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REVIEW ARTICLE

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# Oxygen reduction electrocatalysis: From conventional to single-atomic platinum-based catalysts for proton exchange membrane fuel cells

**Abstract** Platinum (Pt)-based materials are still the most efficient and practical catalysts to drive the sluggish kinetics of cathodic oxygen reduction reaction (ORR) in proton exchange membrane fuel cells (PEMFCs). However, their catalysis and stability performance still need to be further improved in terms of corrosion of both carbon support and Pt catalyst particles as well as Pt loading reduction. Based on the developed synthetic strategies of alloying/nanostructuring Pt particles and modifying/innovating supports in developing conventional Pt-based catalysts, Pt single-atom catalysts (Pt SACs) as the recently burgeoning hot materials with a potential to achieve the maximum utilization of Pt are comprehensively reviewed in this paper. The design thoughts and synthesis of various isolated, alloyed, and nanoparticle-contained Pt SACs are summarized. The single-atomic Pt coordinating with non-metals and alloying with metals as well as the metal-support interactions of Pt single-atoms with carbon/non-carbon supports are emphasized in terms of the ORR activity and stability of the catalysts. To advance further research and development of Pt SACs for viable implementation in PEMFCs, various technical challenges and several potential research directions are outlined.

**Keywords** oxygen reduction electrocatalysis, Pt single-atom catalysts, conventional Pt-based catalysts, design thoughts and synthesis, metal-support interactions

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## 1 Introduction

With the increase of energy demand and the aggravation of environment pollution, it is urgent to develop high-efficient and safe technologies for energy storage and conversion of clean electricity generated from renewable and sustainable energy sources such as solar, wind, waterfall, and geothermal. [1,2]. Electrochemical energy technologies including proton exchange membrane fuel cells (PEMFCs) have been identified as reliable options [3–5], which can achieve the conversion of chemical energy (i.e., hydrogen energy) to electrical energy. However, the sluggish kinetics of oxygen reduction reaction (ORR) at the cathode of PEMFC needs an electrocatalyst to accelerate its rate to meet the requirement of practical application rate [6–8]. Therefore, the development of highly active and stable ORR electrocatalysts is desperately needed. So far, platinum (Pt)-based materials still remain the most practical ORR electrocatalysts. However, such Pt-based catalysts show some drawbacks of scarce Pt resources, high-cost, and unsatisfying activity/stability [9,10]. Currently, the commercially available carbon-supported Pt catalysts with 2–4 nm of Pt nanoparticles have been widely applied in hydrogen-fed PEMFCs. Regarding their performance, some degradation modes have been identified, such as the corrosion of both carbon support and Pt nanoparticles due to their oxidation in acidic solution, high temperature, and oxygen pressure as well as high cathode potentials [11–13].

To tackle the aforementioned challenges, the strategies of Pt-alloying and nanostructuring have been shown effective in reducing the usage of Pt metal loading and improving catalytic ORR performance. Alloying of Pt with cheap transition metals such as Fe, Co, Ni, Cu, and Mn can mainly regulate the electronic/geometric structure effects [14–16], and nanostructuring such as from particles to wires, tubes, cages, plates, and frames can usually create highly active facets and stable skeletons for catalytic ORR [17–20].

In view of the above alloying and nanostructuring strategies for developing Pt-based catalysts, the other important research direction has emerged in recent years, i.e., the development of single-atom catalysts (SACs) with significant reduction of Pt loading and maximum of its utilization as well as the ideal model for a fundamental understanding of the catalysis mechanisms [21–24]. Such SACs strategy has been expected to accomplish the low-cost and high-performance low/ultralow-Pt catalysts. In this paper, the burgeoning Pt SACs are comprehensively summarized, mainly including design thoughts (single-atomic Pt coordinating with non-metals and alloying with other metals to form variously isolated, alloyed and nanoparticle-contained Pt SACs) and metal-support interactions (Pt single-atoms with carbon/non-carbon supports). Overall, this review will present methodologies, fundamentals, mechanisms, and applications to provide insights into the further development of SACs for ORR in PEMFCs.

## 2 Conventional Pt-based catalysts

Fundamentally understanding the catalytic ORR mechanisms from the electronic and geometric structures at an atomic level is conducive to developing high-performance electrocatalysts. Up to the present, there are still no overwhelming consensus because there are no sufficient experimental validation techniques to accurately identify the formed intermediates during the reaction.

### 2.1 Oxygen reduction pathway

Overall, ORR can occur through 4e⁻ reduction from $O_2$ to $H_2O$ in acidic electrolytes, generally involving two different pathway processes. One of the pathways is a direct 4e⁻ reduction to produce $H_2O$ (Eq. (1)); the other is the stepwise 2e⁻ reduction with the hydrogen peroxide ($H_2O_2$) intermediate (Eqs. (2) and 3).

One-step 4e⁻ process:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{1}$$

Stepwise 2e⁻ process:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{2}$$

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \tag{3}$$

The different active catalysts can possess different ORR pathways. For example, less reactive metals (e.g., Au and Hg) are reported to have 2e⁻ reduction, while 4e⁻ reduction can occur on highly-active catalysts. Katsounaros et al. [25] suggested that electrochemistry of $H_2O_2$ on Pt could be useful for the understanding of ORR mechanisms, due to the applied potential determined Pt surface state and reaction direction. $H_2O_2$ could interact with the reduced surface sites to decompose into adsorbed OH. When $H_2O_2$ interacted with the oxidized Pt sites, it was oxidized to $O_2$ via the reducing surface. In general, the 4e⁻ pathway has been agreed to be the favorable route in PEMFCs because the ORR does not lead to peroxides that cause certain degradation of electrodes and electrolyte membranes and the cell can have a high energy efficiency due to the 4e⁻ process. The density functional theory (DFT) calculations confirm that the 4e⁻ path can occur via dissociation or association mechanisms on Pt(111), as shown in Fig. 1 [26]. Additionally, the peroxo mechanism with “tandem” 2e⁻ paths can occur, which is unfavorable because the produced $H_2O_2$ can reduce the electron transfer number and increase the degradation rate of electrode and membrane.

### 2.2 Synthetic strategies

Currently, Pt-based catalysts remain the highest-performance materials in PEMFCs, where massive Pt is used at their cathodes to overcome the sluggish kinetics of ORR. Building upon a moderately bound surface oxygen, Pt and its alloys adhere to the Sabatier principle, expediting the sluggish kinetics of ORR. However, there are some drawbacks in the use of Pt that have an unsatisfying activity/stability and cost effectiveness of catalysts, resulting in possible obstacles to the large-scale sustainable commercial applications of the PEMFC technology [27].

Conventionally, the high-performance ORR catalysts can be reasonably designed from two aspects of modifying/innovating supports and alloying/nanostructuring Pt particles. On the one hand, the modified and innovated carbon materials can be used not only as the catalyst supports but also as the non-precious metal catalysts

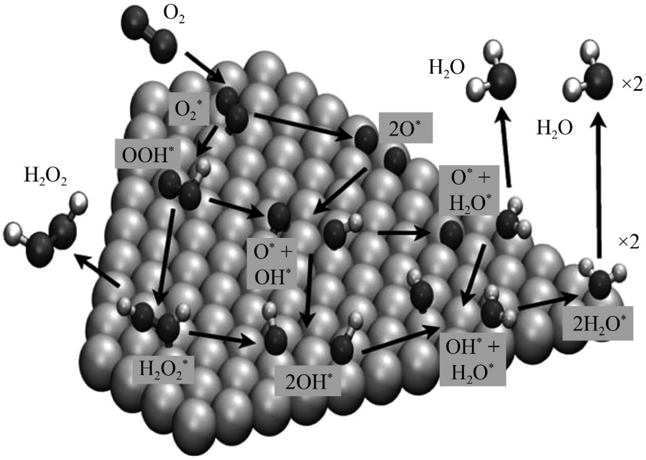


**Fig. 1** Schematic representation of proposed ORR mechanisms on Pt(111) by calculations (adapted with permission from Ref. [26]).

