and demand [3, 4]. Hydrogen gas (H2) is regarded as a promising candidate for energy storage in the future, which can be used in fuel cells, because H2 process the higher gravimetric energy density than other fuels and water is the only byproduct in energy conversion processes [5, 6]. Moreover, Hydrogen is also a basic raw material used for the synthesis of ammonia, the hydrogenation of hydrocarbons, and the production of metals as a reducing agent in industry. However, more than 95% of the hydrogen comes from the gasification of coalsteam or reforming of methane. Such production routes not only consume non-renewable fossil fuels, but also emit large amounts of carbon dioxide and other greenhouse gases [7]. Therefore, it is imperative to develop alternative technologies toward green hydrogen to solve challenges in environment, energy, and sustainability.

Electrochemical water splitting (H2O(l) → H2(g) + 1/2O2(g), ΔG0 = +237.2 kJ mol−1, ΔE0 = 1.23 V vs normal hydrogen electrode) is one of the most promising approach to convert electrical energy derived from intermittent renewable energy to chemical energy (hydrogen) [8]. Compared with the reforming of fossil fuels, this method has some advantages in many aspects, for instance, the raw material is water, which is a renewable and rich resource on the earth. The energy comes from renewable energy source such as wind energy, solar energy, or ground thermal energy etc; Furthermore, such approach does not emit polluting gases or greenhouse gases. Electrochemical water splitting involves two half-cell reactions, namely the hydrogen evolution reaction (HER) on the cathode and the oxygen evolution reaction on the anode.
However, the key prerequisite is to design an electrocatalysts with high performance to achieve the
cost-effective and large-scale production based on electrolytic water splitting technologies [9].

Compared with bulk materials, nanostructured materials usually exhibit enhanced electrocatalytic
activity due to the well-defined structure [10, 11]. In reviewing previous reports, the unique properties
originating from their sizes, shape, composition and electronic structures of nanomaterials will have a
profound impact on their catalytic activity, stability and selectivity [9, 12]. Although conventional
nanocatalysts have made great achievements, there are still many challenges [13]. From the perspective of the
catalytic reaction process, the reactions commonly occur on the surface or interface of the catalyst, and only a
small part of the metal atoms exposed to the reactant can serve as catalytically active sites (rather than the
entire particle), leading to unsatisfactory metal utilization efficiency [14, 15]. From the perspective of
catalytic mechanism, nanoparticles have a complex microscopic environments where the constituent metal
atoms may be located in different chemical environments and serve as multiple active centers to catalyze the
reactants. So it is difficult to establish the relationship between structure and performance. In principle,
reducing the size of nanoparticles to clusters, or even separate metal atoms, can significantly improve the
efficiency of atom utilization, possibly up to 100% [16].

In addition, as the active sites of the single atoms are nearly uniform, the catalytic mechanism can be
explained through rational design and calculation models. In 2001, Zhang et al defined the terminology of
single-atom catalysts (SACs) are as catalysts composed of only atomically dispersed active sites (single atom
sites) [17]. Single Pt atom supported on iron oxide (Pt1/FeOx) was firstly prepared by a co-precipitation
method. Combined with a series of advanced characterization methods, it is confirmed that the structure of
Pt1/FeOx revealed the essence of the high CO oxidation efficiency and stability of Pt single atoms supported on
FeOx.

Since then, researchers have conducted extensive research on various single-atom catalysts, also known as
single-atom site catalysts. Single-atom electrocatalysts (SAECs) has opened up a new way for the
development of advanced electrocatalysts for HER to achieve maximum atom utilization efficiency, excellent
stability and high catalytic activity [18, 19]. In this review, we will first briefly introduce the basic mechanism
of electrochemical HER. Secondly, the leading methods used in the synthesis strategies of SAECs are
summarized. Furthermore, we will summarize recent advances in using these SAECs towards HER from the
aspect of the local structural regulation and the support coupling effect by precise tuning of metal anchoring
sites and supports. And we focus on an in-depth insight into the structure-property relationships of SAECs
towards HER. Finally, perspectives on the current challenges and possible opportunities in SAECs for HER
are also discussed.

2. Mechanistic principles for HER

HER is a cathodic reaction (2H+ + 2e− → H2) that occur on the electrode surface via two electron transfer
reaction with two steps.

In acidic solution, HER takes place through two typical steps [20]:

(a) Starting with proton (H+) discharge to form one catalytic intermediate (H*) by the Volmer mechanism:
H+ + e− + ∗ → H* (where H+ comes from hydronium cation).
(b) In the second step, H* is more willing to join with an electron and a H+ concurrently by the Heyrovsky
mechanism: H* + H+ + e− → H2, or combine with another H* via Tafel mechanism: 2H* → H2 + ∗ to
form a molecule of H2 [21].

In alkaline electrolytes, the generally accepted two process for HER are Volmer–Heyrovsky pathway:

(a) begin with proton adsorption in Volmer reaction: H2O + e− + ∗ → H* + OH− (where the source of
proton is water molecule).
(b) the desorption of H2 gas in Heyrovsky reaction: H2O + H* + e− → H2 + OH− + ∗, or recombine with
research other: 2H* → H2 + * via chemical desorption [22].

Nowadays, it is clear from both theoretical and experimental perspectives that the adsorption free energy
of H* (∆GH*) has been suggested to be a key descriptor for the HER activity. If the catalysts have a negative
∆GH∗, though Volmer step (initial step) is very easy, the subsequent Heyrovsky or Tafel step will be difficult.
On the contrary, if ∆GH* of the catalyst is positive, the entire HER will slow down because of the repulsive
interaction between the surface of an electrode and the protons. Thus, a value of ∆GH* close to zero is
favorable for active catalysts of HER. ∆GH* largely depends on the geometry and electronic structures of the
catalysts. To these end, the rational design of catalysts is the key to improve HER activity.
3. Synthetic methods for SACs

It is one of the most important research focuses for exploration and development of synthetic methodologies toward SAECs to achieve single atom dispersion of metals. However, because of the high surface energy, isolated single atoms can easily migrate and aggregate into particles [23, 24]. Consequently, fabricating SAECs and maintaining atomic dispersion of single metal atoms against agglomeration into particles under realistic synthesis and reaction conditions represent grand challenges.

