Surface/Near-Surface Structure of Highly Active and Durable Pt-Based Catalysts for Oxygen Reduction Reaction: A Review

Fanpeng Kong,* Weize Shi, Yajie Song, Liping Ren, Xue Sun, and Jiajun Wang*

Proton exchange membrane fuel cells (PEMFCs) are highly promising energy-conversion devices because of their zero-emission and high efficiency. A great deal of Pt is of significant necessity on the cathode to accelerate the rate of kinetically sluggish oxygen reduction reaction (ORR) and maintain the long-term operation, leading to the prohibitive cost of PEMFCs and limiting their widespread deployment. In the past decades, numerous efforts including manipulation of composition, morphology, and structure have been devoted to improving their higher activity and stability, but still lag behind the actual requirement. ORR is a typical surface-sensitive electrochemical reaction and its process is mainly determined by surface/near-surface structure. Herein, the recent advances in the manipulation of surface structure are summarized. The ORR mechanism and evaluation method for activity and stability are introduced. Then, solutions toward the engineering of surface structure and its effect on activity and stability are presented. Finally, comments on the future direction of nanocatalysts for ORR are presented in terms of engineered surface structure.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) directly converted carried hydrogen energy into electric energy with zero-carbon footprint, attracting significant amounts of attention from the academic community and industrial community. The widespread deployment of PEMFCs in portable and stationary applications will effectively mitigate global warming and fossil energy shortage. The central bottleneck for limiting PEMFCs commercialization is their prohibitive cost and relatively low operation time. According to the Fuel Cell Technical Roadmap of The United States Department of Energy (DOE), the current cost of a fuel cell system is $50 kW⁻¹ at a volume of 100 000 units per year, whereas the competitive cost in the market is only $35 kW⁻¹. In addition, the durability of the best-performing fuel cell is only 4100 h with 10 % stack voltage degradation, lagging far behind the actual requirement of 8000 h. The high cost of fuel cells is attributed to the loading of numerous Pt, which is utilized to improve the sluggish kinetics of oxygen reduction reaction (ORR). The inevitable dissolution of Pt particles and Ostwald ripening under harsh ORR conditions, including high potential and strong acidity, leads to unsatisfactory long-term stability. Therefore, improving the ORR activity of Pt-based catalysts and their stability is highly feasible to facilitate the practical application of PEMFCs.

ORR is a typical surface-sensitive electrochemical reaction, where the surface/near-surface structure, including coordination environment, electronic structure, and geometric structure, directly controls the interaction between reagents and surface and further affects the ORR process. Massive efforts have been devoted to improving the ORR kinetics by modifying surface/near-surface structures. Markovic’s group found that segregated Pt skin on Pt–M catalysts was beneficial for the enhancement of ORR. The improved ORR activity and stability were observed on Pt monolayer on Pd by Adzic’s group. Strasser and coworkers revealed that shape-selective PtNi nanocrystal with Pt-rich shell of 2–3 layers significantly promoted ORR process but with poor stability. Maillard’s study suggested that distorted surface greatly increased the catalytical activity and antidegradation ability. The composition, atoms arrangement, and order of degree all can affect the ORR activity and stability, achieved by manipulating the surface/near-surface structure. In this context, we focus on the relationship between activity, stability, and surface/near-surface structure. We classified the surface structure into three types which are smooth surface structure, distorted surface structure, and heterostructural surface, respectively. The engineering strategy of surface structure and corresponding tuning mechanism on ORR are also summarized in detail. Also, the future for the development of surface-engineered catalysts is also discussed.
2. ORR and Performance Decay Mechanism in the Acid Electrolyte

2.1. ORR Mechanism in the Acid Electrolyte

There are three main mechanisms for ORR in acid solution, mainly including dissociative mechanism, first associate mechanism, and second associate mechanism, as shown in Figure 1a.[14] The adsorbed oxygen molecular can be directly dissociated into $\text{O}_2^*$, which then combines proton and electron to form $\text{H}_2\text{O}$ (a dissociative mechanism). Also, $\text{O}_2^*$ first combined the proton and electron to form $\text{OOH}^*$ and then dissociated into $\text{O}^*$ and $\text{OH}^*$, which is further reduced into $\text{H}_2\text{O}$ (a first associate mechanism). Alternatively, different from the dissociation pathway of $\text{OOH}^*$, $\text{OOH}^*$ also couples with the proton and electron to form $\text{H}_2\text{O}_2$, denoted as the second associate mechanism. Based on Sabatier’s principle, promising ORR catalysts shows moderate adsorption energy with reactants, intermediates, and production to accelerate the rate for dissociation of reactants, bonding of intermediates, and desorption of production. Among all metal elements, Pt has been found to locate at the apex of the volcano plot shown in Figure 1b,[15] still lagging behind the optimized activity. Further study indicated that the reactivity on Pt surface is limited by the removal of adsorbed $\text{OH}^*$ at 1.23 V, whereas the rate of ORR is dictated by the removal of $\text{OH}^*$ and dissociation of $\text{O}_2^*$ at a cell potential of 0.8 V.

2.2. Activity Decay Mechanism

According to the U. S. Department of Energy (DOE), fuel cells must have a durability target of 8000 h (equivalent to 150 000 miles of driving) with less than 10% loss of performance to compete with internal combustion engines in the market. However, the highest durability in the company-average project is about 4000 h with 10% voltage degradation, significantly lower than the ultimate target of 8000 h. It has been demonstrated that performance losses of PEMFCs under steady-state and cycling conditions are mainly attributed to the dissolution of platinum and carbon corrosion, which has been summarized in many reviews.[16] The extent of dissolution of Pt may be attributed to the electrochemical dissolution, the formation of platinum oxide, and chemical dissolution of oxide. Platinum is prone to be oxidized to insoluble Pt(\text{OH})_2, PtO, and PtO_2 based on Pourbaix diagrams and Lee diagrams.[17] Recently, an in-situ X-ray reflectivity experiment provided strong evidence for the formation of PtO_2 on Pt (111) at high potential, in line with the detection of the chemisorbed O on Pt surface between 0.85 and 1.15 V by in situ X-ray studies.[18] In addition, the oxidation of Pt nanoparticles (NPs) supported on carbon was also observed through in-situ XAFS measurements.[19] Many results for bulk and high-surface-area carbon-supported platinum in acid electrolytes showed slopes lower than expected for the two-electron process, strongly suggesting that the dissolution of Pt is attributed to the oxide rather than metal.[20] 

To in situ monitor the kinetic of Pt dissolution and understand the relationship between surface structure and stability, inductively coupled plasma mass spectrometry (ICP–MS) connected to a stationary probe coupled with a rotating disk electrode (SPRDE) technique possibly enable the measurement of dissolution rate as low as 0.4 pg cm$^{-2}$ s$^{-1}$ in Figure 2a.[21] It was found that coordination of surface atoms directly determined the degree of stability, where less coordinated surface atoms were prone to dissolve (Figure 2b–d). In addition, the Pt nanoparticles have been less stable than the bulk electrode, possibly due to the richness of defect at the nanoscale. For Pt nanoparticles, both size of nanoparticles and homogeneity in size directly determined the dissolution kinetics of Pt. The dissolved Pt content for nanoparticles with the size of 2.8 nm was four times higher than that for 7.8 nm Pt NPs. In addition, the degradation of the catalyst was also accelerated for nonuniform size distribution compared with highly uniform distribution.

