# Advances of PtRu-Based Electrocatalysts for Methanol Oxidation

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**ABSTRACT** Platinum-Ruthenium (PtRu)-based materials are considered the "holy grail" of electrocatalysts for methanol oxidation reaction (MOR) in the fuel cells technique. However, to the best of our knowledge, the exhaustive review report on the advance of PtRu materials for methanol oxidation is rarely summarized for the recent novel achievements. Herein, we summarize and discuss the latest progress of PtRu-based catalysts in MOR. The reaction mechanism of MOR is firstly introduced, and the promotion mechanism is revealed by the relevant activity descriptor, the in-situ spectroscopic analysis and the theoretical calculation. Subsequently, some advanced regulation strategies of PtRu-based catalysts are concluded, including support engineering, morphology design and surface interface regulation. Finally, the challenges and opportunities to improve the MOR performance of PtRu-based electrocatalysts are prospected to further promote the widespread application of PtRu-based catalysts in electrocatalytic systems. It is concluded that many efforts are still required to decipher the atomic scale structure-activity relationship and the structural changes of atoms and electrons in the reaction process by advanced strategies and characterization methods. Hopefully, this review can be helpful for novel PtRu-based catalyst development and understanding their correlation to the structure and performance of energy-relevant electrocatalysis.

**Keywords:** Pt-Ru based catalysts, electrocatalysis, methanol oxidation reaction, regulation strategies
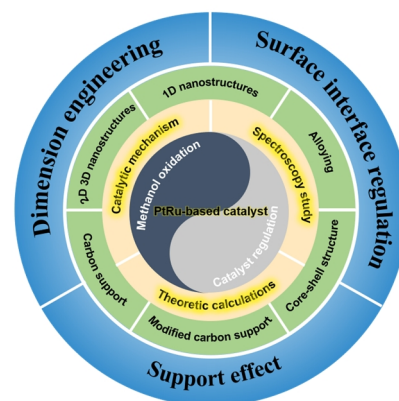
## ■ INTRODUNTION

Platinum-ruthenium (PtRu)-based materials are considered the "holy grail" of electrocatalysts that are widely used in many energy-relevant reactions, especially in fuel cell-related electrocatalysis of methanol oxidation reaction (MOR).[1,2] The unique catalytic ability comes from the synergy effect of PtRu, which can not be realized by other Pt alloys. Because the active sites of Pt catalyst are easily poisoned in the MOR process by the strongly adsorbed CO-like intermediates, and meanwhile, the adsorption of OH species (OH*) is too weak to activate $H_2O$ at low potential for the generation of oxophilic sites for other metals,[3,4] Pt based catalyst can not realize smooth catalytic reaction for MOR compared to the PtRu catalyst.[5-8] Therefore, the development of PtRu-based electrocatalysts has received special attention, and some novel and important advances have been made recently.

Understanding the promotion mechanism of PtRu-based catalysts in electrocatalytic reactions is a prerequisite for the development of high-performance electrocatalysts. The electronic and synergistic effects in Pt-Ru bimetallic metals can effectively improve the anti-CO poisoning ability and adjust the adsorption strength of reaction intermediates.[9,10] To be specific, the addition of oxophilic metal Ru can increase the electron density around Pt and weaken the strength of the bond between Pt and adsorbed CO; as a result, the CO poisoning effect on the Pt surface is reduced.[11] Furthermore, Ru facilitates the dissociation of $H_2O$ at a lower potential to form adsorbed hydroxyl groups (Ru-OH$_{ads}$) which act as oxidants to promote the oxidation of CO adsorbed on the nearby Pt (Pt-CO$_{ads}$).[12,13] At present, many strategies have been used to improve the electrocatalytic activity and stability of PtRu catalysts in MOR. For example, the one-dimensional

PtRu/Cu nanowires showed much higher mass activity in MOR due to the modified d-band center of Pt and weakened binding of Pt and CO intermediates.[14] The PtRu catalyst with interconnected arms is reported active for MOR resulting from its self-supporting porous structure with a high surface area.[15] A highly active PtRu alloy nano-sponge for methanol electrooxidation was proposed, and the Ru-rich $Pt_1Ru_3$ catalyst was found more active by improving the electronic structure of the Pt surface by increased Ru content.[16] It can be seen that the electrocatalytic activity of PtRu-based catalysts can be effectively improved by appropriate metal-support construction, appropriate morphology design, and the surface/interface regulation as well as the electronic structure tuning of the active center.
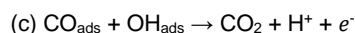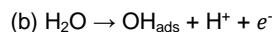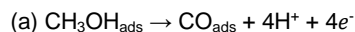
Because of the excellent performance of PtRu-based nanomaterials in the field of electrocatalysis, some discoveries and progress in the early stage have been summarized.[17] For example, a review described the early research results and new fabrication methods of Pt-Ru catalysts and their contributions to the understanding of the functional properties of PtRu-based catalysts.[18] Recent progress in the synthesis and property evaluation of PtRu-based catalysts as anode materials for direct methanol fuel cells and polymer electrolyte fuel cells was reported.[19] Considering the significance of MOR in the energy conversion techniques and the rapid development of PtRu-based catalysts in recent years, herein, the recent progress of PtRu-based nanomaterials as the catalyst for MOR was overviewed. The reaction mechanism of MOR was firstly presented and the promotion mechanism was shown by combining it with the relevant activity descriptor; and their catalytic promotion effect for MOR was also shown based on the spectroscopic characterization and density functional theory (DFT) calculations. The catalytic performance

of PtRu-based catalyst regulation based on some strategies was mainly discussed, which included the support engineering, morphology design, the surface and interface regulation. It is concluded that the rational design and construction of PtRu-based catalysts could enhance MOR activity and stability, while challenges are still faced in terms of accurate control of the atomic/electronic structure of PtRu-based electrocatalysts and deciphering the relationship between structure and activity. We hope this review can be helpful to the scientific community for PtRu-based catalyst development and their catalytic mechanism and promotion understanding.

## n  METHANOL OXIDATION

**Catalytic Mechanism.** Methanol oxidation contains two parallel pathways of the direct and indirect pathways. For the direct pathway, the methanol is directly oxidized to the $CO_2$ without the formation of poisoning intermediates such as CO; and in the indirect pathway, on the contrary, the generation of poisoning species is involved during the catalysis reaction.[20,21] The potential of MOR for the direct and indirect pathways can be defined as $U_{MOR}^d$ and $U_{MOR}^i$, and it is calculated that the potential of the indirect path is equal to or greater than that of the direct path for all surfaces of some transition metals (Figure 1a). The commonly used MOR potential of $U_{MOR}$ corresponds to that of the indirect pathway because the direct pathway only contributes to the current for the surface without CO poisoning.[22] A framework for evaluating MOR was proposed based on two reactivity descriptors: the adsorption free energy of CO* and OH* on the surface.[22,23] Mavrikakis et. al. found that the binding energy of other intermediates is proportional to the binding energy of these two intermediates. Thus, two sets of linear relationships can be established for the states of C-bound species and the O-bound species.[24] Therefore, an excellent catalyst for MOR requires three main capabilities in terms of competitive methanol dehydrogenation, good water activation ability for OH species formation, and the removal of CO* and other intermediates from the surface. By plotting the two surface reactivity descriptors of CO binding energy ($\Delta G_{CO}$) and OH binding energy ($\Delta G_{OH}$) with MOR potential of $U_{MOR}^i$ into a 2 dimension (2D) filled contour map, the minimum MOR potential of $U_{MOR}^i$ = 0.29 V was obtained from the calculation of the volcano plot (Figure 1b). This value matches

well with the thermodynamic barrier for overcoming methanol activation calculated from the free energy of different intermediates on Pt (111) surface.[25] By using $OH_{ads}$ as a model for activating water, the reaction mechanism of a hypothetical indirect pathway can be expressed as follows:

(a) $CH_3OH_{ads} \rightarrow CO_{ads} + 4H^+ + 4e^-$

(b) $H_2O \rightarrow OH_{ads} + H^+ + e^-$

(c) $CO_{ads} + OH_{ads} \rightarrow CO_2 + H^+ + e^-$

When the potentials of the above three processes for a catalyst are equal to each other, the catalyst would be considered as an efficient catalyst, and if the three potentials are equal to zero for a catalyst, it will be an ideal methanol electrooxidation catalyst. Unfortunately, no pure metal surface meets the description of a highly efficient (or ideal) catalyst, but the MOR overpotential can be effectively reduced when catalyzed by the bifunctional structured catalyst, and the PtRu system is the most efficient bimetallic catalyst for methanol oxidation. In the volcano diagram of the bimetallic structure, PtRu alloy lies on the boundary where the potentials of water activation and methanol oxidation to CO are equal to each other (Figure 1c), which is in line with the above description of high-efficiency catalysts, indicating that PtRu has the potential to be a high-efficiency catalyst.