In recent literatures, a range of synthetic methodologies has been reported for the synthesis of SACs [25]. Currently, some primary methods to synthesis SAEC (figure 1) are summarized in detail, mainly including high-temperature pyrolysis method, wet-chemistry method, as well as physical and chemical deposition method.

3.1. High-temperature pyrolysis method

High-temperature pyrolysis methods has been widely used in the synthesis of atomically dispersed materials through decomposing selected precursors at an appropriate temperature under protective atmosphere (such as Ar, H2, or NH3) [26, 27]. In general, in a typical pyrolysis process, SACs can be obtained from various precursors including carbon sources, doped/coordination atoms and metals.

MOF, a well-defined porous materials constructed by organic linkers and metal nodes, and MOF-derived materials have been reported to act catalysts or precursors [28–34]. For instance, Li et al found that during direct pyrolysis process of ZIF-67, a Co-containing MOF, the organic linkers of Co-containing MOFs were converted into N-doped porous carbon. Later, the Co nodes were reduced by the produced carbon and then aggregated, leading to the generation of Co atoms to Co nanoparticles [35]. It is well known that the Zn atoms can be evaporated at 907 °C during the pyrolysis process. Interestingly, after pyrolysis process of Zn1Co1-BMOF, single Co atoms embedded in the N-doped porous carbon matrix was successfully synthesized, which was ascribed to two key reasons. The first one is that the added Zn atoms further enlarged the adjacent distance. The second point is that the Zn atoms was evaporated at high temperature and there will be more N sites to anchor Co atoms (figure 2(a)). Jiang’s group prepared FeSA–N–C SACs via the pyrolysis process of a novel mixed-ligand. FeSA–N–C SACs with FeN4 embedded in a porphyrin ligands exhibited excellent ORR activity and stability. So far, based on the strategies mentioned above, a series of SACs have been successfully obtained, including non-noble metal-based SACs such as Fe [36–45], Co [26, 38, 46, 47], Ni [48, 49], Cu [50], Mn [51], Cr [52] and noble metal-based SACs such as Ru [53–55], Ir [56].

Surprisingly, Li et al observed that noble metal nanoparticles (M: Pd, Pt, Au) encapsulated into ZIF-8 crystal (M-NPs@ZIF-8) can be transformed into thermally stable single atoms anchored on N-doped carbon (M–CN) at above 900 °C under an inert atmosphere [57]. The nanoparticles grew bigger from room temperature to 1000 °C because of intensive collision at the initial stage. However, at 1000 °C, as time goes by, the size of nanoparticles decreased again through collision and coordination of surface metal atoms with the N-doped carbon support (figure 2(b)). Density functional theory (DFT) calculations illustrate that the
more thermodynamically stable precious metal-N$_4$ structure can lead to the formation of single-atom catalysts at a high temperature.

### 3.2. Wet-chemistry method

From a perspective of practical application, SACs can also be prepared by wet chemistry approach which is regarded as a promising synthetic methods, due to its easy operation and practicability of large-scale manufacturing. However, in wet chemical approach, because of the high surface energy, the isolated metal atoms contained in precursor materials have a strong tendency to aggregate. Therefore, it is significant for the synthesis of SACs to take effective strategies to guarantee the atomic dispersion of metal species on the surface of the support and meanwhile to avoid their aggregation.

Controlled construction of defect strategy (vacancies or defects) which process of coordination-unsaturated sites on supports could be an effective approach to stabilize isolated metal atoms. General speaking, the surface vacancies or defects of supports serve as ‘traps’ to capture metal precursors in the pre-treatment process and anchor metal atoms during post-treatment [58–60]. So far, extensive efforts have been devoted to constructing anionic vacancies (such as B vacancies [61], C vacancies [62, 63], O vacancy [64, 65], S vacancies [66]) for the synthesizing SACs. As shown in figure 3(a), the synthesis of Au SACs with a mass percentage of 0.3% was achieved by employing defect-rich TiO$_2$ nanosheets with abundant oxygen vacancies as support (Au–SA/Def-TiO$_2$) [67]. The authors claimed that the oxygen vacancies can effectively stabilize single Au atoms through constructing the Ti–Au–Ti structure which can promote the catalytic performance of CO oxidation reaction via reducing the energy barrier and decreasing the competitive adsorption of O$_2$ and CO on single atomic Au sites. Recently, sulfur vacancies defect can also act as capturing sites for single metal atom. Tsang et al adopted a Li intercalation and chemical exfoliation methods to anchored isolated Co atoms on S vacancies in the basal planes of MoS$_2$ monolayer in, Co–3MoS$_2$) [68]. Yao et al also developed single-atom Ni electrocatalysts supported on defective graphene (A–Ni@DG) through incipient wetness impregnation and then acid etching treatment (figure 3(c)) [69]. It revealed that the exceptionally high activity and stability of A–Ni@DG ascribed to the unique electronic configurations of Ni atoms trapped in the defects. In addition to anionic defects/vacancies, a variety of cationic defects/vacancies (such as Al$^{3+}$ vacancies [70], Ni$^{2+}$ vacancies [71, 72], Ti$^{3+}$ vacancies [73]) also have been recently exploited to prepare SACs. Li et al first synthesized nickel hydroxide nanoboard with rich Ni$_2^+$ vacancy defects (Ni(OH)${_x}$ NBs) and subsequent Ni(OH)${_x}$ NBs can effectively stabilize single-atomic Pt species through a wet impregnation method.