2.3. Electrochemical Evaluation for Activity and Stability

As evaluating catalysts through membrane electrode assembly (MEA) is highly intricate, prohibitive, and time-consuming, rotating disk electrode method has been confirmed to be a promising alternative for the screen of active catalysts due to its convenience and acceleration of oxygen mass transfer. First, catalyst powders are ultrasonically dispersed into the mixture of deionized water, alcohol, and Nafion solution, followed by the transfer of ink onto
the polished glass carbon electrode and drying under argon atmosphere to finish the preparation of thin-film electrode. The thin-film electrode is then transferred into argon-saturated perchloric acid solution or sulfuric acid solution. Cyclic voltammetry (CV) consisting of potential cycles between 0.05 and 1.2 V is applied to the working electrode and the corresponding I–V curve is shown in Figure 3a, where the potential range for the occurrence of the underpotential deposition of a hydrogen atom and its oxidation is lower than 0.4 V and Pt happens to oxidize when the potential is higher than 0.6 V. ORR is evaluated using the CV technique consisting of a potential range between 0.05 and 1.2 V in oxygen-saturated perchloric acid solution rather than a sulfuric acid solution due to the adsorption of sulfate ion on Pt surface, as shown in Figure 3b. A high rotate speed (usually a speed of 1600 rpm) is indispensable to mitigate the concentration polarization. It is worth noting that the rational loading of high-surface-area catalysts on RDE is necessary. The formation of thicker catalyst film at higher loading affects the mass transport characteristics of RDE and some unknown parameters such as agglomerate structure and ionomer distribution also may lead to the negative effect on activity. However, catalysts of lower loading may not spread completely over the whole electrode and uncovered electrode remain. Therefore, catalyst loading that is too high or too low should be avoided and the optimum loading of high-surface-area catalysts is about 14 μgPt cm⁻². The investigation on the durability of catalysts in real PEMFCs is almost impossible because the lifetime should be higher than 5000 h for transportation and 40 000 h for stationary application. Therefore, the standard accelerated degradation test (ADT) is of significant importance for the rational evaluation of catalysts stability. The U.S. DOE proposed valuable ADT protocol mainly including CV at a higher voltage window under oxygen-saturated acid solution.

3. Advanced Pt-Based Catalysts with a Smooth Surface/Near-Surface Structure

3.1. Pt-Based Catalysts with Smooth Pt Monolayer

ORR kinetic is determined by the electronic structure, geometric structure, and coordination environment of surface Pt atoms. The modulation of electronic structure and geometry is achieved by the incorporation of inner heteroatoms due to the difference of electronegativity and lattice parameters between Pt and cheaper metals. The ligand effect and strain effects arising from inner core decay with the increasing of Pt-rich shell. Therefore, the thickness of the Pt-rich shell plays an important role in the surface/near-surface structure of catalysts. Underpotential deposition coupled with subsequent galvanic displacement strategy is proposed by Adzic’s group and utilized to synthesize Pt monolayer on different single-crystal substrates (Pt₄ML/M, M = Pd, Au, and Ir), as shown in Figure 4a. It was found that Pt₄ML/Pd (111) achieves the highest performance due to the compressive strain. The carbon-supporting Pd nanoparticles covered by Pt monolayer are further synthesized by galvanic displacement by a Pt₄ML of a Cu monolayer deposited on Pt.
Figure 3. a) CV in argon-purged solution (black) and the CO curve (grey). The inset shows the conventional correction for capacity in the H upd (upd–under potential deposition) region (black dotted). b) ORR–polarization curves for Pt–poly and the 1 nm catalyst with two different Pt loadings in 0.1 M HClO4. The temperature is 333 K, sweep rate 20 mV s⁻¹, and the rotation rate: 1600 rpm. Only the anodic sweep is displayed for all samples. The estimated specific activities are presented in a Tafel plot (b). Reproduced with permission.[22] Copyright 2008, Elsevier.

Figure 4. a) Schematic of underpotential deposition and galvanic displacement of a Cu UPD monolayer by Pt. Green, blue, and brown balls represent Pd, Pt, and Cu atoms, respectively. Reproduced with permission.[10] Copyright 2020, Elsevier. b) High-angle annular dark-field image of a representative PtML/Pd nanoparticle. c) The mass activity of PtML/Pd/C, Pt/C, and Pt/Ketjen for the ORR as a function of the number of potential cycles during fuel cell operation. The concentration profiles of Pd and Pt element across the cross section of MEA d) before and e) after potential cycles. Reproduced with permission.[27] Copyright 2010, Wiley-VCH. f) Schematic illustrations of self-healing and followed self-retaining on the surface of cube-octahedral PtML/Pd model. Grey, blue, and green balls represent the Pt atoms, Pd atoms at the terrace, and Pd atoms at the edge, respectively. Reproduced with permission.[28] Copyright 2018, The Royal Society of Chemistry. g) HAADF/STEM image of a representative PtML/Pd9Au1 nanoparticle and elements distribution obtained by the line-scan analysis. h) Geometrical illustrations for the segregation of Au atoms and Pd atoms from the core to the defective site in the Pt monolayer through DFT calculations. Blue, sky blue, and orange balls represent Pt, Pd, and Au atoms, respectively. Reprinted with permission.[30] Copyright 2012, Springer Nature.
cores at underpotentials (Figure 4b), revealed by the atomic-resolved line-scan under the high angle annular dark field–scanning transmission electron microscope (HAADF–STEM) mode.\textsuperscript{[27]} The P$_{\text{ML}}$/Pd/C achieved a factor of 3 enhancement in mass activity in comparison with commercial Pt/C under the MEA system. More importantly, the P$_{\text{ML}}$/Pd/C only shows a decrease of 19\% and 23\% in mass activity and electrochemical surface area, respectively, in contrast with a striking loss of 68\% in mass activity and electrochemical surface area (Figure 4c). However, the Pd “band” was formed and observed in the membrane through SEM images for MEAs after ADTs, as shown in Figure 4d,e, possibly because of the dissolution of Pd during stability tests. Different from single crystals, it is impossible to deposit a perfect Cu monolayer on nanoparticles due to the presence of massive defect sites. Therefore, the uncovered Pd cores will be directly in contact with the electrolyte. During the electrochemical condition, Pd dissolution into Pd$^{2+}$ ions occurs at a lower potential than that of Pt due to the lower standard equilibrium potential of Pd. The prior Pd dissolution may exert a certain degree of cathodic protection on Pt by limiting the cathode potential reaching Pt dissolution potential. During the long-term stability test, the Pt monolayer undergoes a contraction to form a more stable structure with the dissolution of Pd, denoted as the self-healing mechanism (Figure 4f). After that, Chen et al. evaluated the long-term stability of P$_{\text{ML}}$/Pd/C at the RDE scale.\textsuperscript{[28]} The robustness and superior activity were also observed on the P$_{\text{ML}}$/Pd/C. Different from the decay mechanism of Pt/C ascribing from the dissolution of Pt, the prior Pd dissolution was revealed by the combination of EDX and STEM. In addition, they found that initial P$_{\text{ML}}$/Pd/C also evolved into defect-free P$_{\text{ML}}$/Pd/C through a self-healing mechanism. Defect-free P$_{\text{ML}}$/Pd/C was confirmed to maintain almost unchanged activity, denoted as the self-retaining mechanism (Figure 4f). The main mechanism for robust stability of P$_{\text{ML}}$/Pd/C was revealed by in-situ X-ray absorption near edge structure (XANES). In-situ characterization results suggested that the preferential Pd oxidation at the defects in Pt monolayer up to 0.91 V and through the place exchange process above 1.11 V imparted cathodic protection for Pt monolayers and thus impeded the dissolution of Pt.\textsuperscript{[29]}