[28–38]. These novel carbons can create active sites, which will synergistically promote the activity and stability enhancement of Pt catalyst particles. Moreover, some carbons can be designed as high-performance non-precious metal catalysts such as the popular iron-nitrogen-carbon (Fe−N−C). On the other hand, the ORR activity/stability of Pt particles can be improved by effective alloying and nanostructuring strategies. The construction of various Pt-based alloys with transition metals and nanostructures with different shapes can reasonably adjust the electronic/geometric structures, alleviate the dissolution of transition metals, and reduce the Pt usage [39–41].

### 2.2.1 Modifying/innovating supports

The ORR activity and stability of a Pt-based catalyst can be seriously affected by the inert/poor activity of commercial carbon support and its susceptible corrosion under high potential/temperature and acidic environment. As identified, there is only a weak interaction (van der Waals forces) between Pt and traditional carbon support due to the fully saturated valence shell and almost zero unpaired surface electrons of carbon, directly resulting in the rapid accumulation of Pt through dissolution, surface migration and separation during the electrochemical operation [42]. With respect to this, the modifying/innovating supports can help improve the electrocatalytic performance [13]. Zhang & Chen [43] prepared the N-doping carbon black (NCB) by annealing commercial Vulcan XC-72R in gaseous ammonia ($NH_3$). The resulted NCB supported Pt nanoparticles (Pt/NCB) catalyst exhibited the enhanced electrocatalytic ORR capacity via a proposed oxygen spillover effect, as can be seen from Fig. 2(a). Cai et al. [44] developed a novel N-doped carbon semi-tube (N-CST) as the functional support of Pt nanoparticles and the interfacial Pt–N–C sites as the new ORR active route could promote the electrocatalytic activity of the obtained Pt/N-CST catalyst (Fig. 2(b)). N-doping into carbons can not only create the additional active sites to improve the catalytic activity but also confer a strong metal-support interaction to enhance the ORR stability. Gong et al. [45] used MOF-derived N-doped carbon skeleton with separated Mn single-atoms (Mn-SAs/N–C) as the support to anchor Pt, in which their strongly coupled interactions could limit the overgrowth of Pt. The designed Pt@Mn-SAs/N–C nanocatalyst with an ultra-low amount of Pt (Fig. 2(c)) showed an excellent mass activity, long-term stability, and methanol tolerance toward ORR. Liao et al. [46] dispersed Pt nanoparticles onto the ZIF-8 derived hollow N-coordination iron atoms embedded in carbon (Fe-NC) dodecahedral nanomaterial (Fig. 2(d)). The prepared Pt@Fe-NC has multiple active centers and hollow porous structure, showing a half-wave potential of 0.936 V, a mass activity of 1.34 A/$mg_{Pt}$, and an excellent electrochemical stability.

To thoroughly eliminate carbon corrosion, non-carbons have been considered to be the effective supports [11]. Lin et al. [47] synthesized the novel $SnS_2/SnO_2$ support to deposit Pt nanoparticles (Pt-$SnS_2/SnO_2$) as an ORR catalyst, as shown in Fig. 2(e), in which Pt nanoparticles are mainly decorated at the $SnS_2/SnO_2$ interface. As a result, the mass activity of Pt-$SnS_2/SnO_2$ catalyst was about 4 times higher than that of Pt/C. In terms of stability, the electrochemically active surface area (ECSA) and mass activity of Pt-$SnS_2/SnO_2$ only decreased by 18.2% and 23.7%, respectively, after 50000 cycles in the high-potential region (1.0–1.6 V).

### 2.2.2 Alloying/nanostructuring Pt particles

Although Pt is the most reliable ORR catalyst to attenuate reaction barrier, it still does not sufficiently meet the practical requirements. Moreover, the scarcity of Pt results in a high-cost. In this regard, Pt-alloying with abundant transition metals seems to be an effective way to overcome the above challenges. On the one hand, the electronic/geometric structure effects can effectively regulate the electrocatalytic ORR performance enhancement [48–50]; on the other hand, the reduced Pt usage can greatly improve the cost effectiveness of fuel cells.

Nanostructured Pt-based alloys can greatly enhance the electrocatalytic performance, which generally have various morphologies such as wires, networks, and dendrites [51]. Tang et al. [52] developed a surface/near-surface composition modulation technique that could enable the one-dimensional Pt–Ni nanowires (NWs) (Fig. 3(a)) to exhibit an excellent catalytic ORR activity and stability. High-temperature pyrolysis under the atmosphere of $NH_3$ produced the final Pt–Ni/C–$NH_3$ NWs where the outermost Pt-skin had a high Ni/Pt atomic ratio. Experimental and theoretical results suggested that Pt–Ni/C–$NH_3$ NWs had the optimal adsorption energy of oxygen intermediate reconstruction of structure and composition, exhibiting an excellent specific activity of 3.86 mA/$cm^2$ and a mass activity of 1.02 A/$mg_{Pt}$ as well as a good stability compared with Pt/C. Liao et al. [53] fabricated the composition-graded $PtCu_3$@$Pt_3Cu$@Pt nanodendrites exposed with high index surfaces (HISs) through a combination of atmosphere-modulation synthesis and electrochemical dealloying (Fig. 3(b)). Both Pt-alloying with Cu and HISs together contributed to the outstanding catalytic ORR activity of such characteristic catalyst with mass/specific activities of 14 and 24 times higher than that of the commercial Pt/C catalyst, respectively. In addition, the characteristic nanodendrite architecture promoted the stability. Zhang et al. [54] presented a novel synthetic process (Fig. 3(c)) of S-doped AuPbPt alloy nanowire-networks (NWNs) in aqueous solution by the conformal growth of Pt onto the pre-formed S-doped AuPb NWNs. The excellent electrocatalytic ORR performance could