The role of Ru in assisting Pt for MOR is generally interpreted by the classical bi-functional mechanisms,[26,27] which was first proposed by Watanabe and Motoo in the 1970s.[28,29] According to this mechanism, Pt works as the active center for adsorption and dissociation of methanol molecules, and the neighboring Ru contributes to the oxygen-containing species formation at a lower potential that assists the oxidation of the CO-like intermediate. A simple model system consisting of a mixture of hydrated $RuO_xH_y$ and Pt/C catalysts was constructed to investigate the mechanism of CO oxidation and understand the bifunctional catalytic effects.[26] The direct contact between Pt and $RuO_xH_y$ was small but the adjacent $RuO_xH_y$ to Pt significantly promoted the CO oxidation through Langmuir-Hinshelwood and Eley-Rideal mechanisms. The bi-functional catalytic mechanism of PtRu catalyst in methanol oxidation can be expressed as below (Figure 2):[30]
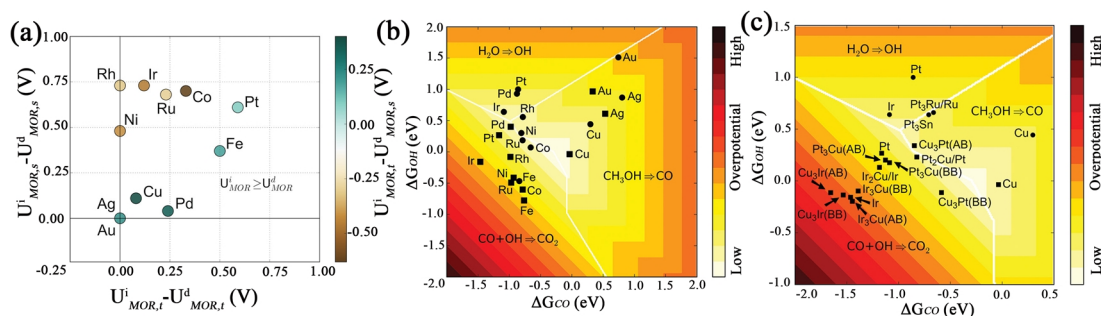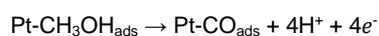
$Pt + CH_3OH_{solution} \rightarrow Pt\text{-}CH_3OH_{ads}$

$Pt\text{-}CH_3OH_{ads} \rightarrow Pt\text{-}CO_{ads} + 4H^+ + 4e^-$



**Figure 1.** (a) Difference between the potential $U_{MOR}^i$ for the indirect and $U_{MOR}^d$ for the direct path for flat (x-axis) vs. stepped surfaces (y-axis). (b) Volcano plot for the indirect path, for stepped surfaces (squares) and flat surfaces (circles). The overpotential minimizes over an area (white) of optimal CO and OH adsorption energies. (c) Volcano plot for the indirect path on stepped (squares) and flat (circles) elemental surfaces and bimetallic alloys. Reproduced with permission from Ref.[22]
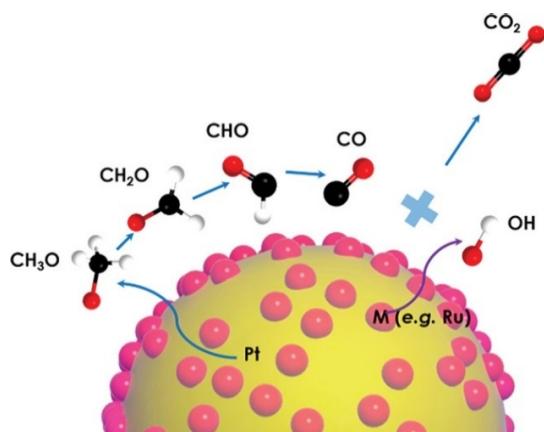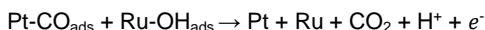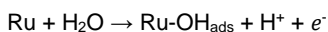
**Figure 2.** A schematic illustration of the bifunctional mechanism of Pt-based catalysts. Reproduced with permission from Ref.[30]

$$Ru + H_2O \rightarrow Ru\text{-}OH_{ads} + H^+ + e^-$$

$$Pt\text{-}CO_{ads} + Ru\text{-}OH_{ads} \rightarrow Pt + Ru + CO_2 + H^+ + e^-$$

**Spectroscopy Study.** Because of the sensitivity of in-situ Fourier transform infrared (FTIR) spectroscopy to the chemical characteristics of the intermediates and products in the electrocatalytic reaction process, it was intensively employed to probe the catalytic intermediate and mechanism for alcohol fuels oxidation.[31,32] The enhanced mechanism of MOR for PtRu alloy catalyst by high-temperature heat treatment was probed by in-situ FTIR spectra for some different samples, in which the PtRu alloy was supported on porous graphitic carbon (PC).[33] PtRu/PC catalyst showed a more negative $CO_{ads}$ potential than Pt/PC, indicating the adsorbed methanol is much easier to dissociate and form $CO_{ads}$. The promotional effect of Ru adatoms on Pt for MOR was further revealed by in-situ FTIR spectroscopy, and a more significant direct methanol oxidation pathway via formic acid was proposed.[34] The spectroscopic analysis showed that the $CO_2$ generation rate of Ru-modified Pt ($\theta_{Ru} = 0.49$) was much higher than that of PtRu/C materials at conditions above 0.15 V. Ramaker analyzed the high oxidation state of Ru on the surface of commercial PtRu alloys by extending the X-ray absorption fine structure (EXAFS), suggesting that $Ru(O)_x$ may be a more efficient ligand than Ru metal.[35] A Ru@Pt nanoparticle model with a submonolayer Ru was used for in-situ X-ray absorption spectroscopy (XAS) surface studies in MOR.[36] It was found that the Ru mainly existed in a metallic state at low potential, and the oxidation state was increased by increasing the potentials. The EXAFS model showed that CO row species was adsorbed on Ru atoms at all potentials and coexisted with OH species on the same Ru atom at potentials of 0.175 V and above. Therefore, the co-adsorption of CO and OH groups on Ru atoms might be crucial during methanol oxidation.

**Theoretic Calculation.** DFT calculation can provide key activity indicators such as Gibbs free energy, band structure and charge analysis to reveal the promotion mechanism of different catalysts in the electrocatalytic process.[37,38] DFT calculation was used to explore the mechanism of CO and OH binding and CO oxidation
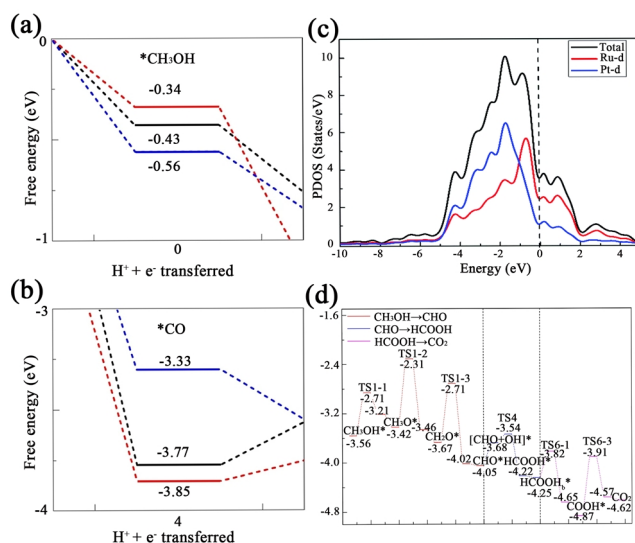