The dissolved Pd ion will be deposited onto the membrane and may diffuse into the anode and further be reduced into to Pt islands, which are harmful for the operation time of PEMFCs. To impede the dissolution of the inner Pt core, small amounts of Au were proposed to stabilize Pd atoms (Figure 4g). The Pt monolayer supported on Pd$_{x}$Au NPs presented higher stability in comparison with P$_{\text{ML}}$/Pd/C, also showing the absence of deposited Pd bands at the side of membrane.\textsuperscript{[30]} The incorporation of Au could not only improve the equilibrium potential of Pd through the electronic structure but also spontaneously diffuse into defect sites due to high segregate energy and suppress Pd dissolution, as shown in Figure 4h.\textsuperscript{[31]} Composition-tunable Pd$_{x}$Au aerogels with self-supported structures were successfully fabricated through a gelation method.\textsuperscript{[32]} The supported-self P$_{\text{ML}}$/Pd$_{x}$Au aerogels achieve the mass activity of 5.25 A mg$_{\text{Pt}}$\textsuperscript{$^{-1}$} and specific activity of 2.53 mA cm$_{\text{Pt}}$\textsuperscript{$^{-1}$} at 0.9 V, respectively. In addition, P$_{\text{ML}}$/Pd$_{20}$Au aerogels exhibited only 8.2\% loss in mass activity after ADTs in comparison with the 27.6\% loss for Pt/C. The enhanced activity and stability were mainly because the incorporation of Au strongly influences the Pd lattice parameters and dissolution potential. On the other hand, the development of nondissolution metal and composite as substrates for the deposition of Pt monolayer is also of importance. Stable Au–Ni with core–shell and alloy structure was synthesized and utilized to prepare P$_{\text{ML}}$ catalysts, showing the improved activity and stability.\textsuperscript{[16a]} Ir and IrNi alloy with higher antidualositional ability was also proposed as substrates for the deposition of Pt monolayer.\textsuperscript{[133]} Underpotential deposition is an electrode-scale technique, leading to the difficulty in mass production of Pt monolayer catalysts. Wang and coworkers used the facile reduction ability of ethanol to deposit a Pt monolayer on Pd nanoparticles and Ru nanoparticles, respectively.\textsuperscript{[34]} A novel self-assembly method is demonstrated to be of high feasibility in the synthesis of Pt monolayer on a nonprecious core, such as WC and TiWC, opening up the possibility for the design of Pt ML on precious metal group metal-free cores.\textsuperscript{[135]} Although substrates Pd with shorter geometric distance led to compressive strain on Pt monolayer, the geometric modulation was still far insufficient. To further apply compressive strain on surface Pt atoms, the 3D transition metals with shorter bond distance, such as Ni, Co, and Fe, were alloyed with Pd. Pt monolayer deposited on single-crystal Pd,Fe (111) showed higher activity than Pt monolayer on Pd (111) single crystals.\textsuperscript{[36]} After that, the Pt monolayer is deposited onto the fabricated Pd-based nanoparticles. Zhang and coworkers synthesized a series of PdNi nanoparticles and found that Pd$_x$Ni$_{1-x}$ nanoparticles covered by P$_{\text{ML}}$ showed the highest ORR activity.\textsuperscript{[137]} Porous active centers with 3D accessibility are beneficial for the improvement of activity.\textsuperscript{[40,5b,38]} A porous PdCu alloy was synthesized by leaching Cu-rich PdCu alloy.\textsuperscript{[39]} The Pt monolayer on porous PdCu exhibited mass activity 14 times higher than Pt/C. Shao et al. also fabricated shape-selective P$_{\text{ML}}$/Pd/C to further enhance the ORR activity,\textsuperscript{[40]} where Pt monolayer was deposited on manipulated Pd nanocrystal such as Pd cubes and octahedral through underpotential deposition technique.\textsuperscript{[41]} To eliminate the dissolution of inner Pt, the interlayer of Au was deposited on the shape-selective Pt by UPD in advance and exhibited a positive role in the improvement of stability.\textsuperscript{[42]}

3.2. Pt-based Catalysts with Smooth Pt Multilayers

Except for monolayer, surface/near-surface structure with multilayers also plays an important role in the manipulation of ORR pathways and long-term stability. Xia et al. developed an advanced Pt shell thickness-tunable strategy by slowly injecting Pt precursors into ethylene glycol containing Pd crystals, such as cubes,\textsuperscript{[43]} octahedra,\textsuperscript{[44]} decahedra,\textsuperscript{[45]} and icosahedra.\textsuperscript{[46]} During the synthesis process, the reduced Pt atoms by ethylene glycol will quickly diffuse onto the Pt surface and form a comfortable deposited shell rather than the self-nuclear of Pt (Figure 5a,b). Among Pd@P$_{\text{ML}}$ with different multilayers synthesized by the variation of Pt precursors, Pt within 2–3 ML achieves the highest ORR performance. The descending ORR activity for Pd@Pt with a thicker Pt shell is mainly due to the decay of ligand effect and strain effect. The partial cover may be the main reason for the relatively low activity of Pd@P$_{1.1}$ in comparison with Pd@P$_{2.3}$L. Among all Pd@Pt nanocrystals, Pd@Pt concave decahedra achieved the highest ORR mass activity of 1.6 A mg$^{-1}$, due to its special surface coordination.
Leaching and dealloying are the main strategies for tuning the surface structure with a multilayer Pt shell. Watanabe and coworkers used the magnetron sputtering technique to prepare the Pt–Fe, Pt–Co, and Pt–Ni thin-film electrode and revealed their significantly enhanced ORR activity. Markovic and coworkers proposed a segregation concept where sputtered Pt–Co electrode was immersed into an acid solution and further treated at 950 K, denoted as Pt-skin electrode. The low-coordinated Pt atoms due to the dissolution of Ni atoms will diffuse and rearrange to form a skin structure at high temperature. The existence of Pt skin surface is demonstrated by the value of $Q_{\text{CO}}/2Q_{\text{H}}$ to be 1.5, where $Q_{\text{CO}}$ and $Q_{\text{H}}$ is the charge related to CO stripping and H underpotential deposition, respectively. They also found that the segregated Pt skin near-surface structure is only formed when the ratio of Pt to M in Pt–M catalysts is higher than 3. Furthermore, they prepared five kinds of Pt$_x$M electrodes ($M = V, Ti, Fe, Co$, and Ni) and found that segregated Pt-skin on Pt$_x$Co achieved the peak performance due to its optimized electronic structure. The in situ X-ray absorption spectroscopy result reveals that the Pt-skin catalysts with the segregated Pt surface bind the adsorbates weakly in comparison with the insufficiently segregated Pt surface. Wang et al. deposited different Pt layers on the PtNi electrode and found that Pt$_x$–3L on the PtNi electrode exhibited the highest activity, as shown in Figure 5c. After that, they prepared Pt-skin/Pt$_x$–3Ni/C catalyst by a wet chemistry method followed by leaching and thermal treatment, as shown in Figure 5d,e. The Pt-rich shell structure after leaching treatment is directly controlled by the initial composition and the highest ORR activity was observed on leached PtNi nanoparticles mainly due to its thinnest Pt-rich shell. Chorkendorff et al. manipulated the activity of Pt-based alloy electrocatalysts through the lanthanide contraction. The ORR activity on eight Pt-lanthanide and alkaline earth electrodes were studied and presented a volcano curve. The active phases consisted of a Pt overlayer formed by
acid leaching and demonstrate that the lanthanide contraction can be used to control strain effects and tune the activity and stability (Figure 5f,g). Pt–Cu with varied composition was synthesized by Strasser’s group by treating Pt–Cu precursors at a different temperature.\(^{[60]}\) The catalysts loaded onto the glassy carbon electrode are dealloyed in acid solution and covered by different Pt-rich layers (Figure 5h). They found that the ligand effect was a short-range interaction only within 2–3 layers, whereas the lattice strain is a long-range interaction within at least 10 layers (Figure 5i). After that, PtNi, PtNi\(_{3}\), and PtNi\(_{2}\) nanocatalysts were also fabricated and dealloyed in acid electrolyte.\(^{[59]}\) The bulk composition also played an important role in the near-surface structure of catalysts, where Pt-rich shell became thicker with the increase in bulk content. Although Pt–M catalysts covered by multi-Pt layers have shown great ORR activity, their stability still cannot meet the actual requirements due to the outward diffusion of non-PGM metal. To stabilize the inner PGM-free metal, Wang et al. synthesized a novel Pt–Co catalyst with an intermetallic compound structure, exhibiting an ultrathin Pt shell in an electrochemical environment.\(^{[60]}\) Significantly enhanced activity and electrochemical stability were observed on intermetallic PtFe@Pt and PtCo@Pt with ultrathin Pt-rich layers.\(^{[61]}\) The high stability of intermetallic structure was mainly because of the anchor of cheaper metal in the superlattice structure. Gan and coworkers studied the relationship between intermetallic compound and composition, revealing that Pt–Fe and Pt–Co phase could evolve from alloy phase into intermetallic at high temperatures, such as 800 °C, whereas Pt–Ni phase maintains their alloy structure even at a high heat-treatment temperature.\(^{[62]}\)