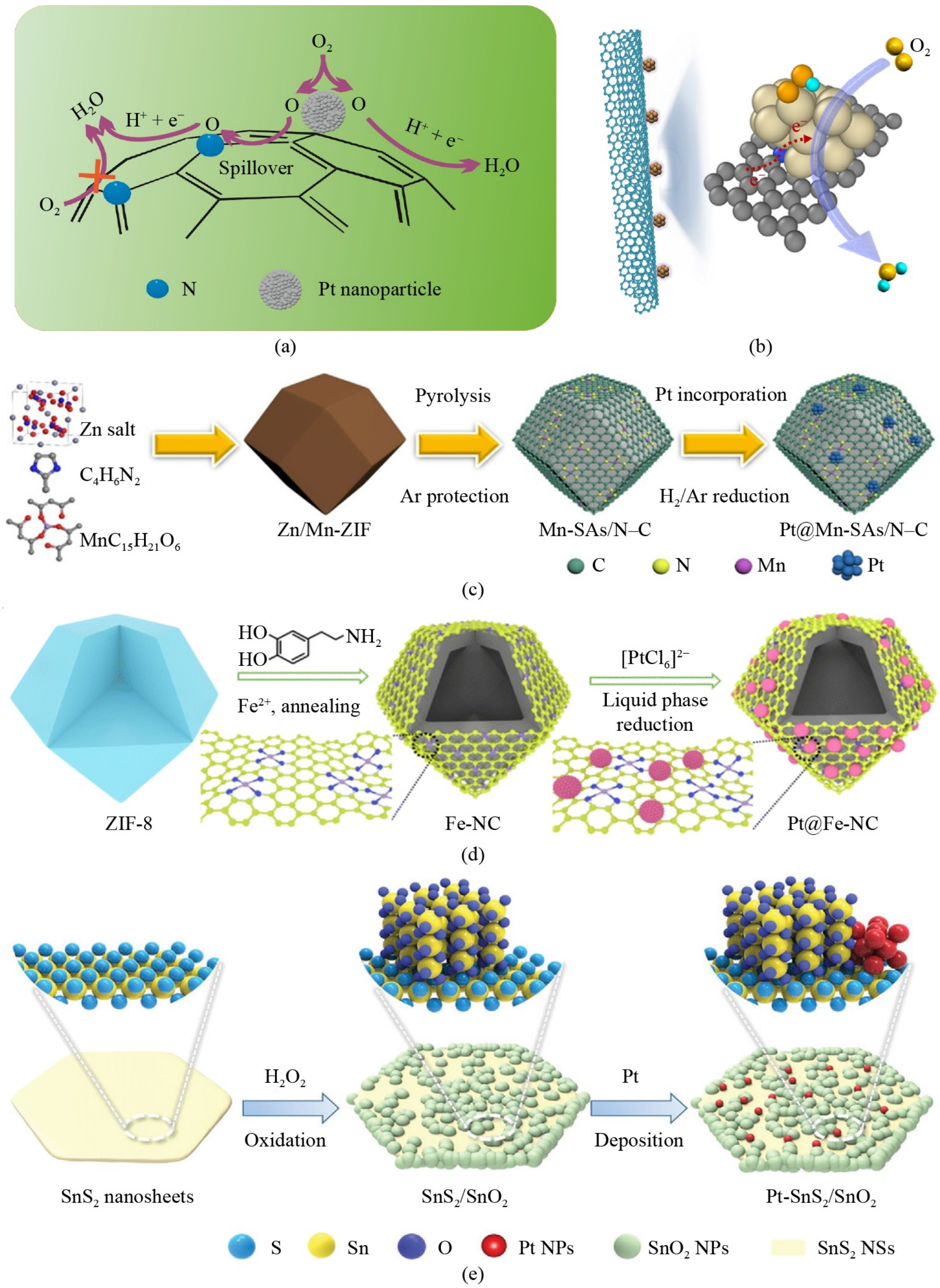


**Fig. 2** Schematic illustrations of various modifying/innovating supports for Pt-based catalysts.

(a) Pt/NCB catalyst and its possible oxygen spillover effect (adapted with permission from Ref. [43]); (b) Pt/N-CST (adapted from Ref. [44] under the terms of CC BY NC ND license; (c) Pt@Mn-SAs/N–C (adapted with permission from Ref. [45]); (d) Pt@Fe-NC (adapted with permission from Ref. [46]); (e) Pt-$SnS_2/SnO_2$ (adapted with permission from Ref. [47]).

benefit from the formation of appropriate amount of PtS in the resulting catalyst.

Alloying-induced ligand/strain effects can promote the ORR kinetics of Pt by regulating the near-surface atomic arrangement [55]. However, during the long-term ORR process, spontaneous surface segregation and subsequent dealloying could occur, resulting in a structural collapse and severe decline in ORR performance of Pt-based nanostructures [56]. Compared with the traditional Pt–M alloys, Pt–rare earth (RE) alloys were found to have an extremely low alloy formation energy which can further enhance the stable presence of RE atoms in characteristic alloys [57,58]. Qian et al. [59] developed a universal, scalable, and green synthetic method for Pt–RE alloy catalysts (Fig. 3(d)). Incorporating RE atoms could well modulate the electronic structure of Pt to accelerate the

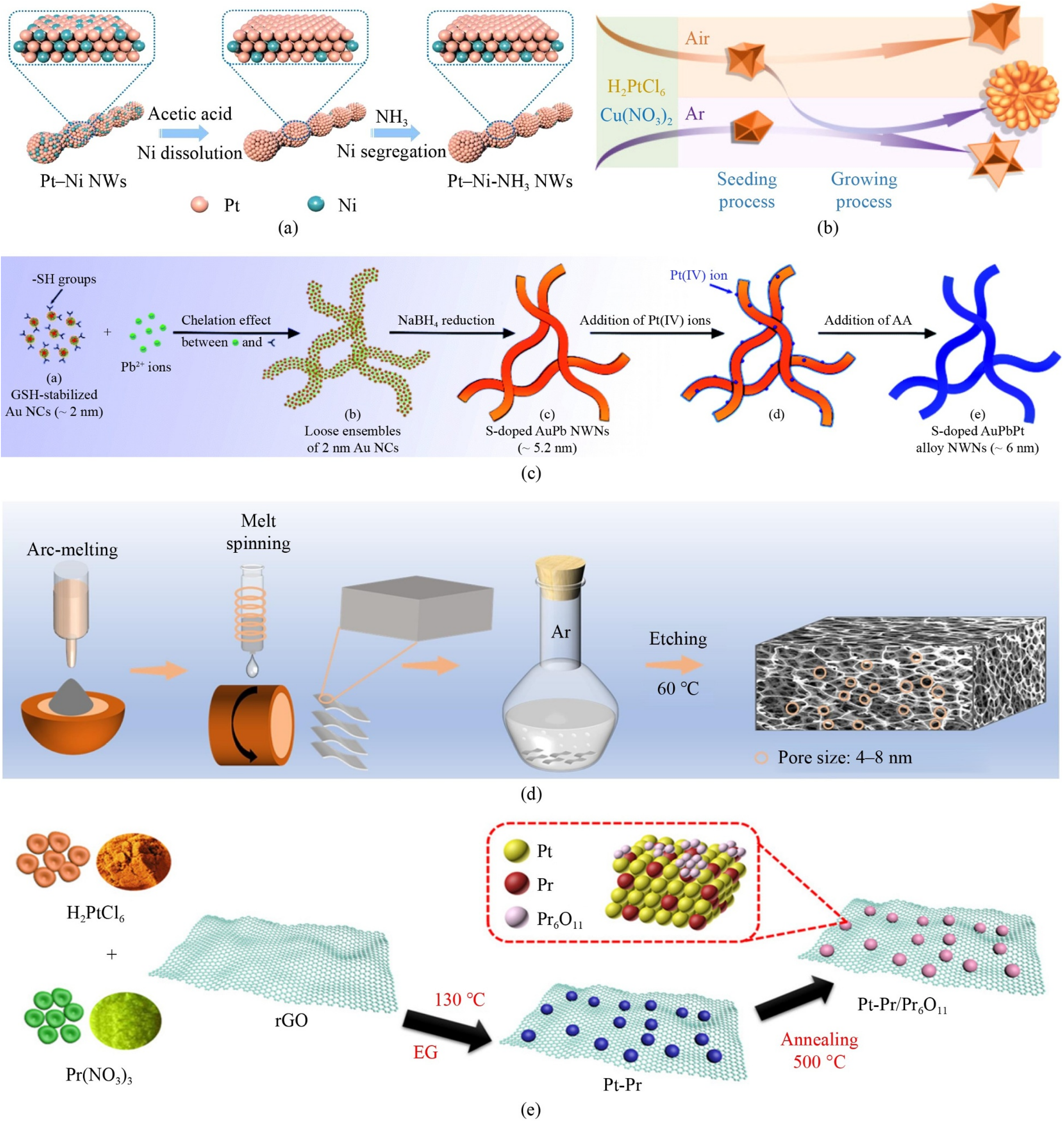


**Fig. 3** Schematic illustrations of various nanostructured Pt-based alloy catalysts.
(a) Pt−Ni−$NH_3$ NWs (adapted with permission from Ref. [52]); (b) Pt–Cu nanocrystals (adapted with permission from Ref. [53]); (c) S-doped AuPbPt alloy NWNs (adapted with permission from Ref. [54]); (d) Pt–RE alloys (adapted with permission from Ref. [59]); (e) graphene-supported Pt−Pr/$Pr_6O_{11}$ (adapted with permission from Ref. [60]).

catalytic ORR kinetics and significantly enhance the energy barrier for Pt demetallation to improve the ORR stability. As a result, the optimal platinum-yttrium ($Pt_3Y$) catalyst showed the best electrocatalytic activity and stability. Its mass activity reached 5.3 times that of commercial Pt/C catalyst, decreasing by only 35.7% after 60000 potential cycles. Wu et al. [60] successfully utilized praseodymium (Pr) for the construction of graphene-supported $Pr_6O_{11}$-assisted Pt–Pr (Pt−Pr/$Pr_6O_{11}$) catalyst by the combined co-reduction of Pt and Pr salts and further thermal oxidation treatment (Fig. 3(e)). The excellent ORR performance could be associated with the electron transfer from $Pr_6O_{11}$ to Pt surface and the strong oxophilicity of Pr to adjust Pt active site to promote $O_2$ adsorption/dissociation.