SACs have been synthesized through rationally designed uniform coordination sites, which would regard as ‘paws’ to anchor metal precursors or metal atoms avoid their migration and agglomeration. It is worth noting that some elements (such as N [74–77], O [78–80], S [81]) or heteroatom-doped carbon materials with lone pairs of electrons can adsorb and bind metal species via forming strong interaction [82–84]. Nitrogen-doped carbon or graphene materials have been explored as a perfect support for SACs. For instance, polymer-derived hollow nitrogen-doped porous carbon materials with large surface area, excellent electrical conductivity and plentiful N sites for coordinating have been exploited for stabilizing atomically dispersed Co sites by a strong interaction with cobalt phthalocyanine in figure 4(a) [74]. Furthermore,
Figure 3. Some examples of metal SAC synthesized by defect engineering strategy. (a) Schematic illustration of preparation process for Au-SA/Def-TiO$_2$ with O vacancies as coordination sites [67]. [67] John Wiley & Sons. Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) HAADF-STEM image (left) and corresponding magnified image (right) for Co–MoS$_2$ with S vacancies as anchoring sites [68]. Reprinted by permission from Springer Nature Customer Service Centre GmbH: [Springer Nature] [Nature Chemistry] [68], (2017). (c) Fabrication schematic of single Ni atoms anchored by C vacancies of graphene [69]. Reprinted from [69], Copyright (2018), with permission from Elsevier.

Figure 4. Some examples of metal SAC synthesized by coordination design strategy. (a) Schematic illustration of Co–N$_5$/HNPCs catalyst with N in nitrogen-doped porous carbon as coordination sites [74]. [74] John Wiley & Sons. Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) Illustration of single Pd atoms with N in mpg-C$_3$N$_4$ as coordination [75]. [75] John Wiley & Sons. Copyright 2015 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (c) Structure of Pt/HSC catalyst with S in zeolite-templated carbon as coordination sites [81]. Reproduced from [81], CC BY 4.0.

graphitic carbon nitrides with the unique N/C-coordinating holes can provide abundant N coordination sites for anchoring various isolated metal precursors or metal species, such as Fe [85], Ru [86], Au [87], Pd [75] (figure 4(b)). Another study showed that the Pt–S$_4$ complex can be obtained adopting a simple wet-impregnation method, which can atomically stabilize dispersed Pt on zeolite-template carbon with rich S coordination sites in figure 4(c) [81].

3.3. Physical and chemical deposition method
Preparation of SACs with uniform geometrical structures can be obtained through atomic layer deposition (ALD) strategy which is a gas-phase deposition method [16, 88]. As shown in figure 5(a), by adjusting the ALD cycle numbers from 0 to 100, Sun et al synthesized Pt SACs and Pt nanoparticle supported by nitrogen-doped graphene nanosheets (NGNs) [89]. And the Pt SACs showed high activity for the HER. The Lu et al produced an isolated Pd catalyst on graphene by precisely tuning the variety and amount of surface oxygen groups anchor on the pristine graphene [90]. The oxygen functional groups can react with Palladium exalfluoroacetacetylacetytate (Pd(hfac)$_2$), and then immobilize the Pd atom after the hfac ligands were withdrew under the ALD conditions. In another research of their team, they accurately synthesized Pt$_2$ dimers on graphene [91]. Pt$_1$/CeO$_2$ SACs can be fabricated catalyst through ALD approach [92].
Electrochemical deposition is a conventional strategy to decorate the surface or to change the surface characteristics of materials [95, 96]. In one study, atomically dispersed Pt atoms on the sidewall of single-walled carbon nanotubes (SWCNT) was fabricated by electroplating method, in which Pt ions from Pt foil counter dissolved in sulfuric acid and then redeposited on SWCNT dropcasted on a glassy carbon working electrode to form Pt SACs-SWCNT during repeating potential cycling in three-electrode systems [97]. Similarly, Luo et al also successfully prepared a catalyst of single Pt atoms on CoP nanotube supported on Ni foam via potential-cycling method (figure 5(b)) [93]. Vacancies also can stabilize single metal atoms during electrochemical process [93, 98, 99]. For example, Tan and collaborators successfully constructed Co vacancies by slight dissolution of Co atoms in np-Co0.85Se, meanwhile Pt atoms were captured by Co vacancies during cyclic voltammetry (CV) in a three-electrode cell (figure 5(c)) [94].

4. Electrochemical HER application of SAEC

When metal species were divided into smaller particles, the surface cohesive energy of a metal increased significantly, which leads that single atoms are generally prone to reunion [100]. An effective way to overcome this property is to reduce the large surface free energy of single metal atoms through anchoring sites in a unique way on the supported materials by a strong chemical bonding interaction between metal atoms and support. Such interaction not only influences the stability of single metal atoms but also alters the activity of the catalyst by manipulating the electronic structure of metal atoms [101].

In very recent years, various support substrates have developed to strengthen coordination bonds and prevent metal species from aggregating during synthesis and catalysis processes of multifarious single-atoms catalysts [69, 81, 101–104]. Tables 1 and 2 shows the summary of SAECs along with the corresponding materials, electrolyte, metal contents, and their HER performances in 0.5 M H2SO4 solution and 1.0 M KOH solution, according to the order: from precious metals to cheap metals. Herein, by classifying the supports into carbon-based materials and metal compound-based materials, we will present a more detailed discussion to adjust and identify the local coordination environment of atomically dispersed metal and their influence toward the HER catalytic performance.

4.1. Coordination sites on carbon-based supports

Having the prominent advantage of high specific surface area, excellent electric conductivity and superior stability and with many superiorities over other supports in anchoring single metal atoms, carbon nanomaterials are the most extensively used as the appropriate supports to stabilize single-atom catalysts for HER [133]. The strong interatomic interactions between the single metal atoms and adjacent carbon atoms
Table 1. Summary of single atom electrocatalysts along with the corresponding HER performance in 0.5 M H₂SO₄ solution except Pt–MoS₂ and Co–MoS₂.