3.3. Shape-Selective Pt-based Catalysts

Surface atoms arrangement is also another important factor besides electronic structure and geometric structure.\(^{[63]}\) Single crystals are the ideal model for revealing the effect of atom orientation on ORR. Markovic et al. studied ORR kinetics on the low-index single crystal, including Pt (100), Pt (111), and Pt (110) and found that the Pt (111) exhibited the top performance in perchloric acid solution.\(^{[64]}\) At the nanoscale, as-synthesized 0D nanoparticles are bounded by low-index facets of (111) and (100) surfaces and bridged by (110) surface.\(^{[65]}\) Shape-selective Pt nanocrystal, such as Pt octahedra, cube, and rhombic dodecahedron nanocrystals, are bounded by Pt (111), Pt (100), and Pt (110), respectively.\(^{[66]}\) The Pt nanocubes were first synthesized by a simple high-temperature organic-phase synthesis, where precise control of Pt nanoparticles was mainly controlled by the presence of oleylamine and oleic acid.\(^{[67]}\) Du et al. developed a facile and green synthetic strategy for the shape-controlled Pt nanocrystal where Pt cube, truncated octahedra, and octahedra were prepared by the addition of different amounts of polydimethyl-diallyl-ammonium chloride (PDDA).\(^{[68]}\) The Pt octahedra enclosed by Pt (111) facets exhibited the highest ORR activity, in line with the single-crystal results. The ORR activity on different-controlled Pt NPs in the acid electrolyte is also revealed by scanning electrochemical microscopy (SECM), demonstrating its surface structural dependency at the nanoscale.\(^{[69]}\)

However, it is a great challenge to synthesize nanocrystals enclosed with high-index facets through conventional wet chemistry-synthesized strategy. Tian et al. made a breakthrough in the synthesis of Pt tetrahedron (THH) by developing a two-step electrochemical method. The first step is the electrochemical deposition of Pt nanoparticles with the size of 750 nm on a glassy carbon electrode.\(^{[70]}\) The second step is the application of square-wave potential onto the deposited Pt nanospheres in sulfuric acid and ascorbic acid mixed solution. (Figure 6a) The periodic adsorption/desorption of hydrogen and oxygen on metal surfaces, caused by the periodic square-wave potential, is demonstrated to be the main reason for the formation of high-index planes.\(^{[71]}\) The drawback of Pt THH crystals is their relatively larger size and limits their application in fuel cells due to the low Pt utilization (Figure 6b,c). Zhou and coworkers synthesized high-index facets Pt nanocrystals supported on carbon using insoluble Cs\(_{2}PtCl\(_{6}\)\(^{[72]}\) Besides Pt THH, Xia and coworkers reported Pt concave nanocubes enclosed by high-index facets including (510), (720), and (830) by the use of a Pt pyrophosphate complex as precursors and the control of reaction rate with a syringe pump (Figure 6d–g). The ORR activity of Pt concave cubes achieves a factor of 3.6 enhancement in comparison with that of commercial Pt/C.\(^{[73]}\)

Although the enhanced ORR activity was demonstrated onto the shape-selective single Pt nanocrystals, it still lagged far behind the actual requirements. Stamenkovic et al. prepared Pt\(_{3}\)Ni (hkI) alloy single crystal in ultrahigh vacuum and found that Pt\(_{3}\)Ni (111) achieved the recorded ORR activity,\(^{[74]}\) which is about an 90-fold enhancement in comparison with Pt/C, as shown in Figure 6h. The near-surface structure of Pt\(_{3}\)Ni (111) was characterized to be a segregated Pt layer and the subsurface was revealed to be a Ni-rich layer. The unparalleled ORR activity on Pt\(_{3}\)Ni (111) triggers larger numbers of studies on the Pt–Ni alloy nanocrystals bounded by (111) facets, such as Pt–Ni octahedra. Fang and coworkers first fabricated the Pt\(_{3}\)Ni octahedra and cube enclosed with (111) and (100) planes, respectively, via a high-temperature organic solution chemistry solution. Pt\(_{3}\)Ni octahedra delivered about 2.8 times enhancement compared with Pt\(_{3}\)Ni cubes.\(^{[75]}\) The Pt–Ni octahedra with other compositions and near surfaces were also successfully prepared, but lagged behind Pt\(_{3}\)Ni (111), mainly because surfactant, essential for the synthesis of nanocrystals, was difficult to remove and thus limit the ORR activity. Cui et al. developed a surfactant-free solvothermal method where dimethyl formamide (DMF) is used as the solvent and reduced agent.\(^{[76]}\) The PtNi with the size of 9.5 nm achieved the mass activity of 1.45 A mg\(^{-1}\) Pt and 3.14 mA cm\(^{-2}\) Pt toward ORR at 0.9 V, respectively. Xia and coworkers used W(CO)\(_{6}\) to alternate CO as reducing agent to reduce the Pt precursor and Ni precursor in benzyl ether.\(^{[77]}\) The 51-fold enhancement in specific activity toward ORR was observed on 9 nm Pt–Ni octahedra in comparison with the state-of-the-art Pt/C. The great enhancement of ORR activity on Pt–Ni octahedra can be attributed to the presence of a clean, well-protected (111) facet. The difference in activity of reported Pt–Ni octahedra may be due to the different synthesis routes, which directly determined their surface and near-surface structure. Huang et al. revealed the high uniformity in element distribution across the whole Pt–Ni octahedra, whereas the compositional segregation was also found in Pt–Ni octahedra.\(^{[78]}\) Strasser and coworkers revealed the compositional segregation across the (111) facets, where the Pt\(_{5}\)Ni\(_{1}{1–\text{o}}\) octahedra featured
a Pt-rich frame along their edges and corners and Ni atoms were preferentially segregated in their (111) facet region, as shown in Figure 6i. The relationship between bulk composition, near-surface, and activity was also revealed in detail by the use of AR–HAADF–STEM. The Pt\(_1\)Ni\(_1\) octahedra exhibited a near-surface structure of 1–4 Pt layers during the electrochemical environment, achieving the mass activity of 1.6 A mg\(^{-1}\)Pt (Figure 6j). However, the near-surface structure of Pt\(_{1.5}\)Ni evolved into 5–12 layers, showing the mass activity of 1.2 A mg\(^{-1}\)Pt. However, Ni-rich Pt\(_{1.5}\)Ni octahedra evolved into an orthorhombic structure with the mass activity of 1.0 A mg\(^{-1}\)Pt. The lowest ORR activity on Pt\(_{1.5}\)Ni was due to the absence of well-preserved (111) facets. The highest ORR activity on Pt\(_{1.5}\)Ni could be attributed to the typical Pt atomic coordination environment and thinner Pt-rich layers, which were of importance for maintaining interior ligand effect and geometric effect. However, in contrast with the 16% loss in mass activity after ADTs for Pt\(_{1.5}\)Ni octahedra, the Pt\(_{1}\)Ni\(_1\) octahedra containing thinner Pt-rich layers presented about 60% loss after ADTs. The striking loss for Pt\(_{1}\)Ni\(_1\) octahedra after ADTs may be because of the massive dissolution of interior Ni atoms and degradation of surface structure. However the high stability on Pt\(_{1.5}\)Ni was rationally ascribed to its near-surface structure with thicker Pt-rich layers, which limited the Ni dissolution and preserved its atomic arrangement. The striking loss on Pt\(_{1.5}\)Ni octahedra with high initial activity was also confirmed by many groups. In short, it is a dilemma for achieving high ORR activity and robust stability at the same time because the near-surface structure cannot meet the requirements of activity and stability.