**Figure 3.** (a) Free-energy diagrams for the adsorption of CH₃OH gas and (b) the formation of adsorbed CO on the active sites of the catalysts. Blue, single Pt atom on a Ru(10$\bar{1}$0) surface; red, Pt island on a Ru(10$\bar{1}$0) surface; black, PtRu(111) surface. The * indicates adsorbed species. Reproduced with permission from Ref.[43] (c) Partial density of states of d-orbitals of the total Ru-Pt/boron doped graphene surface, as well as surface Ru and Pt atoms. Reproduced with permission from Ref.[45] (d) The whole PES of methanol reaction on PtRu/Pt(111) (in eV). Reproduced with permission from Ref.[46]

on the surface of various Pt-Ru alloys.[39,40] It was found that the mixing of Ru and Pt weakened the binding of CO and OH to Pt surface sites, and enhanced the binding of CO and OH to Ru surface sites.[41,42] The adsorption free energy of $CH_3OH$ on Ru(10$\bar{1}$0), Pt-island-on-Ru(10$\bar{1}$0) and PtRu(111) were compared, and the most negative value of $CH_3OH$ on single Pt-atom-on-Ru(10$\bar{1}$0) indicated the strongest adsorption ability (Figure 3a), which is the key factor for its high MOR activity.[43] In addition, the CO binding energy on single Pt atoms on Ru(10$\bar{1}$0) surface is the weakest (Figure 3b), indicating that the single-Pt-atom-on-Ru(10$\bar{1}$0) catalyst was resilient to CO poisoning and the active sites were available for MOR catalysis. Theoretical calculation showed that strong $CH_3OH$ adsorption and weak CO binding are two key factors to understand the MOR catalytic activity.

The density of states (DOS) provides the density occupying the electron energy level, and the projected DOS (PDOS) can be obtained by further deconvolution of the total DOS, which is closely related to the electrochemical properties of electrocatalysts.[44] The total d orbitals of the Ru-Pt/boron-doped graphene surface and the d orbitals of Pt and Ru on the surface of Ru-Pt/Boron-doped graphene were studied, and the PDOS is shown in Figure 3c.[45] The wider properties of the d-band implied stronger delocalization on the Ru-Pt/boron-doped graphene surface; the stronger adsorption at the Ru site was indicated by the peak at the Fermi level contributed by Ru atoms, and the increase in the density of some states of Ru atom at the Fermi level meant the highly active state of these sites. The methanol decomposition path on PtRu/Pt(111) was studied by DFT calcu-

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lations,[46] and the oxidation of methanol on PtRu/Pt(111) preferentially took place through the non-CO pathway: $CH_3OH \rightarrow CH_3O \rightarrow CH_2O \rightarrow CHO \rightarrow CHOOH \rightarrow COOH \rightarrow CO_2$ (Figure 3d). It can be seen that Ru modification of Pt can promote the decomposition of methanol rather than desorption, reduce the energy barrier of the non-CO path, and change the rate-determining step from pure Pt oxidation to $CH_3O$ dehydrogenation, leading to improved catalytic activity and CO tolerance catalyzed by PtRu alloy.

## n   PTRU-BASED CATALYSTS REGULATION

The number of active sites and intrinsic activity of catalysts are key factors affecting catalytic activity and selectivity.[47,48] To obtain high-performance PtRu-based electrocatalysts, one approach is to disperse the active metals on suitable supports to increase the active surface area and preferentially obtain the necessary active sites or specific exposed surfaces of the dispersed metals on the catalyst surface.[49,50] Catalysts with well-defined topographical structures, such as nanowires, nanoflowers, nanocubes, etc., can not only efficiently expose and increase the active site but also improve the mass diffusion and charge transfer. Besides, the catalyst design based on the promotion and structural effect is also reported effective for novel catalyst development. Basically, surface-interface engineering for the catalyst can affect the interactions between catalysts and reaction intermediates, thereby the performance can be boosted by optimizing the adsorption and activation energies of catalysts. We here mainly discussed the effort for PtRu-based catalyst development based on the support effect, morphology design, and surface/interface regulation.

**Support Effect.** For the supported catalyst, the support is an important component of catalyst that not only provides high dispersion and anchoring of noble metal active sites but also improves the stability and conductivity of active components. Moreover, the support will also bring some additional combined advantages to reactant and product diffusion in the catalytic layer.[51-53] In addition, some supports can play the role of a promoter in the system that can adjust the electronic structure of active metals, optimize the bonding strength of active sites and reaction intermediates, and significantly improve the catalytic performance.[54,55] Therefore, effectively optimizing the catalyst support should be carefully considered when developing novel catalysts. Actually, to increase the dispersion and the active surface area of the catalyst, most catalyst systems involve carbon support, and the support can be classified into carbon support and the carbon support modified by other components. In the following section, considering the amounts of the publication in the literature, we mainly discussed the support based on the carbon materials and the carbon modified by a metal oxide or metal phosphide.

**Carbon Support.** Carbon material has been used as catalyst support for more than 100 years because of its advantages like the low cost and high conductivity, excellent corrosion resistance, controllable shape and stable structure.[56] The carbon-supported metal catalysts are widely used in reactions involving noble metals as the large specific surface area of carbon can effectively disperse the active site and increase the available surface area. As early as 1965, Hillenbrand and Lacksonen demonstrated the important electronic interaction between Pt and carbon surface that largely improved the anti-CO poisoning ability of Pt.[57] The carbon support strongly influences the electrocatalyst properties such as metal particle size, metal dispersion, morphology and stability, and it also affects the performance of the whole catalyst system such as mass transport, electrochemical active area and stability during the operation. Various nanostructured carbon materials from carbon black to carbon graphene have been developed. The traditional carbon black and activated carbon have been intensively employed as support because of the high porosity properties, while some problems are encountered such as thermochemical instability and corrosion in electrocatalytic applications;[58] the carbon materials of carbon nanotubes and graphene have attracted more and more attention recently due to their well-defined geometry and excellent mechanical properties.[59-61] As a popular choice of support, the different physical forms and shapes of carbon have been developed to suit the different conditions like the strong acid and alkali resistance; furthermore, the surface modification of the carbon support can improve the surface property by enhancing metal adsorption and catalyst dispersion. Therefore largely improved catalytic performance can also be realized.[62,63]

Carbon black as one of the most popular commercial carbon supports has been intensively used to support noble metals, and the family members of Vulcan XC-72, Black Pearl 2000, Denka Black, Ketjen EC-300J, etc have been reported in the literature.[64] A comparison of several types of carbon black such as Vulcan XC-72R, Ketjen Black EC 300J, and Black Pearls 2000 as additives/support for the Pt catalyst was done, demonstrating the Ketjen Black EC 300J was the most useful support for increasing the electrochemical surface area.[65] The carbon support modification and novel fabrication approaches for the supported PtRu catalyst have been done, while note that the commercial carbon black was still used especially for the comparison with the newly developed catalyst. A glyoxylate reduction approach provided a favorable deposition and high dispersion of Pt-Ru nanoparticles (ca. 3.3 nm) on Vulcan XC-72R carbon support due to the effective interaction of the metal precursor ions and the surface anchoring sites in alkaline aqueous solution.[66] The high dispersion and the increased active sites of the advantageous Pt(0)/Ru concentration ratio led to the high mass activity for methanol oxidation. The carbon black of Vulcan XC-72R functionalized by $H_2O_2$ and $HNO_3$ was employed to support PtRu, and they showed much better performance for methanol oxidation than those obtained by the commercial one.[67]