| Category          | Electrocatalysts                      | $\eta_{10}$ (mV) | Tafel slope (mV dec⁻¹) | TOF (s⁻¹ at a specific overpotential) | Mass activity (A g⁻¹ at a specific overpotential) | Metal content | Reference   |
|-------------------|--------------------------------------|------------------|------------------------|--------------------------------------|-----------------------------------------------|---------------|-------------|
| Carbon-based supports | ALD50Pt/NGNs                          | ~50              | 29                     | N.A.                                 | 2700@0.05 V                                   | 2.1 wt%       | [89]        |
|                   | Pt SAS/AG                             | 12               | 29.3                   | N.A.                                 | 22 4000@0.05 V                                | 0.44 wt%      | [105]       |
|                   | Pt@PCM                               | 105              | 65.3                   | 65.5@0.5 V                           | 4000@0.2 V                                   | 0.53 wt%      | [106]       |
|                   | Pt SA@DG                              | 23               | 25                     | N.A.                                 | 26 2000@0.05 V                                | 2.1 wt%       | [107]       |
|                   | Pt1/MC                                | ~30              | 26                     | N.A.                                 | 10 0000@0.065 V                               | 2.6 wt%       | [108]       |
|                   | Pt–GDY1                               | ~30              | 49                     | N.A.                                 | 7260@0.1 V                                   | 4.65 mg cm⁻²  | [109]       |
|                   | Pt–GDY2                               | ~70              | 38                     | N.A.                                 | 23 6400@0.1 V                                 | N.A.          | [109]       |
|                   | Pt1@Fe–N–C                            | 60               | 42                     | N.A.                                 | N.A.                                         | 2.1 wt% Pt    | [80]        |
|                   | Pt1/NPC                               | 25               | 28                     | 2.93@0.025 V                         | 2860@0.025 V                                 | N.A.          | [110]       |
|                   | Pt–GT-1                               | 18               | 24                     | N.A.                                 | N.A.                                         | N.A.          | [111]       |
|                   | Pt1/OLC                               | >50              | 36                     | 40.78@0.1 V                          | 7400@0.038 V                                 | 0.27 wt%      | [112]       |
|                   | A–CoPt–NC                             | 27               | 31                     | N.A.                                 | 224 000@0.045 V                               | 0.419 mg cm⁻² | [98]        |
|                   | Mo³/GDY                               | 48               | 33                     | N.A.                                 | 15 100@0.07 V                                 | 7.5 wt%       | [113]       |
|                   | Ni/GD                                 | 88               | 45.8                   | 1.59@0.1 V                           | 1260@0.05 V                                  | 0.278 wt%     | [114]       |
|                   | Fe/GD                                 | 66               | 37.8                   | 4.15@0.1 V                           | 3520@0.05 V                                  | 0.68 wt%      | [114]       |
|                   | Mo1NiC₂                               | 154              | 86                     | 2.59@0.2 V                           | N.A.                                         | 1.32 wt%      | [115]       |
|                   | W1NiC₂                                | 105              | N.A.                   | ~4@0.12 V                            | N.A.                                         | 1.21 wt%      | [116]       |
|                   | np-Ni/graphene                        | 50               | 45                     | 0.8@0.3 V                            | N.A.                                         | 4–8 at%       | [62]        |
|                   | aNi@G5775                             | 70               | 31                     | 5.7@0.1 V                            | 1.24 wt%                                     | N.A.          | [69]        |
|                   | Co–NG                                 | ~147              | 82                     | 1.189@0.2 V                         | N.A.                                         | 0.57 at%      | [117]       |
|                   | Co–SAS/HOPNC                          | 137              | 52                     | 3.8@0.2 V                            | N.A.                                         | 0.49 wt%      | [118]       |
|                   | Co₁/PCN                               | 151              | N.A.                   | 5.98@0.1 V                           | ~0.3 wt%                                     | N.A.          | [119]       |
|                   | Co–NG–MW                              | 127              | 80                     | 0.385@0.1 V                         | N.A.                                         | ~1.1 wt%      | [120]       |
|                   | Ru@Co–Sas/N–C                         | 57               | 55                     | N.A.                                 | 0.285 mg cm⁻²                                | N.A.          | [121]       |
|                   | Ru–NC                                 | 29               | 28                     | N.A.                                 | 4 at%                                        | N.A.          | [122]       |
| Metal compound supports | Pt SA/WO₃₋ₓ                          | 38               | 45                     | 35@0.1 V                             | 12 800@0.05 V                                 | N.A.          | [123]       |
|                   | Pt@MoS₂/NiS₂                          | 34               | 40                     | N.A.                                 | N.A.                                         | N.A.          | [124]       |
|                   | Pd/Cu–Pt NRs                           | 22.8             | 25                     | N.A.                                 | N.A.                                         | N.A.          | [125]       |
|                   | NiSA–MoS₂/CC                          | 110              | 74                     | N.A.                                 | N.A.                                         | 1.9 at%       | [126]       |
|                   | Pt/np–Co₀.₈₅Se                       | 58               | 26                     | N.A.                                 | 13 570@0.1 V                                 | 1.03 wt%      | [94]        |
|                   | Pt–MoS₂                               | ~145            | 96                     | N.A.                                 | N.A.                                         | 1.7 wt%       | [127]       |
|                   | Co–MoS₂                               | ~185             | 85                     | N.A.                                 | N.A.                                         | N.A.          | [127]       |

*The unknown data.
Table 2. Summary of single atom electrocatalysts along with the corresponding HER performance in 1.0 M KOH solution except Ru-NC and Co@NG.