Gan et al. first studied the nucleation growth process to understand its principal growth mechanisms. A Pt-rich phase first evolved into the precursor nanohexapods, followed by a slower step-induced deposition of a Ni-rich phase at the concave hexapod surface forming the octahedral facets. Beermann used the in situ electrochemical liquid cell STEM to understand the degradation of Pt–Ni octahedra in real time, where the occurrence of the Ni dissolution process promptly took place after some
electrochemical cycles. Also, the octahedral shape remained stable during the moderate potential cycling up to 1.0 V, whereas the higher upper limiting potential, such as 1.2 and 1.4 V, severely caused the morphology degradation possibly due to the dissolution, migration, and redeposition of Pt atoms. Recently, many efforts have been devoted to improving the stability of shape-controlled Pt–Ni nanocrystal. Huang et al. doped a series of transition metals into the surface/near surface of Pt$_3$Ni octahedra.$^{[83]}$ Among all M ($M = \text{V}, \text{Cr}, \text{and Mo}$)-doped Pt$_3$Ni octahedra, the Mo-Pt$_3$Ni/C showed the best ORR performance, with the mass activity of 6.98 A mg$^{-1}$Pt and specific activity of 10.3 mA cm$^{-2}$Pt (Figure 7a–c). Also, Mo-Pt$_3$Ni/C catalysts only show a 5.5% loss in mass activity after ADTs, in comparison with the 41% loss for Pt$_3$Ni/C. Theoretical calculations suggested that Mo simultaneously diffused into the subsurface positions near the edges and surface vertex/edge sites in oxidizing conditions, where it enhanced both the performance and the stability of the Pt$_3$Ni catalyst. Strasser and coworkers studied the Rh surface-doped octahedral Pt–Ni particles with various Rh levels.$^{[84]}$ It was found that Rh-PtNi with 3% doping content maintained octahedral shape even after 30 000 potential cycles, whereas PtNi nanoparticles showed a complete loss in morphology after 8000 cycles (Figure 7e). Ternary alloy Pt$_2$CuNi octahedra were also demonstrated by its high stability and initial activity.$^{[85]}$ The improved stability was attributed to the uniform element distribution, which promoted the formation of intact Pt surface layers and good retention of the octahedral morphology. Also, the incorporation of Pb was also revealed to be feasible for

\[ \text{Figure 7.} \ a) \text{Cyclic voltammograms of octahedral Mo-Pt}_3\text{Ni/C, octahedral Pt}_3\text{Ni/C, and commercial Pt/C catalysts recorded in nitrogen-saturated 0.1 M HClO}_4\text{ solution.} \ b) \text{ORR polarization curves of octahedral Mo-Pt}_3\text{Ni/C, octahedral Pt}_3\text{Ni/C, and commercial Pt/C catalysts in oxygen-saturated 0.1 M HClO}_4\text{ solution with a sweep rate of 10 mV s}^{-1}. \ c) \text{The electrochemical active surface area, specific activity, and mass activity at 0.9 V (vs. RHE) for these transition metal-doped octahedral Pt}_3\text{Ni/C catalysts. Reproduced with permission.}^{[83]} \text{Copyright 2015, AAAS.} \ d) \text{Low-resolution HAADF–STEM image and atomic-resolution HAADF–STEM image of representative A-MS-Pt}_{1.5}\text{Ni and A-Pt}_{1.5}\text{Ni octahedra. The upper portion shows the image of A-MS-Pt}_{1.5}\text{Ni. The bottom portion shows the image of A-Pt}_{1.5}\text{Ni. Reproduced with permission.}^{[87]} \text{Copyright 2020, American Chemical Society.} \ e) \text{Schematic illustration for the evolution behavior of PtNi and PtNiRh octahedral during the electrochemical process. Reproduced with permission.}^{[84]} \text{Copyright 2016, American Chemical Society.} \]
the improvement of stability. The surface doping strategy has been confirmed to be a feasible strategy to improve ORR stability almost without the compromise of activity. Our group proposed a novel strategy called near-surface structure engineering, to stabilize their morphology and structure, as shown in Figure 7d. The near-surface structure of engineered Pt$_{3.5}$Ni octahedra evolved into the Pt-rich shell with about 2–3 layers, in contrast with the near-surface structure of 5–7 Pt-rich layers for Pt$_{1.5}$Ni. The engineered Pt$_{3.5}$Ni exhibited superior mass activity of 1.9 A mg$^{-1}$Pt and specific activity of 7.7 mA cm$^{-2}$Pt, which is possibly due to the thinner Pt-rich layers. More importantly, the engineered catalysts also showed robust structure and morphology stability after ADTs with just about 10% loss in mass activity. The enhanced stability on engineered catalysts was mainly because the interior Pt-rich composition protected Ni atoms from outward diffusion and further dissolution.

Although the presence of interior metal, such as Pd and Ni, was beneficial for the improvement of activity through lattice mismatch and heterogeneity, the inevitable diffusion significantly lower catalytic activity. Hollow structure featuring ultrathin Pt layers is a kind of stable catalyst, which effectively eliminates the dissolution of a second metal. The hollow core is also an interesting structure because it may induce desirable lattice contraction in a Pt shell, which is beneficial for the improvement of ORR. The template method is an effective strategy to prepare the 0D hollow nanoparticles and shape-controlled hollow nanoparticles, denoted as nanocages. Kirkendall effect, a vacancy-mediated diffusion mechanism, has been recognized as a highly feasible strategy to fabricate hollow nanocatalysts. Wang et al. synthesized Pt hollow nanoparticles by the application of electrochemical dealloying on Ni@Pt nanoparticles. The Pt hollow nanoparticles did not only exhibit enhanced ORR activity, but also showed the much higher thermal stability and electrochemical stability ascribed to the lower diffusivity of Pt and the high-coordination surface sites per Pt mass. The difference for metal diffusion rate was also used to fabricate the engineered near-surface Pt-based binary hollow nanoparticles. Binary PtNi hollow nanoparticles were also found to be higher than that of solid PtNi nanoparticles, which were ascribed to their open porosity, preferential crystallographic orientation, and weakened oxygen binding energy. Wei and coworkers revealed the structural evolution of solid Pt nanoparticles to hollow Pt-skin–PtM nanocatalysts through space-confined pyrolysis and nanoscale Kirkendall effect.

Zhang et al. used Pd cubes and Pd octahedra as hard templates to synthesize Pt cubic and octahedral nanocages by etching shape-selective Pd@Pt$_{5.5}$SL nanocrystals. During the process of Pt deposition on Pd nanocrystals, some Pd atoms diffused into deposited Pt overlayers and formed Pt–Pd alloy. During the etching process, the surface Pd atoms were oxidized upon contact with the etchant and generated the surface vacancies (as shown in Figure 8a). The underlying Pd atoms diffused to these vacancies and were etched away, leaving behind atom-wide channels. During the early stage of etching, the outward diffusion rate of Pd was higher than the Pt diffusion rate inward, leading to the creation of a void in the Pd template. With the increase of etching time, the channels grew in size to allow direct corrosion of Pd from the core. In addition, there were essentially no changes to the shape and morphology by sophisticated control of the etching environment. The Pt octahedra and cubes cages, as shown in b–f, were composed of ultra-thin Pt-rich layers with great 3D accessibility. Also, the ORR activity on Pt nanocages was greatly enhanced where octahedral Pt nanocages achieved the mass activity of 0.75 A mg$^{-1}$Pt at 0.9 V. After that, they also demonstrated that a similar strategy can also be extended to the icosahedral system. The icosahedral nanocages enclosed by (111) facets and multiple twin defects were also synthesized by etching of icosahedral Pd@Pt$_{4.5}$SL. The Pt-based icosahedral nanocages with only six atomic layers showed an extremely high specific activity of 3.5 mA cm$^{-2}$Pt and mass activity of 1.28 A mg$^{-1}$Pt. Except for morphology, the surface composition is also an effective strategy to modulate the near-surface structure of Pt-based nanocages. Recently, Ni atoms were introduced into octahedral Pt-based nanocages through a surface-modification strategy. The incorporation of Ni atoms could tune the electronic structure of surface Pt atoms and further shorten Pt–Pt bond length, leading to the enhancement of ORR activity with the mass activity of 1.17 A mg$^{-1}$Pt. Chen et al. developed novel nanoframes structure to eliminate the dissolution of relatively cheaper metal, prepared by the chemical etching of PtNi$_{4}$ rhombic dodecahedron, as shown in Figure 7j. The Pt-rich Pt$_{3.5}$Ni nanoframes achieved a factor of 36 enhancement in mass activity and a factor of 22 enhancement in specific activity (Figure 7k). The anisotropic phase segregation and migration mechanism allowed for the Pt$_{3.5}$Ni nanoframes to be obtained after chemical corrosion (Figure 7l). The ex situ and in situ X-ray absorption spectrum reveals that the unparalleled ORR activity on nanoframes was attributed to the significant segregation of Pt over Ni-rich subsurface layers.