The carbon nanotube is one of the main carbon materials as support due to its high degree of graphitization, unique tubular structure and strong metal-support interaction;[68,69] it can be divided into single-walled carbon nanotubes (SWCNTs), double-walled carbon nanotubes (DWCNTs) and multi-walled carbon nanotubes (MWCNTs) according to the number of layers. The SWCNTs are an allotrope of $sp^2$ hybridized carbon assembled as cylindrical tubes including six-membered carbon rings similar to graphite, and the diameter of SWCNT differs from 0.4 to 2 or 3
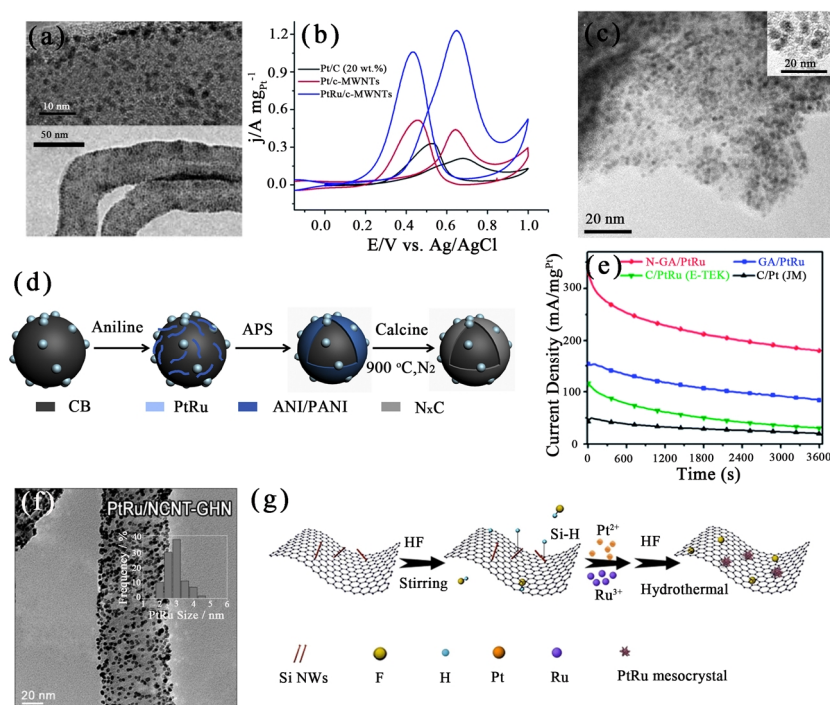
**Figure 4.** (a) Transmission electron microscopy (TEM) images of PtRu/CNTs-PIL. Reproduced with permission from Ref.[74] (b) CVs of Pt-Ru/c-MWNT, Pt/c-MWNT and commercial Pt/C (20 wt%) catalysts in $N_2$-sparged 0.5 M $H_2SO_4$ solution containing 0.5 M methanol at a scan rate of 50 mV s$^{-1}$. Reproduced with permission from Ref.[75] (c) TEM images of PtRu/PMo$_{12}$-graphene catalysts. Reproduced with permission from Ref.[86] (d) Synthetic routine of PtRu/CB@N$_x$C electrocatalyst. Reproduced with permission from Ref.[92] (e) Chronoamperometric curves of different samples in an aqueous solution containing 0.5 M $H_2SO_4$ and 0.5 M $CH_3OH$ at an applied potential of 0.4 V. Reproduced with permission from Ref.[93] (f) Well-dispersed PtRu nanoparticles on NCNT-GHN. Reproduced with permission from Ref.[94] (g) Schematic illustration of the catalyst fabrication process. Reproduced with permission from Ref.[97]

nm with the length in the micrometer range;[70-72] double-walled carbon nanotube consists of exactly two concentric carbon nanotubes. Compared to SWCNTs, DWCNTs have much higher mechanical strength and thermal stability. The MWCNTs consist of several tubes in concentric cylinders varying from 6 to 25 or more, and the diameter of MWCNTs can be as high as 30 nm. Pt-Ru catalysts supported on SWCNTs, DWCNTs and MWCNTs were prepared by the ethylene glycol reduction method, and the best catalytic activity with 2.17 times the current density of that of Pt-Ru/C was observed on the double-walled carbon nanotube supported Pt-Ru catalyst due to the larger surface area and better conductivity.[73] PtRu nanoparticles loaded on the carbon nanotubes functionalized by ionic-liquid polymer were found to have good dispersity and narrow size distribution with an average diameter of about 1.3 nm (Figure 4a), which showed the catalytic activity for MOR of 2.32 times higher than that of pristine PtRu/CNTs.[74] The PtRu nanoparticles supported on carboxylate-functionalized multi-walled carbon nanotubes were prepared by ultrasonic-assisted synthesis method that showed excellent performance for MOR of 5.77 times higher than that of commercial Pt/C catalyst (Figure 4b).[75] After 500 cyclic voltam-mograms (CVs) cycles, the forward peak current density of the Pt-Ru/c-MWNT catalyst is 83.7% of the initial value, which is much higher than 39.7% of the commercial Pt/C. PtRu nanopar-

ticles uniformly distributed on CNTs were prepared by the modified impregnation method, effectively preventing the aggregation of PtRu nanoparticles, and the obtained Pt-Ru/CNTs catalyst showed the current density of 1.4 times that of the commercial Pt-Ru/C for MOR.[76]

Graphene as a two-dimensional carbon (2-D) form has a one-atom-thick planar flat sheet with a thickness of 0.34 nm consisting of sp$^2$ bonded carbon atoms packed in a regular atomic-scale chicken wire (hexagonal) pattern.[77,78] Its theoretical specific surface area can be as high as 2630 m$^2$ g$^{-1}$, much higher than that of carbon black (lower than 900 m$^2$ g$^{-1}$) and carbon nanotubes (100 to 1000 m$^2$ g$^{-1}$).[79] The high surface area of graphene, especially for the functionalized graphene, makes it very promising as metal support for better catalyst dispersion and high conductivity.[80-83] Graphene-supported PtRu nanoparticles were evaluated for MOR compared with the PtRu supported on Vulcan XC-72R carbon black, and much higher methanol oxidation efficiency was observed due to its excellent electrical conductivity and large surface area.[84] PtRu/graphene with good dispersion and high electrochemical active surface area (ECSA), which showed the catalytic performance for MOR of 4.17 times higher than that of commercial Pt/C catalysts can be prepared by uniformly anchoring small PtRu nanoparticles onto graphene sheets via a simple one-step reduction method without surfac-

tant.[85] The PtRu catalysts supported on $PMo_{12}$-functionalized graphene nanosheets were prepared by microwave irradiation in ethylene glycol solution and the self-assembly and negatively charged properties of the $PMo_{12}$ monolayer improved the dispersion and stability of the supported PtRu nanoparticles (Figure 4c).[86] The as-prepared catalyst exhibited much higher methanol oxidation activity and better cycle stability compared to unmodified PtRu/graphene catalysts.

Carbon support modification by hetero-atom is an effective strategy to endow it with good supporting properties; as a result, the physicochemical properties of electrical conductivity and hydrophilicity can be changed resulting in structural deformation and charge density changes.[87-90] N-doping is commonly employed to modify the carbon support, and the high electron density induced by the insertion of nitrogen would enhance and improve the catalytic ability.[91] PtRu alloyed nanoparticles decorated by nitrogen-doped carbon ($N_xC$) were prepared by carburization of in-situ polymerized polyaniline over the surface of PtRu/C (Figure 4d); the aniline monomer was polymerized over the carbon surface via preferential π-π conjugation, and partially oxidized Ru was formed by partial electrons donation from Ru driven by nitrogen atoms;[92] Much higher CO tolerance ability was demonstrated compared to other PtRu based catalyst, and $N_xC$ protected PtRu catalyst showed good catalytic stability. About 10% of active sites was lost after the stability test by the potential sweeping from 0.6 to 1.0 V vs. RHE, much better than that of bare PtRu electrocatalyst (50%) due to the suppression of Ru dissolution and Pt nanoparticles migration/coalescence protected by $N_xC$. PtRu nanoparticles uniformly distributed over the porous three-dimensional N-doped graphene aerogel (N-GA) support were fabricated by a rapid microwave reduction methanol.[93] Compared with PtRu/GA and PtRu/C, PtRu/N-GA exhibited much better CO tolerance and stability in acidic methanol oxidation (Figure 4e). A hierarchical N-doped carbon nanotube-graphene hybrid nanostructure (NCNT-GHN) was fabricated to support the PtRu nanoparticles (Figure 4f) because of the high electron affinity of nitrogen by activating the carbon atoms nearby. The conductivity and metal anchoring ability were improved, which promoted the dispersion of PtRu nanoparticles and catalytic performance for methanol oxidation.[94]

In addition to element N, other elements such as B, P, and F have also been studied as dopants for carbon support.[95-97] There is a synergistic effect and strong interaction between doped atoms and metals, and the stability of the supporting structure is improved.[98,99] Meanwhile, more sufficient OH adsorbed species can be generated to improve MOR activity.[100,101] The current density of MOR catalyzed by PtRu supported on the P-doped carbon prepared by heat-treating commercial carbon with $H_3PO_4$ was about twice that of PtRu/C because of the reduction of average particle size and/or the more active Pt and Ru species resulting from metal-support interactions.[96] PtRu nanocatalysts supported on F-doped graphene were synthesized by the wet chemical method.[97] During fabrication, silicon nanowires and hydrofluoric acid were used to form Si-H bonds that acted as reducing agents to reduce Pt and Ru ions and form PtRu on reduced graphene oxide (rGO) (Figure 4g). The catalytic

activity for MOR of PtRu/rGO catalyst is 2.2 times higher than that of commercial Pt/C catalyst due to the F doping and flower-like mesogenic structure in graphene. In addition, the current retention rate of PtRu/rGO is much higher than that of Pt/C catalyst after 4000 s chronoamperometry (CA) test and 500 cycles of accelerated decay test, indicating its excellent durability.