| Category                  | Electrocatalysts | $-\eta_{10}$ (mV) | Tafel slope (mV dec$^{-1}$) | TOF (s$^{-1}$) at a specific overpotential | Mass activity (A g$_{metal}$$^{-1}$) at a specific overpotential | Metal content | Reference |
|---------------------------|------------------|-------------------|-----------------------------|------------------------------------------|----------------------------------------------------------------|---------------|-----------|
| Carbon-based supports     | Pt@PCM           | 139               | 73.6                        | N.A.$^a$                                 | N.A.                                                            | N.A.          | [106]     |
|                           | A–CoPt–NC        | 50                | 48                          | N.A.                                    | 45 000@0.07 V                                                   | 0.419 mg cm$^{-2}$ | [98]      |
|                           | Mo$_3$Ni$_2$C$_2$| 132               | 86                          | 1.46@0.15 V                             | N.A.                                                            | 1.32 wt%      | [115]     |
|                           | Fe–N$_4$         | 202               | 123                         | N.A.                                    | N.A.                                                            | 1.96 wt%      | [128]     |
|                           | SAs/NPC          |                   |                             |                                         |                                                                 |               |           |
|                           | Co–NG            | >250              | N.A.                        | N.A.                                    | N.A.                                                            | 0.57 at%      | [117]     |
|                           | Co$_3$/PCN       | 89                | 52                          | 5.98@0.1 V                              | N.A.                                                            | N.A.          | [119]     |
|                           | Ir$_1$@Co/NC     | 55                | 119                         | N.A.                                    | N.A.                                                            | N.A.          | [56]      |
|                           | Ru@Co–SAs/N–C    | 7                 | 30                          | N.A.                                    | 500@0.01 V                                                      | 0.285 mg cm$^{-2}$ | [121]     |
|                           | Ru–NC            | 12                | 14                          | N.A.                                    | N.A.                                                            | 4 at%         | [122]     |
|                           | Ru–NC            | 47                | N.A.                        | N.A.                                    | N.A.                                                            | 4 at%         | [122]     |
|                           | Co@NG            | 172               | 42.5                        | N.A.                                    | N.A.                                                            | 1.32 wt%      | [129]     |
|                           | Ni$_5$P$_4$–Ru   | 54                | 52                          | N.A.                                    | 1601@0.05 V                                                     | 3.83 wt%      | [130]     |
|                           | SAni–MoS$_2$/CC  | 70                | 60.3                        | N.A.                                    | 11 800@0.07 V                                                   | 6 at%         | [131]     |
| Metal compound supports   | NiS@–MoS$_2$/CC  | 98                | 75                          | N.A.                                    | N.A.                                                            | 1.9 at%       | [126]     |
|                           | Pt/np–Co$_{0.85}$Se | 58              | 39                          | N.A.                                    | 1280@0.1 V                                                     | 1.03 wt%      | [94]      |

$^a$The unknown data.
can significantly tune the charge density and electronic structure of active metal sites. Such characteristics could be exploited to enhance the stability and catalytic performance of the electrocatalyst.

Single Pt atoms anchored on nanocarbon-based supports have also been widely synthesized and examined for HER catalysts [134], such as ALD50Pt/NGNs [89], Pt SASs/AG [105], Pt@PCM [106], Pt SAs/DG [107], Pt/MC [108], Pt–GDY1 (C1–Pt–Cl1) [109], Pt1@Fe–N–C [80], Pt1/NPC [110], A–CoPt–NC [98], Pt–GT-1 [113]. Sun et al used the ALD technique to fabricate novel Pt catalysts supported by NGNs for
the HER [89]. The size of the Pt catalysts on the NGNs ranged from single atoms (Pt1–NGNs) to NPs (Pt–NGNs), which were precisely controlled by simply adjusting the number of ALD cycles. Interestingly, both of them displayed better catalytic performance towards the HER than commercial Pt/C catalysts in 0.5 M H₂SO₄. Figures 6(a) and (b) show the annular dark field (ADF) STEM images of ALD Pt/-NGNs with different sizes of the Pt electrocatalysts anchored on NGNs: ALD Pt 50/-NGNs and ALD Pt 100/NGNs with ALD cycles of 50 and 100. There are a lot of individual Pt atoms and very small Pt clusters on the NGNs surface in the ALD 50 Pt/NGNs catalysts. For ALD 100 Pt/NGNs catalysts, some single Pt atoms and small Pt clusters are still present, whereas many Pt clusters have grown to form NPs at a larger quantity. Surprisingly, the ALD Pt/NGN catalysts show even much higher HER activities than the commercial Pt/C catalysts (figure 6(c)). The HER catalytic activity of the ALD Pt/NGNs reduced when increasing the number of ALD cycles, which was attributed to the extra wasted Pt. The ALD 50 Pt/NGNs catalysts, normalized to the Pt loading (figure 6(d)), displayed a small Tafel slope. Meanwhile, the Pt mass activity of the ALD 50 Pt/NGNs catalysts at the overpotential of 0.05 V RHE for HER can reach 10.1 A mg⁻¹, which was 7.8 times than the ALD 100 Pt/NGNs catalyst (2.12 A mg⁻¹), and 37.4 times greater than that of the Pt/C catalyst (0.27 A mg⁻¹). The excellent performance of the single Pt atoms and clusters arise from the partially unoccupied density of states (DOS) of the 5d orbitals of single Pt atoms on the N-doped graphene.

The long-term stability of the ALD Pt/NGNs catalysts can be observed by extended electrolysis at fixed potentials. The stability of ALD 50 Pt/NGNs can be confirmed by accelerated degradation tests (ADT)
Figure 9. (a) HAADF–STEM image of Co$_1$/PCN, exhibiting that Co single atoms are well-dispersed in PCN matrix. (b) First-shell fitting of EXAFS spectra of different fitting paths for the Co$_1$/PCN under ex situ and open-circuit conditions and at $-0.04$ V$_{RHE}$. Black and red lines represent experimental and fitting curves, respectively. (c) Calculated energy diagram of H$_2$O dissociation. Insets: corresponding atomic configurations of the water dissociation step on the surface of HO–Co$_1$/PCN and Pt(111) [119]. Reprinted by permission from Springer Nature Customer Service Centre GmbH: [Springer Nature] [Nature Catalysis] [119], (2019). (d) Hydrogen adsorption free energy diagram of Ni-doped graphene (Ni$_{ab}$/G, Ni$_{sub}$/G, and Ni$_{def}$/G) and Pt catalyst for HER [62]. [62] John Wiley & Sons. [Copyright 2015 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim].