## 3 Burgeoning Pt single-atom catalysts

To achieve the low/ultralow-Pt usage for advanced ORR catalysts, many different strategies such as alloying [61–63], core-shell/Pt-skin nanostructuring [64], and Pt SACs designing [65] have been proposed to improve the utilization of Pt. Pt SACs show great promise in reducing catalyst loading and cost to achieve high-performance due to their maximum atomic utilization and atom-adjustable active structure [66]. SACs are a new class of heterogeneous catalysts in which each active metal atom can be atomically dispersed and fixed on the support. In fact, they have similarities to homogeneous catalysts. When these metal single-atoms are coordinated with or anchored by a surface atom of support, surface atoms can be regarded as the ligands in homogeneous catalysts which can not only stabilize metal atoms but also participate in catalytic reactions [67]. The preparation methods of SACs mainly include chemical vapor deposition [68], atomic layer deposition [69], pyrolysis [70], wet chemical method [71], photochemical method [72], co-precipitation [73], atomic capture [74], and so on. However, the content of individual metal atoms in the whole catalyst is usually less than 5 wt.% (mass fraction), greatly restricting the number of catalytic sites and thus the activity of the catalyst [75]. Moreover, the stability of monoatomic structures is often poor, making it easy for them to aggregate into nanoparticles [76].

So far, great progresses have been made in the synthesis, characterization, and preliminary application of SACs. However, the issues of low atomic density and poor stability still hinder the wide practical applications of SACs. To obtain highly active and stable Pt SACs, some effective strategies can be continually considered to pursue high-density atomic Pt sites and strong metal-support interactions.

### 3.1 Design thoughts

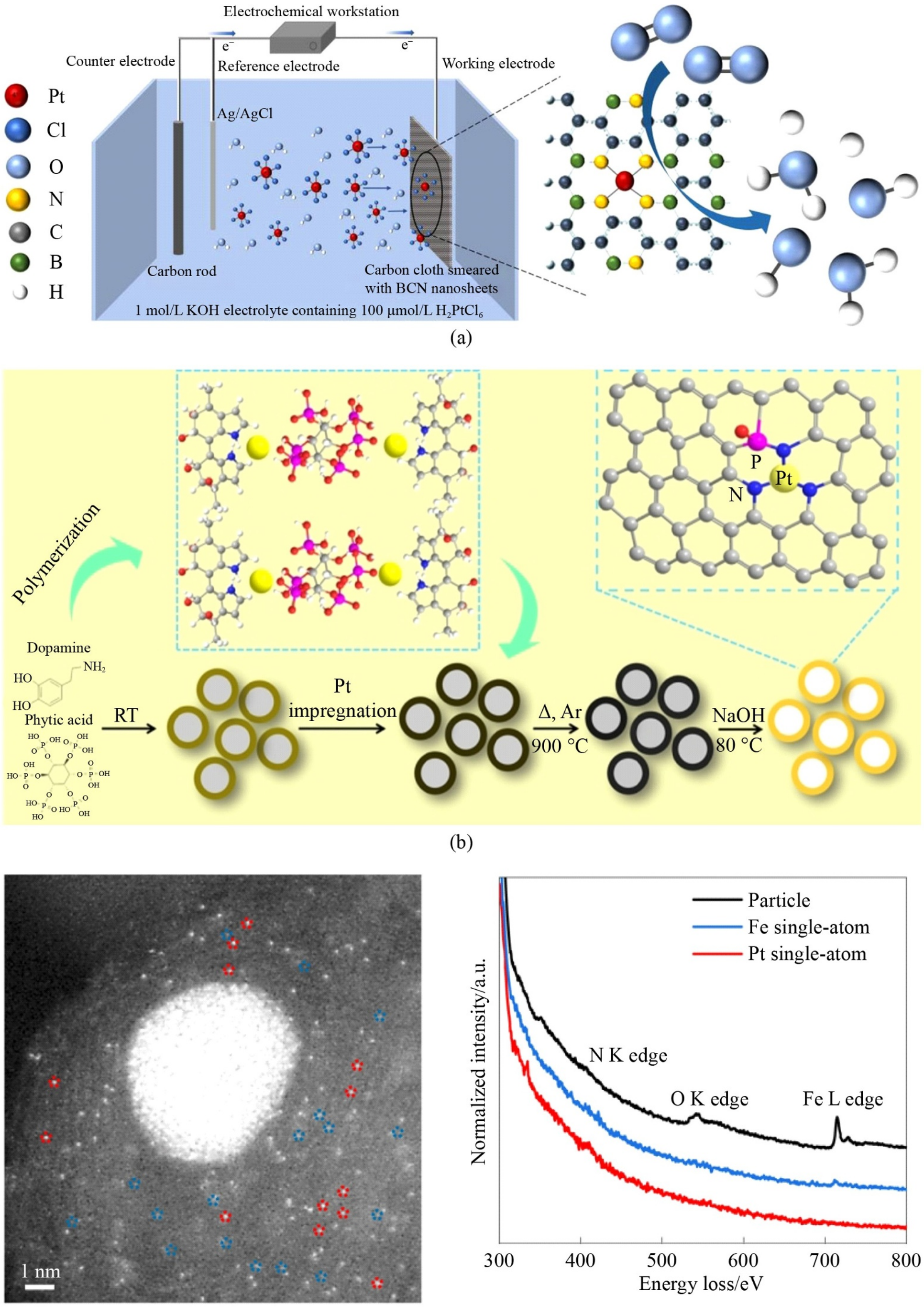
It is well known that the catalytic activity and selectivity of SACs are directly related to its electronic structure, which can be effectively regulated depending on metal atom types, local coordination environments, supports, and so on. Thanks to the maximum metal utilization, Pt SACs can give a high intrinsic catalytic activity. In terms of ORR selectivity, in general, there will be an expected $4e^-$ selection path. However, controversies on the $2e^-/4e^-$ selectivity are noted for different Pt SACs and a high selectivity for $H_2O_2$ production can be found in most cases. Some factors like the Pt coordination environments (coordination element and coordination number) can affect the ORR selectivity of product type and its concentration, essentially depending on the manipulation of dissociative and associative mechanisms.

Mainly, Pt single-atoms can reside in the Pt SACs by coordinating with non-metals and alloying with metals through a reasonable design. With Pt single-atom as the center, different types and numbers of non-metal/metal atoms can coordinate and/or alloy with Pt atoms. Notably, the neighboring atoms can also participate in the ORR process and the first/second coordination shells of Pt can have significant effects on its activity and selectivity by regulating the local geometry and charge density of centered Pt atom. In the first coordination shell, Pt single-atoms can couple with the adjacent atoms by Pt-nonmetal/metal interactions. Moreover, it is also found that some carbon atoms in the second coordination shell can act as active sites for enhancement of electrocatalytic ORR performance.

#### 3.1.1 Single-atomic Pt coordinating with non-metals

Generally, the single-atomic Pt can coordinate with non-metallic atoms such as B, C, N, O, P, and S in the carbon substrates for the construction of Pt SACs. For example, the $Pt-N_x$ coordinations are the most popular ones. N-doped carbons containing pyridinic-N, graphitic-N, or pyrrolic-N have been shown to be the promising supports for coordinating Pt single-atoms due to their porous structure, high specific surface area, and abundant N-sites [77–79]. ORR electrocatalysis on an N-coordinated single-atomic Pt ($Pt_1-N_x$) site can be proceeded by a $2e^-$ pathway to the production of $H_2O_2$ on Pt SACs and a $4e^-$ pathway to the production of $H_2O$. The $Pt–N_4$ site of a Pt atom coordinating with four pyridinic-N is well-known for electrocatalysis [80,81]. Song et al. [82] investigated the graphene-supported different Pt species (nanoparticle, cluster, and single-atom) and found that the isolated Pt single-atoms could follow a two-electron pathway while the Pt nanoparticles had a complete $4e^-$ reduction.