4. Advanced Pt-based Catalysts with a Distorted Surface/Near-Surface

4.1. Generalized Coordination Number and ORR Activity

Sabatier’s principle has been extensively used as a criterion to design and screen the catalysts, stating that ideal catalysts balance the strength of adsorption and desorption of key reaction intermediates. The volcano curves, correlating surface adsorption energies of intermediates with the catalytic activity of different materials, confirmed the validity of Sabatier principle. Several studies have used this criterion to successfully find catalysts with high ORR activities, such as Pt$_{5.5}$/Pd. However, it still is a great challenge to bridge a correlation between single-crystal and nanoparticle design principles, which creates a huge gap between controlled laboratory experiments and technological implementation. Calle-Vallejo et al. proposed a new descriptor, called generalized coordination number ($\mathcal{C}_N$), which enabled a clear distinction between deleterious and beneficial defects for the ORR activity in nanoparticles as well as extended surfaces. Although conventional coordination numbers are a count of the first nearest neighbors that capture trends on adsorption energies on extending surfaces, they fail on nanoparticles. The $\mathcal{C}_N$ weighted each first-nearest neighbor atom ($j$) by its coordination number ($\text{cn}(j)$). It was also worth noting that the generalized coordination number of surface Pt atom at (111) surface was 7.5, located on the left side of the volcano plot. It was also...
revealed that the sites with the $\text{CN} < 7.5$ bound $^\circ\text{OH}$ more strongly and led to a larger overpotential, whereas the sites with the $\text{CN} > 7.5$ bound $^\circ\text{OH}$ more weakly and produced the smaller overpotential. Such highly coordinated sites could not be assigned to the convex surface, as shown in Figure 9a, which well explained their lower activities. The concave sites with highly coordinated sites were pointed out to be the high activity region. For all convex shapes including cube, octahedra, and truncated...
octahedra, the upper limit $\langle CN \rangle$ is 7.5. However, the $\langle CN \rangle$ for small nanoparticles is lower than 7.5 due to the presence of edge and vertex, which rationally explained that the ORR activity for small nanoparticles is substantially lower than the extended surface. In addition, nanoparticles with highly coordinated numbers have been found in the framework, coalescent, and cross structure, as shown in Figure 9b–d, which are expected to exhibit higher activity and have been confirmed by experiment. They further used the generalized coordination number principle to engineer the active sites at Pt (111), as shown in 9e. The first strategy was the dealloying of Cu/Pt (111) surface alloy. The second strategy is the galvanic displacement between deposited Cu overlayer with Pt ions in solution. The last strategy was the formation of subsurface Pt oxide through electrochemical polarization. Electrochemical measurement results indicate that the various (111) defective electrodes significantly enhanced ORR activity in comparison with smooth (111) surface (Figure 9f). The great enhancement can be attributed to the presence of concave sites with $\langle CN \rangle = 8.3$ rather than the traditional ligand effect, geometric effect, and the increase in the accessible sites. Also, the Pt (111) surface with cavities possesses ORR activity that outperforms many kinds of active alloy and core–shell structures, as shown in Figure 9i. Therefore, it is manipulating surface coordination number that is a promising way to enhance ORR performance, besides the optimization of electronic structure and geometric structure.

4.2. Distorted Pt-Based Catalysts

Based on the generalized coordination number principal, 1D Pt catalysts are expected to accelerate ORR rate because the at $\langle CN \rangle$ junctions of nanowires is higher than the smooth surface (Figure 9c). Huang et al. used the dodecyl dimethyl ammonium bromide (DDAB) as a structure-direct agent to synthesize Pt nanowires with a diameter of about 2 nm. The ultrathin Pt nanowires achieve a factor of 5 enhancement and a factor of 4 enhancement in mass activity and specific activity, respectively, in comparison with commercial Pt/C. Li et al. synthesized ultrathin jagged Pt nanowires by the thermal treatment of NiO@Pt

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**Figure 9.** a) Summary of the predictions of the coordination–activity plot and their relationship to the geometry of Pt sites. Four types of sites exist: flat (111) sites (black); convex sites (red) that are less active than flat sites; concave sites (blue) that are more active than flat sites; and concave sites with steric hindrance (blue cross). Most active sites on various Pt nanostructures. b) “Classical” convex nanoparticle; c) coalescent convex nanoparticle, at the contact of which a concavity is formed; d) cross nanoparticle. Reproduced under the terms of the Creative Commons Attribution 3.0 Unported License. Copyright 2017, The Royal Society of Chemistry. e) Schematics of three approaches used to create defects at Pt (111). Cu atoms appear in red and Pt atoms in gray or black, according to the depth concerning the surface layer. f) Kinetic current densities in O$_2$-saturated 0.1 M HClO$_4$ for defective PtPc (dotted line); Pt(111)(black); dealloyed Cu–Pt(111) SA, (SA) dealloyed (orange); Pt(111) electrodes modified via galvanic displacement, Pt(111)$_{1GD}$ (1 Cu monolayer displaced, green) and Pt(111)$_{5GD}$ (5 monolayers Cu displaced, red); and electrochemical destruction (10 cycles, blue), Pt(111)ED. g) ORR activities for defective Pt(111)$_{ED}$ and other reported catalysts with high activity toward ORR. Reproduced with permission. Copyright 2015, AAAS.
under reduced atmosphere, followed by the electrochemical dealloying in acid solution.\textsuperscript{[104]} Atomic resolution-transmission electron microscopy (TEM) images revealed the highly jagged surface with rich atomic steps on the dealloyed surface in contrast to the relatively smooth surface observed in typical synthetic Pt nanowires, as shown in Figure 10a–c. The jagged nanowires achieved the peak performance among all reported nanocatalysts with the mass activity of 13.6 A mg\textsuperscript{−1} Pt\textsuperscript{2} and the specific activity of 11.5 mA cm\textsuperscript{−2} Pt\textsuperscript{1} (Figure 10d). The presence of highly stressed, undercoordinated rhombus-rich surface configurations led to the enhanced ORR activity on jagged nanowires, revealed by the reactive molecular dynamics simulations. The second metal was also introduced to engineer the electronic structure and geometric structure of highly coordinated sites to further enhance the ORR activity. Bu et al. reported hierarchical Pt–Co nanowires with engineered surface structure by dispersing Pt(acac)\textsubscript{2}, Co(acac)\textsubscript{3}, glucose, and cetyltrimethylammonium chloride (CTAC) into oleylamine at 160 °C for about 8 h.\textsuperscript{[105]} It was also found that the presence of Co(acac)\textsubscript{3} is of vital importance for the formation of a hierarchical structure, as shown in Figure 10e,f. The uneven Pt–Co nanowires enabled remarkable performance for ORR, where the mass activity and specific activity of hierarchical catalysts are 34/40 times higher than commercial Pt/C catalysts, respectively. The unprecedented ORR activity was attributed to the active threefold hollow sites on Pt-rich high-index facets. Luo et al. adopted a similar synthesized strategy to fabricate the zigzag-like PtFe nanowires enclosed by highly uneven surfaces.\textsuperscript{[106]} The scanning transmission electron microscopy image revealed that the high-index facets such as (211) and (311) planes dominated the uneven surface (Figure 10g,h). The zigzag surface endowed catalysts with a mass activity of 2.11 A mg\textsuperscript{−1} Pt\textsuperscript{1} and a specific activity of 4.34 mA cm\textsuperscript{−2} Pt\textsuperscript{2}. Li et al. utilized third metal Rh to stabilize the low-coordinated Pt sites in ultrathin trimetallic nanowires, which was beneficial for the improvement of long-term stability.\textsuperscript{[107]} The uneven multimetallic Pt nanowires exhibited significantly enhanced ORR activity and substantially improved stability compared with the commercial Pt/C catalysts. Maillard and coworkers synthesized four kinds of catalysts with the different atomic arrangements, including solid, hollow, sea sponge PtNi alloys, and Ni@Pt core-shell.\textsuperscript{[108]} Different from the single solid nanoparticles, the sea sponge PtNi alloys are composed of individual nanocrystallites