The ALD50Pt/NGNs only showed a loss of only 4% of its initial current density, which was lower than the ALD50Pt/NGNs (~24% loss) catalyst and the commercial Pt/C catalysts (19% loss) when the polarization curve was cycled 1000 times. In addition, another main issue with these single-atom catalysts is that their tendency to get agglomerated to form nano/microparticles during the course of the reaction. For that, ADF STEM images acquired from the ALD50Pt/NGNs after the ADT (figure 6(f)) revealed that there was only a slight increase in the Pt size without significant aggregation. To further understand the effect of a strong interaction between the support and the deposited metal on the stability of the Pt atoms and clusters, the authors synthesized ALD-deposited Pt on graphene nanosheets (GNs) for comparison. It can be considered that the larger particles formed on the GNs (figure 6(g)) during the ALD process can be led to the weaker interaction between the Pt and the graphene support, compared with the N-doped graphene support. Furthermore, after the ADT test, the ALD50Pt/NGNs sample was examined using ADF imaging (figure 6(h)) and found that the frequency of larger clusters and NPs increased. It can be suggested that the increased Pt particle size during cycling on the GNs may be caused by the weaker adsorption energy, thus leading to a decreased stability of the Pt atoms, clusters and NPs, making them susceptible to degradation mechanisms [135]. The Pt/C catalyst will coalesce into larger particles, and the average size of Pt NPs increases from 4.2 to 5.5 nm after ADTs, according to the high-resolution transmission electron microscope image. The growth of NPs may be caused by the migration of Pt owing to weak interaction between Pt and the support [136]. This indicates that compared with ALDpt/NGNs and Pt/C catalyst, the increased strong interaction between the Pt catalysts and support anchored on NGNs leads to the higher stability and activity.

On the contrary, single Pt atoms were confirmly supported on onion-like nanospheres of carbon (OLC) as a electrocatalyst (Pt$_1$/OLC), leading to high durability and activity [112]. In acidic medium, Pt$_1$/OLC (0.27 wt% Pt) displayed very small $t_{10} = 38$ mV with low Tafel slope of 36 mV dec$^{-1}$, high TOF of 40.78 H$_2$ s$^{-1}$ at 100 mV and impressive stability after 6000 CV sweeps, which is comparable to commercial Pt/C. The extended x-ray absorption fine structure (EXAFS) analysis exhibited that the single Pt atoms on the OLC support were anchored with one C-atom and two O-atoms in the form of Pt$_1$O$_2$C$_3$ (figure 7(a)). The x-ray absorption near-edge structure (XANES) spectra measurements revealed that the oxidation states...
of the single Pt atoms in Pt$_1$/OLC were situated between the Pt$^6$ and Pt$^{IV}$. First-principle calculations demonstrate that a tip-enhancement effect at the Pt site of the curved OLC surface leads to gather the localized electrons and induces strong local electric fields, which may enhance the electrocatalytic performance for HER (figure 7(b)). Another study by their team designed a microwave reduction method to anchor single Pt atoms on aniline-stacked graphene (AG) with excellent HER performance (Pt SASs/AG) [105]. EXAFS exhibited that atomically dispersed Pt site was anchored on graphene and it coordinated with four aniline molecules to form Pt–N$_4$ configuration (figure 7(c)). Density functional theory (DFT) calculations found that the coordination of single-atom Pt with the N of aniline molecules optimized the electronic structure of the single Pt atomic sites and the free energy of hydrogen adsorption, finally promoting HER stability as well as activity (figure 7(d)). Lou et al reported a dynamic reaction method to modulate and stabilize the isolated Pt atoms in the mesoporous carbon matrix (Pt@PCM) [106]. They confirmed that the single Pt atoms were coordinated by surrounding carbon/nitrogen atoms. To understand the HER performance of Pt@PCM, the DOS calculation suggested that the electron transfer from central Pt sites to neighboring C/N atoms can increase the electronic states of C/N atoms, which resulted in the enhanced hydrogen adsorption ability as well as thereby enhanced the HER activity. The DFT further indicated that the adjacent C and N atoms can be triggered by the isolated Pt sites, making both confined Pt atoms centers and adjacent C/N atoms become the active sites. In the studies by Chen et al, ruthenium and nitrogen codoped carbon nanowires are prepared as effective HER electrocatalysts [19, 122, 137]. Notably, the HER performance of Ru–NC catalysts was better than those of commercial Pt/C in alkaline media [122].

In recent years, the non-noble metals (such as Fe, Co, Ni, Mo and W) carbon-supported SACs catalysts make rapid progress on the enhancing the performance of HER. For instance, Fei et al synthesized uniformly dispersed Co atoms on nitrogen-doped graphene (Co–NG) by simply heating graphene oxide and a small amount of cobalt salt in NH$_3$ atmosphere [117]. The high-angle ADF scanning TEM (HAADF-STEM) measurements demonstrate that, the bright dots about 2–3 Å in size are corresponding to isolated Co atoms in figure 8(a). Fourier-transformed EXAFS (FT-EXAFS) analysis showed that there are no substantial differences in the coordination environments of Co atoms which exist in the Co–NG and Co–G samples. The wavelet-transformed EXAFS analysis confirmed a location of maximum at 3.2 Å$^{-1}$ for forming Co–C bonds in Co–G, similarly that at 3.4 Å$^{-1}$ for forming Co–N bonds in Co–NG (figures 8(b) and (c)). The above-mentioned analyses revealed that the single Co atom were introduced into the NG support to form a strong binding interaction between Co and N atoms. The Co–NG (which contains only 0.57 at% Co) exhibited a very small onset $\eta$ of $\approx$ 30 mV, and a $\eta_{10}$ of only $\approx$ 147 mV, much lower than NG ($\approx$ 195 mV) or Co–G ($\approx$ 225 mV) in 0.1 M H$_2$SO$_4$ (figure 8(d)). More importantly, the Co–NG catalysts exhibited much higher HER activity than recently catalysts reported in that period (figure 8(e)) [138–144]. Co–NG also showed an excellent stability in both 0.5 M H$_2$SO$_4$ and 1 M KOH electrolyte solution tested by cyclic voltammetry and galvanostatic measurements (figures 8(f) and (g)), which is attributed to a strong coordination of Co sites with N atoms in NG.