To maintain a good catalytic performance at a low Pt content, it is necessary to further improve the inherent catalytic ORR activity and stability of the single-atomic Pt site, which needs a reasonable change of its electronic structure and coordination environment. The two-dimensional boron carbon nitride (BCN) materials with a graphene-like structure have the advantages from boron nitride and graphene, such as high specific surface area and good electrochemical catalytic activity and stability [83]. The electron-rich N atoms and electron-deficient B atoms on the surface of BCN can make BCN have excellent electrochemical properties and provide abundant sites for anchoring Pt atoms. Zhang et al. [84] used electrochemical deposition for realizing the BCN nanosheets as a substrate to preserve Pt single-atoms (Pt SAs-BCN) (Fig. 4(a)) with densely accessible $Pt-N_4$ active sites. Such catalyst with an efficient and stable ORR activity exhibited a maximum power density of 936.31 $mW/cm^2$ in microbial fuel cells. Zhu et al. [85] studied a Pt SAC of the atomic Pt sites with N and P co-coordination on a carbon matrix (PtNPC) with the P-modified $Pt-N_3$ sites (Fig. 4(b)), which promoted the intrinsic catalytic ORR activity by altering the d-band center of Pt. Moreover, the introduction of a second isolated metal single-atom site has been shown to further improve the catalytic performance. For instance, the isolated bimetallic sites SACs show an excellent electrocatalytic performance compared to monometallic SACs. A case in point is that, Cao et al. [86] prepared a Fe/Pt SAC ($Fe_1Pt_1$/NC) with uniformly dispersed $Fe{-}N_4$ and $Pt{-}N_4$ active sites which showed enhanced bifunctional electrocatalytic ORR performance and hydrogen evolution reaction (HER). Zhong et al. [87] successfully synthesized a bimetallic SAC of isolated Pt and Fe single-atoms anchored on the N-doped carbon (PtFeNC) through a novel strategy of capsulating Pt species into the cavities of Fe-doped zeolite imidazolate framework. This PtFeNC catalyst with isolated $Pt{-}N_4$ and $Fe{-}N_4$ sites exhibited a high activity and stability, with a specific capacity of 807 mAh/g in the zinc-air battery. Additionally, the metal nanoparticles presented in the local environment can also affect the properties of single-atomic Pt site [88]. Xiao et al. [89] designed a hybrid Pt–Fe–N–C catalyst consisting of Pt–Fe alloy nanoparticles and Pt and Fe single-atoms in N-doped



(a)

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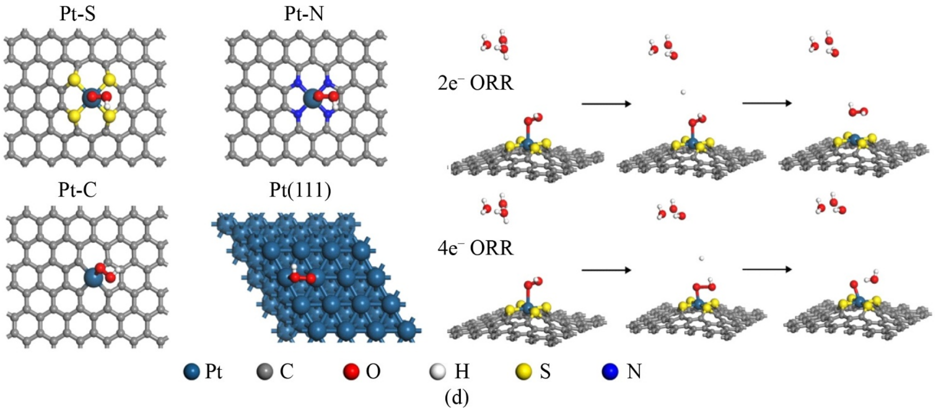


**Fig. 4** Schemes of various SACs by single-atomic Pt coordinating with non-metals.

(a) Pt SAC prepared by electrochemical deposition (adapted with permission from Ref. [84]); (b) PtNPC sample (C, H, O, P, N, and Pt atoms being represented by gray, white, red, pink, blue, and yellow balls, respectively) (adapted with permission from Ref. [85]); (c) HAADF-STEM image of Pt−Fe−N−C electrocatalyst and its corresponding EELS analysis (Fe and Pt single-atoms being marked by blue and red circles, respectively) (adapted from Ref. [89] under the terms of CC BY license); (d) configurations of Pt single-atom coordinated with neighboring S/N/C atoms in two-dimensional carbon matrix (left) and illustration of oxygenated intermediates adsorption on Pt−$S_4$ motif (right) (adapted from Ref. [90] under the terms of CC BY license).

carbon support (Fig. 4(c)). The synergistic effects among different active sites could promote the electrocatalytic activity and stability. In a fuel cell, such Pt−Fe−N−C catalyst demonstrated a Pt mass activity surpassing that of commercial Pt/C by 3.7 times, alongside the remarkable stability of maintaining 97% of the activity after 100000 cycles.

In addition to atomical Pt−N coordination, other non-metallic atoms can also coordinate with Pt single-atom for the development of high-performance Pt SACs. Zhao et al. [90] manipulated the ORR pathways through studying the local Pt single-atom coordination environment of Pt−C, Pt−N−C and Pt−S−C (Fig. 4(d)) using a combined experimental and theoretical approach. The Pt−C motif could be conducive to the dissociative reduction, while direct protonation into $H_2O_2$ for Pt−S and Pt−N motifs. Furthermore, Choi et al. [91] selectively synthesized atomically dispersed Pt catalyst on S-doped zeolite template carbon (ZTC) with an extra-large S-content of 17 wt.% and a high surface area of approximately 2800 $m^2/g$. The rich S-functional groups could stabilize the atomically dispersed Pt to form a unique Pt−$S_4$ coordination with a high selectivity for $H_2O_2$ product. Zhang et al. [92] established isolated Pt atoms stabilized by amorphous tungstenic acid ($H_2WO_4$) on $WO_3$ nanoplates using an *in situ* photodeposition strategy. Pt atoms could coordinate with oxygen atoms from the [$WO_6$] octahedra of $H_2WO_4$, and the strong Pt−O bonding provided both an excellent catalytic ORR activity and stability.

### 3.1.2 Single-atomic Pt alloying with metals

Noteworthily, alloying single-atomic Pt with metals through metal bonds has also attracted more and more attentions. Typically, the single-atom alloy (SAA) catalysts have been developed in which atomically dispersed metal sites are on the surface of metal or throughout the metal catalyst [93]. The properties of active single-atoms can be regulated by controlling both the electronic and geometric structures [94]. Through fine selection of matrix metals and adjustment of local atomic structure, the high-performance Pt SAA catalysts can be well designed. For instance, Chen et al. [95] reported the outstanding CO-tolerance and ORR performance by the “neighboring Pt atoms” in the ultrathin wrinkled FePt nanosheets with a high ECSA of 545.54 $m^2/g_{Pt}$ (Fig. 5(a)). Liu et al. [96] synthesized the typical $Pt_3Co$@Pt-SAC catalyst by a versatile bioinspired self-assembly method (Fig. 5(b)), in which the $Pt_3M$ nanoparticles are coated with single-atom Pt−$C_4$ decorated carbon. As depicted in Fig. 5(c), the strong electronic interaction between single-atoms and nanoparticles can be confirmed by the DFT calculated differential charge densities of $Pt_3Co$/in-plane Pt and $Pt_3Co$/edged Pt (a single-atom Pt placed in-plane on a $Pt_3Co$-decorated graphene sheet or at the edge of the sheet). Compared with the commercial Pt/C, this catalyst exhibited both exceptional mass and specific activities with an order of magnitude higher, and only a 10 mV decay could be in half-wave potential throughout 50000 cycles.