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**Figure 10.** Representative HRTEM images of the a) Pt/NiO core–shell nanowires, b) PtNi alloy nanowires, and c) jagged Pt nanowires. d) Comparison of specific activities and mass activities of the jagged Pt nanowires, Pt nanowires, and Pt/C catalysts at 0.9 V versus RHE. Reproduced with permission.\textsuperscript{[104]} Copyright 2016, AAAS. e) An atomic resolution HAADF–STEM image of Pt\textsubscript{3}Co nanowires. f) Indexes of the flat planes of the Pt\textsubscript{3}Co nanowires. Reproduced under the terms of the Creative Commons Attribution 4.0 International License.\textsuperscript{[105]} Copyright 2016, Springer Nature. g,h) The HAADF–STEM image of zigzag-like Pt\textsubscript{3}Fe nanowires. Reproduced with permission.\textsuperscript{[106]} Copyright 2018, Wiley-VCH GmbH. i) Relationships between the kinetic current for the ORR and SD for the different kinds of catalysts. j) DFT-derived schematic describing different approaches toward enhanced ORR kinetics: the scattergun approach (SD > 0) versus the homogeneously optimized surface approach (SD = 0) for structurally disordered and structurally ordered catalysts, respectively. Reproduced with permission.\textsuperscript{[109]} Copyright 2018, Springer Nature.
interconnected with each other via grain boundaries, which was demonstrated by the existence of CO stripping peak located between 0.4 V and 0.7 V (vs. reversible hydrogen electrode [RHE]). Also, the sea sponge PtNi alloys exhibited higher values of microstrain revealed by the synchrotron wide-angle X-ray scattering patterns (WAXS), which is due to the deviation of the atoms from their ideal positions due to the presence of structural defects. The sea sponge PtNi alloys composed of aggregated PtNi particles showed about 9.3-fold and 3.3-fold enhancement in ORR specific activity compared with Pt/C and PtNi/C, fully revealing that structural defects could remarkably enhance ORR rates at fixed Ni atom %. The higher ORR activity on structural defects such as the grain boundaries is ascribed to the higher generalized coordination numbers. Chattot et al. pointed out that the microstrain in bimetallic nanocatalysts was ascribed from the surface effect and bulk effect, where the surface effect meant the introduction of grain boundaries and (electro)chemical-treated surface and the bulk effect was the variation of chemical composition. The surface distortion (SD) was proposed as a surface structural parameter to eliminate the bulk effect. Based on SD, the synthesized six catalysts, including sphere, cube, octahedron, hollow, aerogel and sponge, were classified into two branches. The left branch with small or null SD values was composed of monocristalline catalysts with the homogeneously strained and densely packed surface (Figure 10i). The ORR activity was controlled by the affinity for oxygenated species, where the Pt$_2$Ni (111) achieved the highest performance. However, the other branch represented the structurally disordered catalysts where the ORR activity increased with the values of SD (Figure 10i). It was also worth noting that the operating modes on structurally ordered and structurally disordered catalysts were highly different. Structurally disordered catalysts exhibited a wide distribution of catalytic site configurations, and the sites with optimal binding to the ORR intermediates dominated the global reaction rate, as shown in Figure 10j. The structurally ordered catalysts such as Pt–Ni octahedra presented a sharp decrease in ORR activity after ADTs, whereas the structurally disordered catalysts just showed milder ORR activity changes. By analyzing the relationship between the activity of degraded catalysts and the changes of structural parameters, SD rather than lattice parameter and composition controlled the ORR activity in the long term. It was also confirmed that different from the decay of electronic structure and geometric structure, the structural disorder was maintained during the stability test. Our group also prepared highly stable 1D Pt nanowires which exhibited only 17% performance loss. The extreme stability D–O$_2$–Pt nanowires were attributed to the structural effect. Therefore, it is a great promising way for the ORR activity enhancement by promoting initial surface defectiveness in comparison with the surface science-inspired approach, where the inevitable occurrence of surface buckling leads to the degradation of activity.

5. Advanced Pt-Based Catalysts with a Heterostructural Surface

The surface structure of Pt-based catalysts is also modulated through heterostructure to govern reaction pathway, besides the manipulation of order and disorder structure. The heterostructural surface means the interface of Pt–cocatalysts compositions. Zhang et al. used the UPD and followed galvanic displacement to deposit Au submonolayer on Pt nanoparticles supported on carbon. The Au submonolayer transformed into Au clusters by applying several potential sweeps up to 1.2 V. It is of considerable interest that the Au clusters on Pt with decreased electrochemical surface area of one-third exhibited a similar ORR activity to that of Pt. The enhanced specific activity on Au clusters-modified Pt was possible because of the efficient spillover of hydrogen peroxide from Au clusters to the Pt surface, where the hydrogen peroxide was reduced into H$_2$O immediately. Au clusters-modified Pt also exhibited almost unchanged activity in the harsh ADT environment consisting of 30 000 cycles between 0.6 and 1.1 V in oxygen-saturated acid solution, in contrast to significant losses observed with Pt/C under the same conditions. The robust stability on Au cluster-modified Pt was attributed to the enhanced Pt oxidation potential, revealed by in-situ X-ray absorption near-edge spectroscopy. Recently, the role of Au was explored by the deposition of controlled submonolayer on Pt (111) surface. It was found that there was a negligible impact on the ORR activity at Au coverages up to $\theta_{Au} = 0.2$ ML, whereas the higher Au coverage led to a significant decrease in ORR activity. The atomic force microscopy images indicated that the Au atoms with the cover degree lower than 0.2 preferentially deposited at the step-edges sites and spill over onto terraces at higher coverages, as shown in Figure 11a,b. The impact of different Au coverages on the dissolution rates of surface Pt atoms was revealed by the SPRDE–ICP–MS coupling techniques. The SPRDE–ICP–MS measurements showed that the selective blockage of undercoordinated sites by Au atoms, such as $\theta = 0.16$ ML, induced a threefold decrease in Pt dissolution rate in comparison with Pt (111) (Figure 11c). Further increases in Au coverage only lead to a modest decrease in dissolution rate, comprising the activity loss due to the blockage of terraces by excessive Au atoms. Two important findings were found, which were of vital importance for the design of real-world catalysts. The first finding was that the deposited Au atoms tend to neighbor with the undercoordinated Pt atoms, decreasing the Pt dissolution rates. The second one was the definition of threshold surface coverage of Au which limited the dissolution of Pt atoms and did not affect the ORR activity. Further study revealed that the utilization of gold promotes ordering of Pt surface atoms toward a (111) structure, whereas Au on the surface selectively protects low-coordinated Pt sites. Li and coworkers utilized the dealloying process to experimentally fabricate the interface between Pt–Ni alloy and amorphous nickel boride membrane (Figure 11d). The nickel boride membrane worked as an electron acceptor to modify the electronic structure, and heterostructural catalysts showed a 27-times enhancement in mass activity compared with Pt/C for ORR, as shown in Figure 11e. Density functional theory (DFT) calculation demonstrated that the adsorbed BO$_2$ in BO$_3$/Pt hybrid systems led to a weaker binding energy of O$^\circ$, OH$^\circ$ on Pt surface and further accelerated rate-determining step (RDE) of ORR process. The interface between Pt and NiB also resulted in great stability with almost unchanged activity. Except for the deposition of Au cluster to limit the Pt dissolution, Sung and coworkers proposed the ultrathin carbon shell to protect thermodynamically unstable Pt nanoparticles.
The Pt@C core-shell structure with few layers of carbon (Pt@CS/CNT, $T = 600, 700, \text{ and } 900 \, ^\circ\text{C}$) was prepared by heat treating the Pt-aniline complex coating to carbon nanofibers at different temperatures. The Pt@CS/CNT catalysts delivered the similar ORR activity to Pt/C. However, Pt@CS/CNT, especially Pt@CS/CNT900 ^\circ\text{C}, showed considerably enhanced long-term stability, where MEA loading of Pt@CS/CNT900 ^\circ\text{C} exhibited slightly increased current density at 0.6 V after 30 k cycles in comparison with the strikingly decreased current for the MEA loading of Pt/C. The improved stability of Pt@CS/CNT was ascribed to the higher graphitization degree, which protects wrapped Pt nanoparticles from dissolution. The ultrathin carbon-coating strategy also exhibited high validity in alloy, core–shell, and intermetallic systems. PtFe alloys covered by N-doped carbon shell (PtFe@N doped C) were obtained by thermal annealing of polydopamine-coated PtFe nanoparticles,\cite{117} showing high catalytical activity and stability, as shown in Figure 11f–g.