However, in this work, Wei et al monitored the atomic-level dynamic catalytic-site structure of Co single atoms catalysts (Co$_0$/PCN) under alkaline HER by using operando x-ray absorption spectroscopy [119]. Generally, Co$_0$/PCN processed a high HER activity comprising single Co atoms in phosphorized carbon nitride (PCN). In 1.0 M KOH electrolytes, Co$_0$/PCN showed superior HER catalytic performance with a low overpotential of 89 mV to deliver a current density of 10 mA cm$^{-2}$, compared with Co$_0$/CN and pristine PCN where $\eta_{10}$ = 138 mV and $\eta_{10}$ = 268 mV, respectively. This material also displayed a small Tafel slope of 52 mV dec$^{-1}$, although slightly worse than that of commercial Pt/C ($\zeta$ = 38 mV dec$^{-1}$). HAADF-STEM images exhibited that the bright dots, single Co atoms, were evenly distributed on the surface of PCN nanosheets (figure 9(a)). Combining operando XANES analysis and DFT calculations, the author identified the changes of active structure in single Co sites under alkaline HER reaction. They found that single Co sites with unsaturated coordination were very sensitive to the alkaline electrochemical conditions, and thereby enhancing the species of OH$^-$ adsorption the valence state changed into high-valence HO–Co$_0$–N$^2$ moiety (figure 9(b)), which probably account for the improved alkaline HER performance. For the adsorption energy of H$_2$O molecule, HO–Co$_0$/PCN (0.94 eV) are more beneficial than Pt (111) facet (0.46 eV). The HO–Co$_0$/PCN catalyst exhibited much easier dissociation of H$_2$O as shown in figure 9(c). In addition, the formation of highly oxidized Co sites reduce the energy barriers for water dissociation and boost their catalytic activity for HER.

Interestingly, Chen et al also reported a single Ni atoms catalysts anchored on 3D nanoporous graphene (Ni-doped graphene), which showed a $\eta_{10}$ of 50 mV and a Tafel slope of 45 mV dec$^{-1}$ in 0.5 M H$_2$SO$_4$ solution [62]. DFT calculations exhibited that the configuration of Ni dopants occupying the carbon vacancy of the graphene lattice (Ni$_{dol}$/G) in Ni-doped graphene (figure 9(d)), having a lower $\Delta$G$^\ast$ value of 0.10 eV (figure 9(e)), very similar to Pt catalyst (0.09 eV), which is beneficial to improve the HER activity. In another study, single Ni atoms anchored on graphene were synthesized by carbonizing Ni-based
metal-organic framework (denoted by A–Ni–C) \[145\]. The unique electronic structures were formed due to a strong chemical interaction between Ni species and supports, and thus optimized the Gibbs free energy of H* adsorption and ensured a faster electron transfer, which result in an excellent HER performance as well as a satisfactory durability. Li et al successfully prepared single Mo atoms supported by N-doped carbon via templated method and pyrolysis precursors \[115\]. In 0.1 M KOH solution, this material displayed superior HER catalysis with an overpotential (\(\eta_{10}\)) of \(-132\) mV, in comparison to MoN or MoC where \(\eta_{10} = -225\) mV and \(-195\) mV individually. Moreover, the catalyst also showed better long-term durability than 20% Pt/C in both alkaline environment (0.1 M KOH solution) and acidic condition (0.5 M H\(_2\)SO\(_4\) solution). EXAFS characterization clearly confirmed that Mo atoms were anchored by one N atom and two C atoms. The DFT studies revealed that Mo\(_1\)Ni\(_1\)C\(_2\) sites have the lowest adsorption free energy of H* (0.082 eV), in contrast with MoN (0.401 eV), N-doped graphene (0.672 eV) and Mo\(_2\)C (0.260 eV). The DOS calculation demonstrated that Mo\(_1\)Ni\(_1\)C\(_2\) possessed a much larger electronic density near the Fermi level than MoN and Mo\(_2\)C, which was benefit for charge transfer. Furthermore, the charge density of Mo\(_1\)Ni\(_1\)C\(_2\) close to the Fermi level was primarily own to \(d\)-orbital of Mo atoms, therefore the single Mo atoms played a crucial role in optimizing DOS near the Fermi level and promoting HER catalytic performance.

4.2. Anchoring sites on metal compound support

In recent years, metal compounds (such as carbides \[146\], oxides \[17\], chalcogenides \[127\], and phosphides \[130\]) also have been used to stabilize metal atoms though forming a strong single metal atom-support interaction. Generally, metal oxides suffer from poor stability and unsatisfactory conductivity in alkaline or acidic environment, because of that it is not suitable as a substrate for electrochemical HER applications. Interestingly, when single-atom Pt was supported on WO\(_{3-x}\) (Pt SA/WO\(_{3-x}\)), Pt SA/WO\(_{3-x}\) displayed a higher corrosion resistance, improved Pt mass activity and lower overpotential at 10 mA cm\(^{-2}\) for HER in comparison to single atom Pt anchored on carbon matrix (Pt SA/C) and Pt nanoparticles anchored on WO\(_{3-x}\) support (Pt NP/WO\(_{3-x}\)), due to the higher degree of hydrogen diffusion from the interface between atomically dispersed Pt atoms and WO\(_{3-x}\) support.

Bao et al synthesized a single Pt-doped MoS\(_2\) nanosheets (Pt–MoS\(_2\)) in which single-atom Pt replaced the positions of the Mo atoms and formed Pt–S bonds \[127\]. The Pt–MoS\(_2\) catalyst exhibits a significantly enhanced HER performance and stability contrast to initial two-dimensional MoS\(_2\) nanosheets (figure 10(a)), which is due to the doped Pt enhanced the H adsorption ability in-plane neighboring S atoms.
The XANES and HAADF-STEM images results clearly verified that the Mo sites in the 2D MoS\(_2\) plane have been successfully substituted by atomically dispersed Pt atoms (figures 10(b) and (c)). The DFT calculations confirmed that the doped Pt atoms tuned the absorption behavior of in-plane adjacent S atoms, leading to a greatly enhanced HER activity. As further illustrated in the volcano plot, a number of single-atom metal dopants can significantly improve the catalytic performance of the inert MoS\(_2\) surface for HER via adjusting the adsorption behavior of H atoms on the neighboring S sites (figure 10(d)).