Pd and Au are ideal substrates for the deposition of isolated Pt atoms due to their comparable lattice constants, making it possible to further regulate the coordination environment and catalytic activity [97]. For example, Zhang et al. [98] used atomic layer deposition to prepare the N-doped carbon nanotubes supported Pt/Pd SAA catalyst of Pt atoms being deposited on octahedral Pd surfaces, which showed both significantly improved HER and ORR activities. Besides, for Pt SAA catalysts,

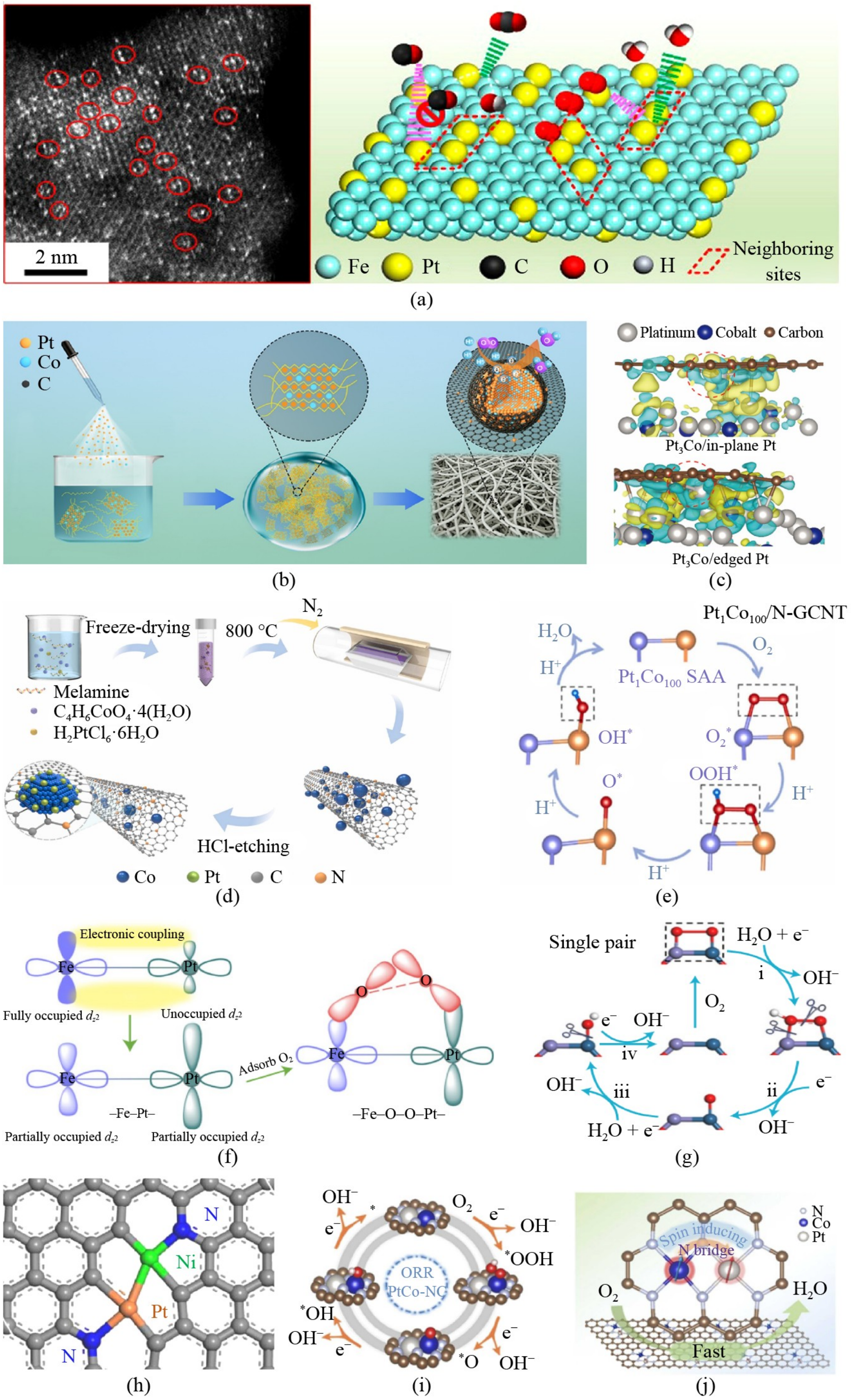


**Fig. 5** Schemes of various SACs by single-atomic Pt alloying with metals.

(a) HAADF-STEM image (left), and schematic diagram of neighboring Pt atom sites in an ultrathin FePt nanosheet (right) for carbon monoxide (CO)-tolerant ORR (adapted with permission from Ref. [95]); (b) $Pt_3M$@Pt-SAC hybrid catalysts (adapted with permission from Ref. [96]); (c) differential charge density of $Pt_3Co$/in-plane Pt and $Pt_3Co$/edged Pt (cyan and yellow areas representing the depletion and accumulation of charge, respectively, and the red circles showing the charge distribution around Pt atoms) (adapted with permission from Ref. [96]); (d) preparation schematic of $Pt_1Co_n$/N-GCNT (gray, orange, blue, and green balls representing C, N, Co, and Pt atoms, respectively) (adapted with permission from Ref. [101]); (e) presented ORR mechanism on $Pt_1Co_{100}$/N-GCNT (gray, purple, orange, red, and blue representing C, Co, Pt, O, and H, respectively) (adapted with permission from Ref. [101]); (f) Pt–Fe electronic coupling effect for $O_2$ activation (adapted with permission from Ref. [102]); (g) proposed ORR mechanism on Pt single-site and Pt–Fe pairs (violet, red, dark blue, and white representing Fe, O, Pt, and H, respectively) (adapted with permission from Ref. [102]); (h) optimized $PtNiN_2C_4$ structure by DFT calculation (adapted with permission from Ref. [103]); (i) transition states (adapted with permission from Ref. [104]); (j) proposed mechanism of PtCo-NC toward ORR (adapted with permission from Ref. [104]).

depositing isolated Pt atoms on the surface of cheap metals will be a more meaningful strategy [99–102]. Cheng et al. [101] reported an excellent SAA catalyst wherein Pt−Co dual sites were wrapped within N-doped graphitized carbon nanotubes ($Pt_1Co_{100}$/N-GCNT). This configuration led to the dispersion of isolated Pt atoms on the surface of Co nanoparticles (Fig. 5(d)). As the proposed mechanism in Fig. 5(e), the unique Pt-Co dual sites can provide a high-efficient four-electron ORR pathway, which is beneficial for OOH* immobilization and OH* dissociation to enable the excellent equilibrium of adsorption and desorption of the oxygen intermediates. Gao et al. [102] constructed the single-site Pt–Fe pairs on $\alpha$-$Fe_2O_3$(012) facets. The partially occupied orbitals driven by strong electronic coupling could be highly active for $O_2$ adsorption and dissociation (Fig. 5(f)), and the proposed ORR mechanism (Fig. 5(g)) suggests that the kinetics of ORR primarily stem from the facile activation of $O_2$ at the Pt–Fe single-site pair and the subsequent desorption of OH* at the Pt single-site.