## Hybrid Support

**Metal Oxide-based Support.** Metal oxides have been introduced into the carbon support to further increase the catalytic performance due to their abundant resources and low cost.[102,103] The use of metal oxides could also prevent the agglomeration of metal particles due to the strong interaction between metal oxides and precious metals.[104] Moreover, metal oxides can provide a large number of $OH_{ads}$ species, and modify the electronic states of precious metals to improve the electrocatalytic performance of MOR through a bifunctional mechanism.[105-107] Titanium oxides are potential supports for catalysts due to their good stability in the fuel cell operation environment, low cost, and commercial availability.[108-110] The strong interaction between titanium oxide and metal nanoparticles can avoid the agglomeration of metal particles and change the electronic properties of metal nanocatalysts.[111] A double-shell PtRu catalyst supported on $TiO_2$ was synthesized by the microwave-assisted method,[112] and the enhanced methanol electrooxidation activity observed showed the peak current density of twice that of commercial Pt/C (Figure 5a). The composition of metal oxides can be changed to further improve the MOR performance of the catalyst.[113] When $TiO_2$ was doped by Nb, the charge compensation for $Nb^{5+}$ substituting $Ti^{4+}$ was realized either by the creation of one Ti cation vacancy per four Nb atoms or by the stoichiometric reduction of $Ti^{4+}$ to $Ti^{3+}$.[102] The Nb-doped $TiO_2$ as PtRu catalyst support showed the catalytic activity comparable to that of commercial PtRu/C in MOR benefiting from the enhanced conductivity after Nb doping.[114] Conformal ultrathin $TiO_2$ films deposited on oxygen-functionalized N-doped carbon nanotubes (ONCNT) were used to support PtRu nanoparticles.[115] Enhanced CO oxidation kinetics and MOR activity of the catalyst were observed and the mass activity and long-cycle stability were superior to that of commercial PtRu/C catalysts due to the continuous electron conduction network, and the increased hydroxyl groups provided by the ultrathin defect hydrogenated $TiO_2$ coating on ONCNT (Figure 5b).

$SnO_2$ has been intensively employed as catalyst support for fuel cells catalyst fabrication.[116,117] It is an n-type semiconductor with high conductivity and good corrosion resistance in acidic media, and the hydroxyl groups generated on the surface of $SnO_2$ can inhibit the CO poisoning effect according to a bifunctional mechanism. The chemically modified CNTs covered by $SnO_2$ shell were used to support the PtRu alloy nanoparticles by a hydrothermal method (Figure 5c).[118] It is found that $SnO_2$ could promote the formation of reactive OH species from water, and then enhance the CO poisoning tolerance ability; in addition, the homogeneous and porous $SnO_2$ layer over CNT could enhance the catalyst and fuel interaction; As a result, a lower onset potential and much higher mass activity for methanol oxidation were observed compared with PtRu/CNT catalyst. The interaction

among different elements in the PtRu/SnO$_2$/C catalyst was probed by reduction treatment in H$_2$ at 300 °C followed by alkaline etching to engineer the surface structure and composition (Figure 5d).[119] PtRu-enriched surface with SnO$_2$-riched core was formed, and compared with other catalysts, this catalyst showed much higher activity for CO and methanol electro-oxidation due to the enriched PtRu surface and the enhanced interactions between the surface PtRu and SnO$_2$ beneath.

Some other metal oxides like tungsten oxide,[120] molybdenum oxide,[121,122] cerium oxide,[123] etc. have also been studied as the catalyst support promoter of PtRu for MOR. Similarly, these metal oxides are also beneficial to the oxygen-containing species formation at a lower potential, which could promote the anti-poisoning ability of the PtRu active phase for MOR. Three-dimensionally ordered macroporous WO$_x$ with a large specific surface area was used as the support for anchoring PtRu nanoparticles.[124] Due to the effective interface formation between PtRu and WO$_x$, the initial potential and peak potentials of CO$_{ads}$ electrooxidation for PtRu/WO$_x$ catalyst were more negative compared with that for PtRu catalyst; and effectively improved MOR performance was observed due to the high anti-CO poisoning ability (Figure 5e). Carbon-CeO$_2$ composite nanofibers (C-CeO$_2$)NF fabricated by electrospinning were used as a support for PtRu nanoparticles, and the parameters of the catalyst loading and the Nafion content in the catalyst layer were optimized for MOR.[125] Under optimum conditions, the catalyst showed a three times higher mass activity for the methanol oxidation than that of the commercial PtRu/C catalyst due to the

addition of CeO$_2$ into the catalyst layer (Figure 5f). A similar case was reported for carbon-supported PtRu-MoO$_x$ nanoparticles prepared by the impregnation-sol two-step method.[122] Although some metal oxides have been introduced into the PtRu catalyst system for MOR, improved performance was observed due to the ligand effect and the electronic effect.[126,127] However, the low charge transfer ability, low surface area, and low stability accompanied by the metal oxides should be carefully considered for the novel catalyst design and fabrication.

**Transition Metal Phosphide Based Support.** Transition metal phosphide (TMP) was reported efficient in assisting PtRu active phase for MOR. The strong electron-rich surface of TMP can optimize the atomic and electronic structures of the catalyst surface and improve the active site density and electrical conductivity.[128,129] The strong coupling between TMP and noble metals can reduce the noble metal dissolution and agglomeration, and the good water activation ability can produce more OH$_{ads}$ and accelerate the removal of poisoning intermediates.[130,131] Until now, TMPs of CoP, Ni$_2$P, and FeP have been reported as supports for MOR electrocatalyst fabrication.[132,133] The synergistic effect between CoP and PtRu was reported to largely increase the stability and resistance to CO poisoning of PtRu catalysts.[134] The electronic structure of metal nanoparticles was regulated by the metal-support interaction that weakened the binding of Pt to the poisoning intermediates (Figure 6a). As a result, the largely improved catalytic performance for MOR was observed; specifically, the peak current of PtRu-CoP/C was 670.5 mA mg$^{-1}$$_{PtRu}$, about 2.89 times that of the commercial PtRu/C-JM (231.9 mA
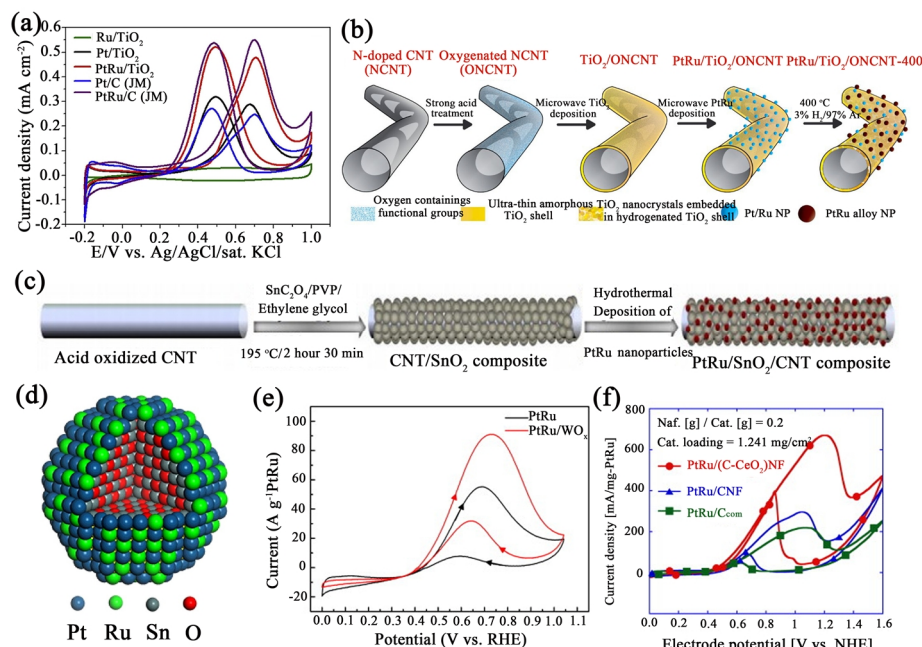