In addition, Tan et al constructed atomically dispersed Pt supported on nanoporous Co\(_{0.85}\)Se material (Pt/npc-Co\(_{0.85}\)Se), which showed high HER performance in neutral electrolyte \([94]\). The Pt/npc-Co\(_{0.85}\)Se exhibited a low overpotential of 55 mV at 10 mA cm\(^{-2}\) and it displayed a small Tafel slope of only 35 mV dec\(^{-1}\) for HER in 1.0 M phosphate buffer solution (PBS). Results of experimental investigations and theoretical calculations demonstrated that the original inert Co atoms can be triggered by single-atom Pt, and the initial inert Co atoms become new active sites for water dissociation. Furthermore, there will be strong electronic interactions between atomic-level Pt and npc-Co\(_{0.85}\)Se, which reduce energy barriers for dissociating water and obviously boost the adsorption/desorption behaviors of hydrogen, therefore synergistically improving HER performance. CoP can also be a great support to stabilize the single Pt atoms. Luo et al synthesized a PtSA-NT-NF catalyst, which was anchored on CoP-based nano-tubes supported by a Ni foam. The PtSA-NT-NF exhibited a low overpotential of 24 mV at 10 mA cm\(^{-2}\) and displayed a small Tafel slope of only 30 mV dec\(^{-1}\) for HER in 1.0 M PBS. The mass activity at the overpotential of 50 mV can be achieved 70 Ag\(^{-1}\), which is about four times of that of Pt/C. Meanwhile, the PtSA-NT-NF catalyst demonstrates an excellent durability in neutral media. The great HER performance of PtSA-NT-NF was attributed to the high Pt mass utilization and the positive modulation of SAC electronic structure by substrates. Ru single atoms catalysis were synthesized in metal compound by incorporating Ru\(^{3+}\) species into the nickel-vacancy defect of nickel hydroxides and then phosphorization treatment (Ru SAs@PN) \([130]\). Ru SAs@PN was tested to process great HER activity.

Besides precious metal, nonprecious metal can be trapped by MoS\(_2\) nanosheets. Feng et al introduced Ni sites into MoS\(_2\) nanosheets (denoted as Ni–MoS\(_2\)) which can effectively accelerate the kinetics of HER \([132]\). The DFT calculations first investigated the energy barrier of initial water dissociation (\(\Delta G(H_2O)\)), adsorption free energy of –OH (G(OH)) and the combination of H\(^+\) intermediates into H\(_2\) (\(\Delta G(H)\)) for MoS\(_2\) nanosheets, Fe-doped MoS\(_2\) (Fe–MoS\(_2\)), Co-doped MoS\(_2\) (Co–MoS\(_2\)) and Ni–MoS\(_2\) (Ni–MoS\(_2\)). As shown in figure 10(e), the \(\Delta G(H_2O)\) is 0.66 eV for Ni–MoS\(_2\), which is much lower than 1.17 eV for pure MoS\(_2\). The decreased \(\Delta G(H_2O)\) values on Ni–MoS\(_2\) speed up the kinetics of water dissociation and facilitate the desorption of –OH. As a result, the Ni–MoS\(_2\) catalysts displayed a remarkable activity in 1.0 M KOH aqueous solution, with the onset overpotential of 45 mV, and an extremely low overpotential (\(\eta_{10}\)) of 98 mV, in comparison to pure MoS\(_2\), \(\eta_{10}\) = 308 mV and reported MoS\(_2\)-based catalysts \([147–152]\).

### 5. Conclusions and perspectives

Electrochemical water splitting is one of the most promising approach for producing pure hydrogen. Because of remarkable characteristics such as the maximal atom utilization efficiency, high catalytic performance, selectivity and durability, the SAECs have shown great application potential for HER. In this review paper, after a brief introduction of mechanistic principle for HER, primary strategies for the fabrication of SAECs have been summarized, such as high-temperature pyrolysis method, wet-chemistry method as well as physical and chemical deposition method. Atomically dispersed single metal atoms in these SAECs are usually achieved through anchoring metal atoms on the carbon-based or metal compound substrates by coordination. We focus on recent advances in adjusting the local structure and the interaction between metal atom and support of SAECs to obtain a significant understanding of catalytic mechanisms and clarify the electronic structure-activity relationship of single metal sites. SAECs supported on both carbon and metal compound matrix have shown extraordinary activity toward HER. SAECs mainly involve metal atoms bonded to non-metallic elements of the support matrix, such as carbon, nitrogen, oxygen, sulfur, and phosphorus, according to the coordination environment of metal–matrix and the supporting matrix, which determines the bonding strength of atomic hydrogen (H\(^+\)) and subsequently the electrocatalytic activity of HER.

Despite numerous efforts in the exploration of electrochemical water splitting into pure hydrogen production. However, there are still many challenges to be addressed.

(a) The activity and stability of SAECs for HER can be further optimized by different strategies. For activity, one important prerequisite is to increase the intrinsic activity of active sites for improving the activity of SAECs \([1, 153]\). Various factors, such as the coordination environment of the metal moieties,
metal–support interfacial interaction, the element properties of the metal, the nature of the support and heteroatom-doped supports, can effective regulate the intrinsic activity of SAEC [133, 154–156].

(b) Increasing the density of centers is another approach to promote catalytic activity by enhancing the isolated metal mass loading and the exposed active site area [25, 80, 157].

(c) The stability issues must be addressed to make the large-scale production of SAECs. Improving the interaction between metal atoms and the supports and choosing a suitable support is one of the most essential strategies to solve its stability problem.

(d) To accurately tune the geometric and electronic structures of the metal centers and identify the coordination environments of single metal atoms, advanced characterization techniques are highly desired [155, 158]. Some effective characterization techniques such as, XANES simulation, spatially resolved APT and EELS, should be combined with EXAFS [159]. Besides, in situ or operando characterization techniques are very important in probing the mechanism and dynamic structure evolution of the SACs catalysis during the catalytic reaction.

(e) Both the theoretical calculations and machine learning for data analysis are effective approach to rationally design and predict the new-generation high catalytic performance SAECs [160–162].

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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