More importantly, the metal atoms in the adjacent bimetallic sites SACs can also produce direct interaction [103–105]. Particularly, this interaction may originate from the synergistic effect of homo/hetero-nuclear adjacent bimetallic sites by tuning the d-band center and orbital coupling to optimize the electronic structure and distribution, significantly boosting the activity, selectivity and stability for ORR. Duc Le et al. [103] synthesized a novel electrocatalyst ($PtNi_{SA\text{-}NPS}$-NDC) composed of Pt–Ni dual single-atoms and Pt–Ni alloy nanoparticles deposited on the N-doped carbon (NDC) surface. DFT calculations showed that the $PtNiN_2C_4$ (Fig. 5(h)) could be one of the main active sites for improved ORR performance. Cheng et al. [104] rationally designed the PtCo-NC binary-atom catalyst with atomically dispersed Pt and Co on N-doped carbon by a mechano-thermal milling strategy and Fig. 5(i) depicted its proposed ORR pathways. Theoretical calculations revealed that Co atom induced spin polarization of adjacent Pt atom could accelerate the catalytic ORR kinetics (Fig. 5(j)). Moreover, the resulted PtCo-NC catalyst showed a long-term stability.

### 3.2 Metal-support interactions

The nature of metal-support interactions can play a pivotal role in dictating the electrocatalytic performance of SACs, influenced by various parameters like the type and size of metal, chemistry of support, interface quality, and surface structure [106]. The metal single-atoms in SACs can be anchored by or coordinated with the surface atoms of the support with almost 100% metal utilization. This maximum utilization means that in the SACs each metal atom can establish a direct contact with the support. However, the supported nanoparticle catalysts contact only along the periphery of their metal atoms [107]. Therefore, SACs would provide a maximized metal-support interaction. In fact, the free energy of metal single-atoms can increase dramatically, leading to a propensity for their clustering and aggregation [108]. In this regard, suitable supports are essential as they can interact with metal single-atoms, facilitating their stable dispersion and enhancing both the electrocatalytic activity and the electrochemical stability of SACs. Therefore, the supports have significant effects on the electrocatalytic performance, similar to the effect of ligand molecules in homogeneous catalysts [109].

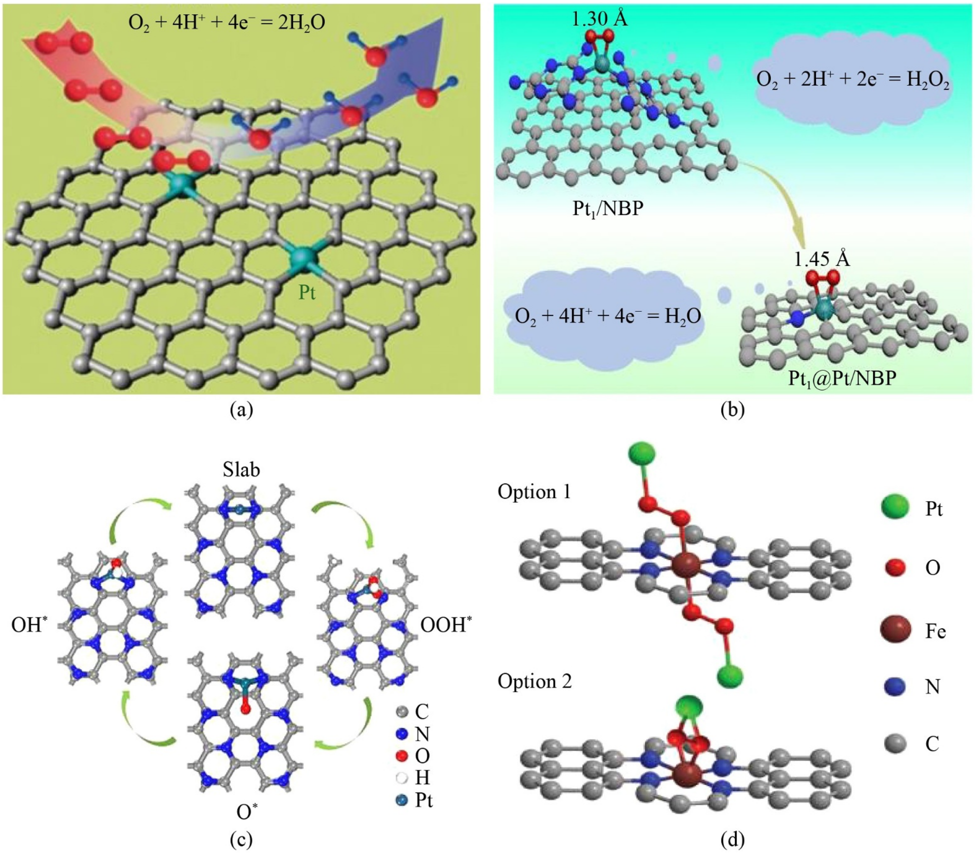
Up to this point, the supports employed for SACs encompass both carbon-based and non-carbon materials [110–114]. In general, non-carbon supports such as metals, metal oxides, hydroxides, sulfides and nitrides exhibit minimal vacancy defects which can result in extremely low monatomic loads. Carbon-based materials can achieve higher monatomic metal contents, such as defective graphene, covalent triazine framework, graphitic carbon nitrides, and heteroatoms-doped carbons [76]. However, the weak interaction of supports and metal does not facilitate the stable dispersion of individual metal atoms. In addition, the insufficiently understanding of metal-support interaction mechanisms is still an issue in improving both activity and stability of the prepared SACs. Therefore, it is of great value to explore the metal-support interaction of Pt atoms with various carbon/noncarbon supports for the preparation of high-performance Pt SACs [115].

#### 3.2.1 Interaction of Pt single-atoms with carbon supports

The structure and chemistry of carbon supports can greatly influence the key properties of single-atomic Pt active center, and such factors can be the geometric configuration, electronic structure, and metal-support interaction [116]. Considering the unique role of carbon supports in stabilizing metal atoms, the type and abundance of active sites can be controlled by rationally designing the structure and chemical properties of carbon materials. The interaction between carbon support and metal atom is usually relatively weak, resulting in the aggregation of metal atoms to particles and degradation of catalytic activity [117]. Carbon materials can capture higher single-atom metal content by confining or embedding metal atoms into the carbon defects [118]. Some studies have investigated the interaction of carbon defect with Pt single atom and its effect on ORR activity of the resulted Pt SAC [119]. Liu et al. [120] presented a carbon defect anchored Pt SAC ($Pt_1$/C), showcasing a remarkable ORR performance and an exceptionally high utilization of Pt. Typically, the main active sites are Pt single atoms coordinated by four carbon atoms neighboring carbon divacancies (Pt−$C_4$ sites). Through Pt−$C_4$ coordination (Fig. 6(a)), such $Pt_1$/C catalyst can provide an efficient $4e^-$ conversion pathway and an excellent performance in the acidic $H_2/O_2$ single cell.

Heteroatoms-doping into carbon materials can proficiently modulate the electronic structure [121], and the most popular is N-doping due to its larger electronegativity than carbon. N-doped carbon materials have been widely used as the platforms for anchoring metal atoms, and usually their supported Pt SACs can produce a better electrochemical performance and stability through the Pt−N coordination interaction. For example, integration of N into a carbon matrix has the potential to significantly modify the functions of support, where abundant coordination sites can facilitate the formation of single-atomic Pt sites [122]. The isolated metal atom is covalently bonded with the adjacent N atom, which can realize the fine modulation of active site and maximize the metal-support interaction effect [98]. Liu et al. [123] used the N-doped Black Pearl (NBP) carbon black support to synthesize an atomically dispersed $Pt_1$/NBP catalyst, in which the Pt atom was coordinated with imine nitrogen groups in a nonplanar structure. After high-temperature pyrolysis of this $Pt_1$/NBP, the coordination environment could be reconstructed as shown in Fig. 6(b). A new active center emerged, wherein a Pt single-atom coordinated with a pyridinic-N and two carbon atoms within a planar structure. This led to the creation of a catalyst with isolated Pt atoms and finely-dispersed Pt nanoparticles on the substrate, denoted as $Pt_1$@Pt/NBP. This catalytic configuration significantly advanced the ORR performance, achieving a high-efficiency $4e^-$ pathway for ORR. Yang et al. [124] synthesized $C_4N$ by a one-step hydrothermal method using 2,3-diamide phenazine as the raw material, which was then used as a functional support for Pt single-atom to form a new Pt@$C_4N$ electrocatalyst. X-ray absorption fine structure revealed the coordination number of Pt−N is 2 with an average distance of 2.02 ± 0.02 Å. Based on the coordination information, the ORR models (Fig. 6(c)) for Pt@$C_4N$ were established to perform the DFT calculations, suggesting that the strong adsorption of reactant species was the reason for the excellent performance.