**Figure 5.** (a) The CVs of different catalysts in 0.5 M H$_2$SO$_4$ containing 0.5 M methanol at a scan rate of 50 mV s$^{-1}$. Reproduced with permission from Ref.[97] (b) Synthesis process for PtRu/TiO$_2$/ONCNT-400. Reproduced with permission from Ref.[115] (c) Schematic diagram of the formation of catalyst supported on CNT/SnO$_2$ composite. Reproduced with permission from Ref.[118] (d) Structural model of PtRu/SnO$_2$/C catalyst. Reproduced with permission from Ref.[119] (e) Cyclic voltammograms of methanol electro-oxidation on PtRu/WO$_x$ and PtRu catalysts in 0.1 M HClO$_4$ + 0.5 M CH$_3$OH at 25 °C. Scan rate: 20 mV s$^{-1}$. Reproduced with permission from Ref.[124] (f) MOR activity of the PtRu/(C-CeO$_2$)NF, PtRu/CNF and PtRu/C catalysts. Reproduced with permission from Ref.[125]

mg$^{-1}_{PtRu}$) and 3.86 times that of the home-made reference (PtRu/C-H) catalyst (173.6 mA mg$^{-1}_{PtRu}$) (Figure 6b). The catalytic stability was evaluated by the CA technique, and after 2 h measurements, the initial current retention of the PtRu-CoP/C catalyst was 1.28 times that of PtRu-JM. Furthermore, the highest maximum current density of 85.7 mW cm$^{-2}$ was obtained at 30 °C, much higher than that of the commercial PtRu/C catalyst of 63.1 mW cm$^{-2}$ at 70 °C (Figure 6c). A similar report of PtRu-Ni$_2$P/C catalysts prepared by anchoring PtRu nanoparticles to Ni$_2$P/C support was also reported.[135] In addition, a core-shell structured PtRu catalyst system with the PtRu as shell and FeP as the core was reported to show excellent catalytic performance for MOR.[136] This catalyst system showed efficient ligand effects and electronic effects resulting from the noble metal active sites and adjacent promoters in the core-shell structure (Figure 6d). High anti-CO poisoning ability was found due to the facile formation of oxygen-containing species and the electronic effects when compared with the case of the benchmark commercial PtRu/C catalyst, which was 110 and 60 mV less for the peak and onset potentials for CO oxidation (Figure 6e). Much higher catalytic activity and stability were also obtained where the peak current density was about 3 times higher than that of the commercial PtRu/C catalyst and home-made PtRu/C for MOR (Figure 6f), and excellent catalytic stability was demonstrated by 1000 cycles of cyclic voltammetry measurements. It can be concluded that the transition metal phosphide introduced in the hybrid support could largely promote the catalytic performance of PtRu active phase, while the relevant research was still rare; the promotion effect mechanism and the relationship between structure and performance were still not touched in the previous reports. Hopefully, more efforts can be done in the future to develop more catalyst systems and decipher their catalysis promotion effect.

**Dimension Engineering.** The morphology of the catalysts also largely influences their catalytic performance because the exposed surface area and active sites are different for the catalysts with different morphologies. Therefore, proper morphology design is an effective approach to enhance the catalyst activity and stability of catalysts.[137-140] The well-designed morphology can effectively expose the active sites on the catalyst surface and promote electron and mass transport.[50,141-143] In this sub-section, the PtRu-based catalysts for MOR classified by the dimensions like 1D, 2D and 3D were selectively summarized and discussed.

1D nanostructures, such as nanowires (NWs) and nanotubes (NTs), show many unique properties like anisotropic structures with fewer lattice boundaries and faster electron and mass transfer; the unique size combination of 1D structure at multiple length scales enables it to have a high surface area and avoid the problem of carbon corrosion; the large scale of 1D structure makes it reduce the dissolution of precious metals and avoid the agglomeration of nanoparticles during the electrochemical reaction.[144] As the most common 1D nanostructures, PtRu-based nanowires with different compositions were prepared by the electrospinning method.[145] Benefiting from the efficient charge transport and better physical and interfacial properties arising from the one-dimensional features, the Pt$_1$Ru$_1$ nanowires with the best atomic ratio showed a performance of 1.3 times higher than that of the Pt$_1$Ru$_1$/C catalyst for MOR. In addition, the template-assisted synthesis approach is an effective method to prepare 1D nanostructures.[146] Using copper nanowires (NWs) as a template, PtRu coated copper NWs were synthesized by galvanic replacement reaction;[14] the 1D morphology of PtRu/Cu NW showed the highest methanol oxidation activity with a peak
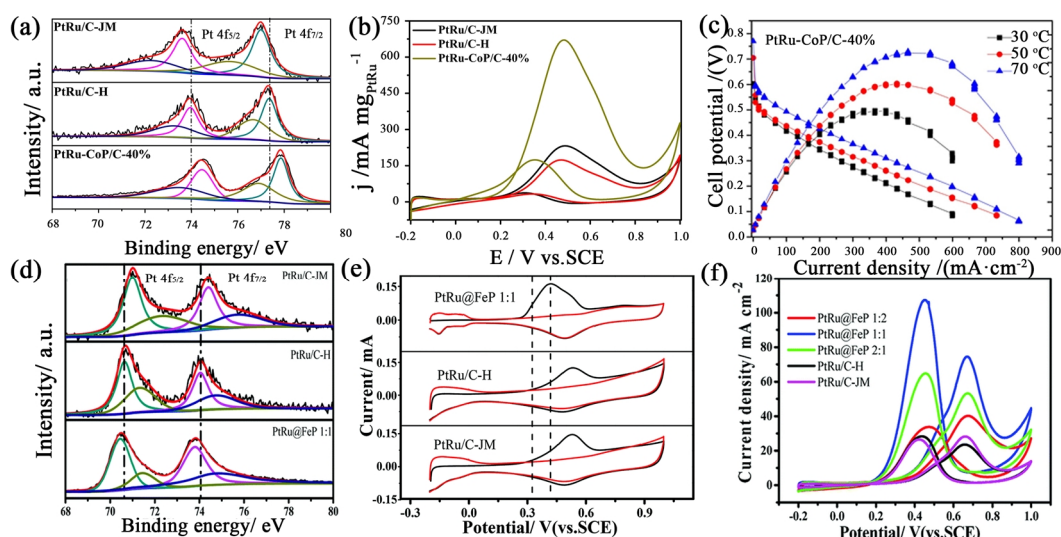