The higher oxidation potential of Pt in PtFe@N-doped C, revealed by in situ XANES, was known as the main reason for the great long-term stability. Recently, carbon shell-protected Pt–M intermetallics were synthesized through heat treating bimetallic compound of [M(bpy)$_3$]$^{2+}$[PtCl$_6$]$^{2-}$ (M = Fe, Co and Ni), which decomposed on carbon surface and formed intermetallic nanoparticles protected by the nitrogen-doped carbon layer.\cite{118}

The protected PtFe intermetallic nanoparticles endowed robust stability and activity, which showed 18 times higher than Pt/C in specific activity for ORR without degradation over stability tests.

### 6. Summary and Perspectives

Manipulating the surface structure of Pt has been confirmed to be a highly effective strategy to improve ORR kinetics. The
surface structure can be roughly classified into order and disor-
der surface. The electronic and geometric environment of Pt atoms at the order and disorder surface also can be modified by the incorporation of cheaper second metals. Various surface-engineered Pt-based catalysts have demonstrated their recorded activity toward ORR. Surface Mo-doped PtNi octahedra achieves the mass activity of 6.98 A mg⁻¹Pt and specific activity of 10.3 mA cm⁻²Pt. Jagged Pt nanowires with the distorted surface exhibited the highest activity at the nanoscale with the mass activity of 13.6 A mg⁻¹Pt and specific activity of 11.5 mA cm⁻²Pt. Therefore, it is a promising way to fabricate highly active and durable Pt-based catalysts by engineering the structural and coordinative environment of surface Pt atoms.

Although significant achievements on Pt-based nanocrystals electrocatalysts have been made, there still are great challenges in the development of promisingly practical catalysts. Several important areas for future research into the development and exploration of next-generation surface-engineered Pt-based catalysts are listed as follows.

A large number of catalysts with the smooth or distorted surface have been demonstrated by their exciting ORR activity, whereas most of the stability behavior and its mechanism is still in debate. Up to now, only a few catalysts degradation mechanism has been studied in detail. The performance loss on Pt/C is mainly because of the dissolution of Pt and Ostwald ripening. Shape-selective Pt-based nanocrystals have been revealed by their poor stability due to the vanishing of morphology. The positive role of Au on stability enhancement is because of preferential blockage of low coordinate sites revealed by the SPRDE–ICP–MS coupling techniques. The main reason for surface Rh-doped PtNi octahedra with high stability is that Rh effectively protects Pt atoms from their migration, confirmed by the HAADF–STEM images at different cycles. The self-healing and self-retaining mechanisms are accountable for the promising stability of P₃ML/Pd/C. Up to now, the mechanism for enhanced stability on most of the catalysts is still unclear. Therefore, it is highly necessary to study the change of morphology, composition, and surface structure in detail during the ADTs.

2) Although catalysts with smooth surface have attracted extensive attention, the focus on the distorted surface catalysts is still relatively rare. For the catalysts with a smooth surface, the incorporation of cheaper metal is the most conventional strategy to modify the electronic structure and geometric structure at the surface. However, the spontaneous outward diffusion of inner cheaper metal inevitably weakens the ligand effect and strain effect, leading to the activity loss. A structurally disordered surface is a promising catalyst because its high activity is determined by the typical types of defects, such as concave site, rather than ligand effect and strain effect. However, the present strategy for the engineering distorted surface is in trial-and-error. The detailed atomic-resolution defect structure with high activity is still unclear. The design principle that how to fabricate structurally disordered catalysts is also ambiguous. The evolution of different defects during ADTs and their effect on activity still have to be solved.

3) Although engineered catalysts have achieved excellent activity and stability at the RDE scale, their performance in MEA is still unclear. Compared with the condition of RDE, the operation environment in MEA is highly complicated. The higher operating temperature such as 80°C, will further accelerate the deactivation of nanocatalysts. In addition, different from the thin-film electrodes at the RDE scale, MEA systems exhibits significant mass transfer resistance at the cathode due to their long-range transportation path. Therefore, high electrochemical surface area and great 3D accessibility have to be considered for the design of practical catalysts in MEA. The catalysts design should also focus on the interaction between catalysts and ionomer. It has been found that the adsorbed ionomers, such as Nafion, strongly poisoned Pt surface and reduced its catalytical activity. In addition, the uniform dispersion of Nafion also is found to significantly enhance the MEA performance by accelerating the transportation of proton and oxygen. Future research should focus on the improvement of activity and stability in MEA systems and optimization of the interaction between catalysts and ionomer by engineering surface/near-surface structure.

In short, although the ORR activity on Pt-based catalysts achieved a significant enhancement through rational modulation of d-band centers and surface environment, the effective descriptor governing the stability of Pt-based catalysts is still in debate. Numerous efforts should be devoted to unraveling the relationship between stability and surface structure of Pt-based catalysts and enhancing the long-term stability. Also, the sophisticated surface engineering strategy is also developed in future research, which is beneficial for understanding the effect of atomic Pt structure on activity and stability. Finally, the actual fuel cell operation conditions, such as high mass transfer resistance, inhomogeneous dispersion of ionomer, and the interaction between Ionomer and active sites, must be considered in the design of next-generation Pt-based catalysts.

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Conflict of Interest
The authors declare no conflict of interest.

Keywords
activity, fuel cells, oxygen reduction reaction, stability, surface structures

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Fanpeng Kong is a post-doctoral at Professor Jiajun Wang’s group at Harbin Institute of Technology. He received Ph.D. in 2019 at the HIT supervised by Professor Geping Yin. He studied at Professor Xueliang (Andy) Sun’s Group (Western University, Canada) as a visiting student in 2018. His current research interest mainly focuses on the design and preparation of single atoms and nanomaterials for oxygen reduction in acid electrolyte.

Jiajun Wang is a professor in School of Chemistry and Chemical Engineering at Harbin Institute of Technology (HIT). He received his Ph.D. in electrochemistry from HIT in 2008. He had been a beamline staff at National Synchrotron Light Source II, Brookhaven National Laboratory. Prior to Joining BNL, he was a postdoctoral fellow in Professor Xueliang Sun’s group at University of Western Ontario. His research interests are developing synchrotron X-ray techniques for electrochemical energy material research.