Additionally, Zeng et al. [125] reported a Pt single-atom grafted Fe–N–C catalyst ($Pt_1$@Fe–N–C) through the process of "single-atom to single-atom" grafting,



(a) (b) (c) (d)

**Fig. 6** Schematic diagrams of Pt single-atoms interacting with carbon supports.

(a) Path diagram of Pt−$C_4$ coordination catalyst (adapted with permission from Ref. [120]); (b) pathway transform of Pt−N coordination catalyst from $2e^-$ to $4e^-$ (adapted with permission from Ref. [123]); (c) ORR reaction process on 1%Pt@$C_4N$ model (adapted with permission from Ref. [124]); (d) $Pt_1$−$O_2$−$Fe_1$−$N_4$−$C_{12}$ as an active moiety in $Pt_1$@Fe−N−C catalyst (adapted with permission from Ref. [125]).

where a Pt atom was successfully integrated into the Fe–$N_4$ center. This yielded a novel $Pt_1$–$O_2$–$Fe_1$–$N_4$ configuration via the adjacent $Fe_1$ and $Pt_1$ atoms coordinating with a bridging oxygen molecule (Fig. 6(d)), which could result in both the remarkably improved electrocatalytic ORR activity and stability.

### 3.2.2 Interaction of Pt single-atoms with non-carbon supports

Non-carbon materials with high corrosion resistance can effectively mitigate or eliminate the oxidative corrosion of carbon supports. Non-carbon materials as supports of Pt SACs can not only stabilize the dispersed single-atom metal centers but also changes their electronic and geometric structure, thus altering the catalyst performance [126,127]. Therefore, the interactions of single-atom Pt with non-carbon support should be given great attention.

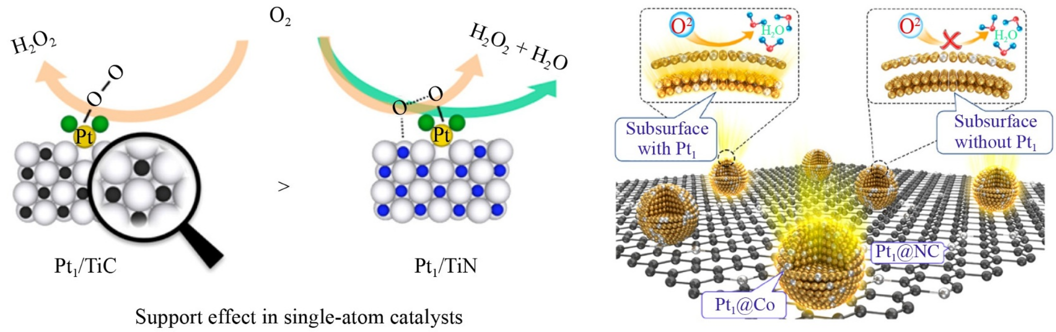
In the effort to improve catalyst stability, titanium nitride (TiN) and titanium carbide (TiC) have been suggested as non-carbon supports for Pt SACs due to their high corrosion resistance and excellent electrical conductivity [128]. By using TiN and TiC as supports, Yang et al. [129] prepared two Pt SACs of $Pt_1$/TiC and $Pt_1$/TiN to demonstrate the support effects (Fig. 7(a)). Compared to $Pt_1$/TiN, $Pt_1$/TiC exhibits a higher activity, selectivity, and stability in electrochemical production of $H_2O_2$. Usually, $H_2O_2$ is thought of as a byproduct of ORR, but it is actually a valuable chemical [130]. DFT calculations showed that $Pt_1$/TiC could retain more oxygen-oxygen bonds for the higher selectivity of $H_2O_2$ generation but $Pt_1$/TiN had a strong oxygen affinity. Additionally, this work revealed that the support could actively participate in electrocatalytic reactions rather than simply acting as anchoring sites of Pt single-atoms.

As is well-known, the performance of Pt SACs can be greatly affected by the coordination environments of metal single-atoms in near-surface regions of support, including surface and subsurface. Lai et al. [131] successfully synthesized a Pt SAC, where individual Pt atoms are uniformly dispersed on a heterogeneous substrate comprising cobalt particles and an N-doped carbon framework ($Pt_1$@Co/NC). In addition to the surface, there were Pt single-atoms in the subsurface Co nanoparticles which could strongly regulate the catalytic ORR efficiency of surface Pt through the change of electronic structure and shift of d-band center. The theoretical and experimental results revealed that $Pt_1$@Co/NC could exhibit a remarkable performance by the alloyed Pt in the subsurface to augment the ORR performance of surface Pt single-atoms (Fig. 7(b)), but the corresponding catalyst was inactive without Pt single-atoms dispersion in the subsurface.

## 4 Summary, challenges, and perspectives

### 4.1 Summary

Pt-based materials can largely meet the practical requirement for ORR electrocatalysis in PEMFCs. However, several drawbacks could compromise the large-scale industrial application, such as the limited reserve of Pt, high cost, and insufficient activity/stability. With commercial Pt/C catalyst as a reference, the advanced Pt-based catalysts have been traditionally developed by alloying/nanostructuring Pt and modifying/innovating supports to reduce cost and enhance performance. To achieve the maximum utilization of Pt, single-atom catalysts are gradually becoming hot research materials. This review summarizes various Pt single-atom catalysts including isolated, alloyed, and nanoparticle-contained ones through single-atomic Pt coordination with non-metals and alloying with metals. Moreover, it discusses the metal-support interactions of Pt single-atoms with carbon/non-carbon supports. Overall, in light of advancing cost-effective and high-performance conventional



Support effect in single-atom catalysts

(a)

(b)

**Fig. 7** Schematic diagrams of Pt single-atoms interacting with non-carbon supports.
(a) Support effect in single-atom catalysts (adapted with permission from Ref. [130]); (b) structural diagram of $Pt_1$@Co/NC with $Pt_{subsurf}$ and $Pt_{Surf}$@Co/NC without $Pt_{subsurf}$ for ORR (adapted with permission from Ref. [131]).

Pt-based catalysts, this paper provides an encompassing overview of burgeoning Pt single-atom catalysts, involving design thoughts, functional properties, electrocatalytic fundamentals and mechanisms, metal-support interactions, application progresses, and so on.

### 4.2 Challenges and perspectives

While significant strides have been taken in designing and synthesizing high-performance Pt single-atom catalysts for ORR, there are still several challenges. First, the site density of atomic Pt is low and its high-dispersion is difficult. In addition, during the synthetic and electrocatalytic process, Pt single-atoms will have a tendency to form clusters or nanoparticles. Moreover, there is insufficient knowledge on the influence factors of peripheral environments on active Pt sites and its electrocatalytic mechanisms. Furthermore, there still exists a huge gap between research and industrial application. To overcome these challenges in advancing high-performance Pt single-atom catalysts, this review presents several perspectives for future research.

(1) Adopting some effective strategies to achieve a high density and optimal dispersion of Pt single-atoms to improve catalytic ORR activity.

(2) Developing modified/novel supports to acquire good corrosion resistance and strong metal-support interaction to enhance electrochemical stability.

(3) Investigating the influences of peripheral environments on active Pt site, such as heteroatoms-doping, defects, curvature, supports, and substituted groups.

(4) Performing high-precision *in situ*/operando physical and electrochemical characterization techniques and advanced theoretical calculations based on machine learning and artificial intelligence to comprehensively explore the electrocatalytic ORR mechanisms.

(5) Pushing the large-scale preparation and industrial production of high-performance single-atom catalysts to accelerate their commercial application in electrochemical energy devices.

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