**Figure 6.** (a) X-ray photoelectron spectroscopy (XPS) patterns of PtRu/C-JM, PtRu/C-H and PtRu-CoP/C-40% for Pt 4f binding energy. (b) The electro-catalytic performance of PtRu/C-JM, PtRu/C-H and PtRu-CoP/C-40% catalysts for methanol electrooxidation in 0.5 M H$_2$SO$_4$ + 1.0 M CH$_3$OH at 50 mV s$^{-1}$. (c) Steady-state polarization, and power-density curves for fuel cells employing PtRu-CoP/C-40%. Reproduced with permission from Ref.[134] (d) XPS spectra of the Pt 4f region for the PtRu/C-JM, PtRu/C-H and PtRu@FeP 1:1 catalyst. (e) CO$_{ads}$ stripping voltammograms of PtRu@FeP 1:1, PtRu/C-H and PtRu/C-JM catalysts in 0.5 M H$_2$SO$_4$ solution at a scan rate of 20 mV s$^{-1}$. (f) The electrocatalytic performance of all the catalysts for methanol electro-oxidation in 0.5 M H$_2$SO$_4$ + 1 M CH$_3$OH solution at a scan rate of 50 mV s$^{-1}$. Reproduced with permission from Ref.[136]
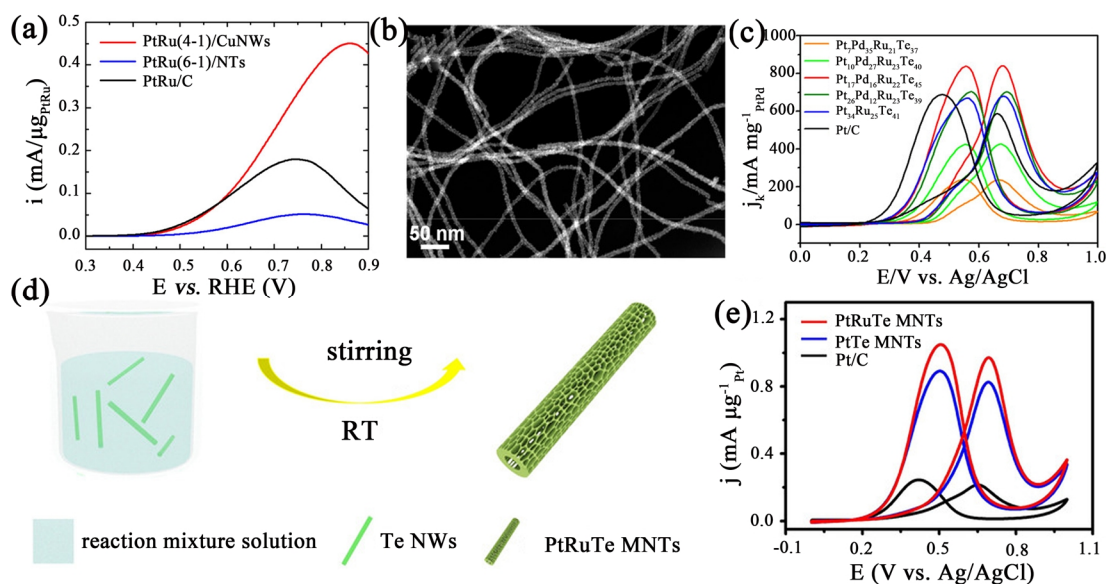
**Figure 7.** (a) Cyclic voltammogram (forward scan) of PtRu(4-1)/CuNWs, PtRu(6-1)NTs, and PtRu/C in terms of mass activity. Reproduced with permission from Ref.[14] (b) HAADF/STEM images of the $Pt_{17}Pd_{16}Ru_{22}Te_{45}$ NTs. (c) CV curves of PtPdRuTe NTs, PtRuTe NTs, and Pt/C catalysts for the MOR in 0.5 M $H_2SO_4$ + 1.0 M methanol solution at a sweep rate of 50 mV s$^{-1}$. Reproduced with permission from Ref.[147] (d) Schematic illustration of the fabrication of the PtRuTe MNTs and (e) mass-normalized CV curves of different catalysts in 0.5 M $H_2SO_4$ with 1 M $CH_3OH$ at a scan rate of 50 mV s$^{-1}$. Reproduced with permission from Ref.[148]

current density of 1.6 mA cm$^{-2}_{PtRu}$, which is 5.5 times that of PtRu/C due to the increased ECSA and improved charge transfer capability (Figure 7a). By normalizing the current in the CA curve to the initial current, the PtRu/Cu NW catalyst showed a higher current for PtRu/C after the 1800 s test, indicating its excellent stability. PtPdRuTe nanotubes (NTs) with different compositions and controllable shapes were prepared using ultrathin Te NWs as sacrificial templates (Figure 7b);[147] by adjusting the composition of the catalyst, the $Pt_{17}Pd_{16}Ru_{22}Te_{45}$ NTs showed much higher mass activity than Pt/C catalyst in methanol oxidation due to the hollow one-dimensional structure and the synergistic effect between the components (Figure 7c). In addition, ternary PtRuTe mesoporous nanotubes (PtRuTe MNTs) were prepared using ultra-long Te NWs and F127 triblock copolymers as self-sacrificing templates and soft film plates, respectively (Figure 7d).[148] The high surface area and fast mass transfer rate induced by the mesoporous surface and hollow interior make this catalyst have good activity and stability for MOR; specifically, the specific activity is 3.71 times that of Pt/C catalyst (Figure 7e).

2D nanostructures, such as nanosheets (NS) and nanodendrites, have some new advantages including the high electron mobility, high aspect ratio, high surface area, and abundantly exposed active sites, which makes them ideal for surface-active applications such as MOR.[149] The high aspect ratio, high surface area and a large number of exposed active sites can effectively improve the utilization rate of precious metals of MOR catalyst, and significantly improve the electrocatalytic performance of MOR catalyst. Therefore, the advantages of two-dimensional nanomaterials can effectively improve the catalytic activity of the PtRu-based catalyst.[150,151] The controllable syn-

thesis of PtRu nanodendrites was done by the co-reduction of Pt and Ru precursors in oleylamine with $H_2$ gas.[15] The PtRu nanocrystals with well-defined branching morphology have a high surface area and self-supported porous structure; and excellent catalytic activity and durability in MOR were demonstrated with the forward current density of 4 times higher than that of commercial Pt/C catalysts (Figure 8a). An ultrathin PtRuNi-O nanosheet with a diameter of about 6.2 nm was reported to have good methanol oxidation activity.[152] The optimized catalyst of $Pt_7RuNi_2$-O NS showed the highest methanol oxidation mass activity of 3.57 A mg$_{Pt}^{-1}$, which was 10.5 times as high as that of the commercial Pt/C catalyst (0.34 A mg$_{Pt}^{-1}$) (Figure 8b). In addition, by comparing the CV curves after 1000 cycles, the mass activity of $Pt_7RuNi_2$-O NS catalyst was decreased by only 8.1% compared with the initial value, indicating good stability of the $Pt_7RuNi_2$-O NS catalyst.

The complex structures of 3D nanostructures make them have unique physical and chemical properties;[153,154] the common 3D nanostructures mainly include nanocages, nanoframes, nanoflowers, nanospheres, etc., and they tend to be a hollow and porous structure with more exposed surfaces and active sites for catalysis reaction.[155,156] The large specific surface area of 3D structure can effectively avoid the aggregation of noble metal particles, which helps improve the catalytic performance of the catalyst. The porous or mesoporous structure brings about rapid charge transfer and contributes to the improved electrocatalytic reaction kinetics. The tunable hollow Pt@Ru dodecahedrons were fabricated for MOR by controlling the precursor concentration via a galvanic replacement method.[12] Employing the Pt as the skeleton of the dodecahedron, Ru was deposited over the
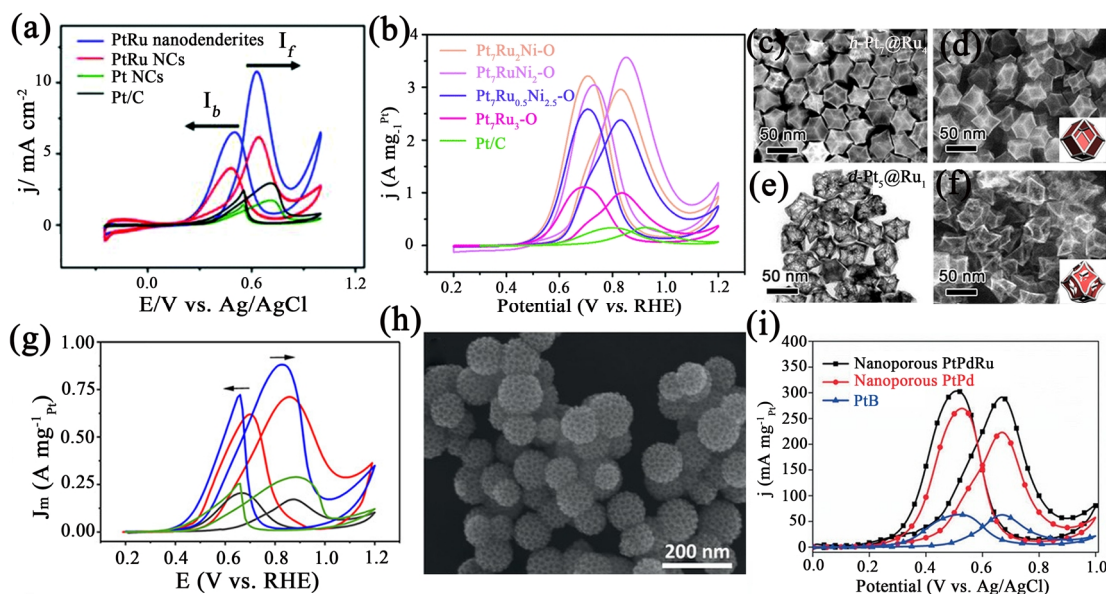
**Figure 8.** (a) CVs of the catalysts measured in $N_2$-saturated 0.1 M $HClO_4$ in the presence of 1 M $CH_3OH$ at a scan rate of 50 mV s$^{-1}$. Reproduced with permission from Ref.[15] (b) Mass activity curves of different catalysts in $N_2$-saturated 0.5 M sulfuric acid and 0.5 M methanol. Reproduced with permission from Ref.[152] (c) TEM dark-field image and (d) scanning electron microscopy (SEM) image of h-Pt@Ru. (e) TEM bright-field image and (f) SEM image of d-Pt@Ru. The insets show the corresponding structure models. (g) CV curves of methanol oxidation at 20 mV s$^{-1}$ in 0.5 M $H_2SO_4$ with 1.0 M $CH_3OH$. Reproduced with permission from Ref.[12] (h) Low magnification SEM image of trimetallic mesoporous PtPdRu spheres. (i) Cyclic voltammograms for methanol oxidation reactions catalyzed by different catalysts. Reproduced with permission from Ref.[158]

surface along the edge of Pt, forming a deformed hollow Pt@Ru (d-Pt@Ru) dodecahedron and hollow Pt@Ru (h-Pt@Ru) dodecahedron (Figure 8c-f). The two hollow Pt@Ru dodecahedrons exhibited much better methanol electrooxidation activity and stability than PtRu NPs and commercial Pt/C catalysts resulting from the hollow dodecahedral structure with optimal spatial element distribution (Figure 8g). Dendritic PtRuNi nanoframes were synthesized by a simple two-step co-reduction-leaching process, and the mass activity of PtRuNi FDs catalyst for MOR could reach up to 1.49 A mg$_{Pt}^{-1}$, about 2.9 times that of commercial Pt/C catalysts due to the unique three-dimensional open structure and suitable composition.[157] By comparing the peak current density of the catalysts at the initial stage and after 1000 cycles, the current retention of PtRuNi FDs is 78.5%, which is much higher than that of Pt/C catalysts of 58.5%, indicating its excellent durability performance. In addition, using ascorbic acid as a reducing agent and triblock copolymer F127 as a pore directing agent,[158] mesoporous trimetallic PtPdRu spheres were synthesized with well-defined spherical morphology and uniformly sized pores (Figure 8h). The MOR catalytic performance expressed by mass activity was about 4.9 times that of commercial platinum black catalysts resulting from the well-defined 3D spherical shape and homogeneous mesoporous structure (Figure 8i). In addition, due to the low aggregation of mesoporous structure, the mesoporous trimetallic PtPdRu sphere exhibits slow current attenuation in the stability test.

**Surface Interfaces Regulation.** The surface/interface of the catalyst is highly related to the electrocatalytic performance because the surface-interface structure can affect the interaction between the catalyst and the reaction intermediates, thereby optimizing the adsorption and activation energies of the catalyst.[159] Effective design and regulation of the surface interface of the catalyst can effectively improve the reactivity and catalytic performance of the catalyst. Here, we summarize and discuss the commonly used approaches to design and optimize the surface and interface of PtRu-based catalysts including alloying and core-shell structures in MOR.

**Alloying.** Alloying can effectively modulate the electronic structure of the active site on the catalyst surface due to the different atomic arrangements of different metal atoms. It is considered as a feasible strategy to improve the electrocatalytic activity.[160-163] PtRu nanoalloy supported on porous graphitic carbon was prepared by Sun et. al.[33] using co-reduction of the precursors of Pt and Ru at 300 °C by $H_2$ (PtRu/PC-L) followed by thermal treatment at a high temperature (700 °C, PtRu/PC-H) (Figure 9a). The as-fabricated PtRu/PC-H sample exhibited good catalytic performance compared with PtRu/PC-L and Pt/C nano-catalysts due to the higher alloying degree and strong electronic interaction between Pt and Ru atoms. The mass activity and specific activity of PtRu/PC-H are 1674.2 mA mg$^{-1}_{Pt}$ and 4.4 mA cm$^{-2}$ for MOR are 4.08 and 8.80 times higher than that of the Pt/PC nano-catalyst. After 7200 s stability test, the limiting current density of PtRu/PC-H is 5.32 times that of Pt/C, which further confirmed the good durability of PtRu/PC-H for MOR; the maximum power density of 83.7 mW cm$^{-2}$ was obtained in a single methanol fuel cell test which is more than three times of the commercial Pt/C (Figure 9b). Benefiting from the modification of the Pt electronic structure and Ru chemical properties on the nano-
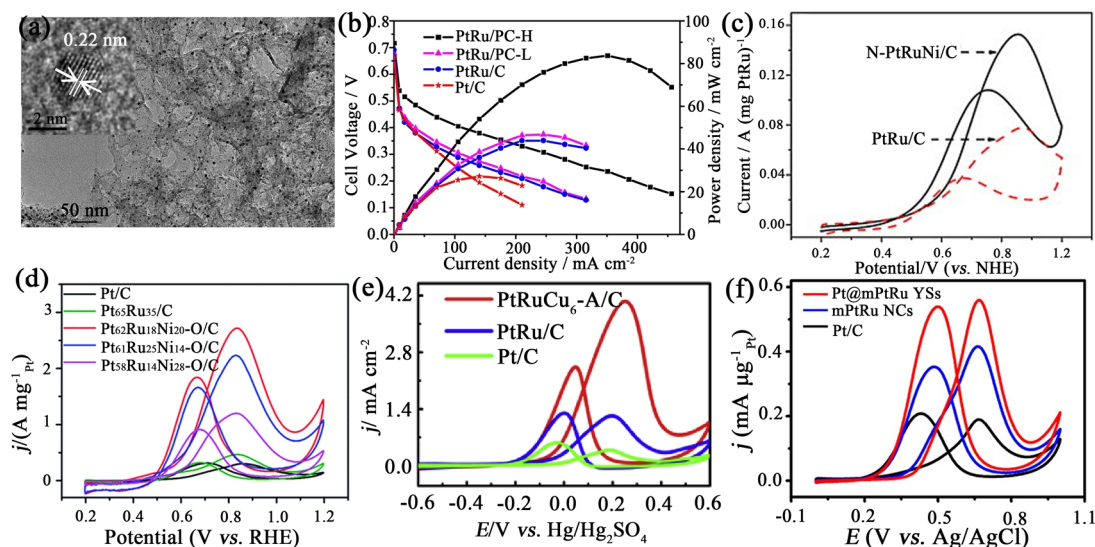
**Figure 9.** (a) TEM image of PtRu/PC-H. (b) Steady-state polarization and power density curves for fuel cells employing PtRu/PC-H, PtRu/PC-L, commercial PtRu/C and commercial Pt/C as anode catalysts. Reproduced with permission from Ref.[33] (c) Cyclic voltammograms for methanol oxidation on the solid PtRu/C and N-PtRuNi/C catalysts. Reproduced with permission from Ref.[170] (d) Mass activity in 0.1 M HClO4 + 1 M CH3OH solution for different catalysts. Reproduced with permission from Ref.[171] (e) CVs on different catalysts at 50 mV s$^{-1}$. Reproduced with permission from Ref.[174] (f) Mass-normalized CV curves of different catalysts in a 0.5 M H2SO4 with 1.0 M CH3OH at a sweep rate of 50 mV s$^{-1}$. Reproduced with permission from Ref.[190]

particle surface by strain and ligand effects, a porous flower-like Pt$_{72}$Ru$_{28}$ nanometer alloy catalyst was prepared and it showed specific activity and mass activity of 4.19 and 3.54 times higher than those of commercial Pt black.[164] Using MgO nanoparticles as sacrificial templates, PtRu black catalysts with a high alloying degree and small particle size were obtained, which also showed largely improved performance for MOR by comparison with the commercial PtRu-JM catalyst.[165]

A ternary alloy of PtRu-based catalysts by introducing the third transition metal element in the PtRu alloy can further improve the catalytic activity by utilizing the synergistic effect between different components.[166,167] The introduction of Ni into the PtRu system can effectively improve the CO poisoning effect due to the enhanced oxidation of CO$_{ads}$ by nickel hydroxide and the high proton and electronic conductivity of hydroxide.[168,169] A nanoporous PtRuNi ternary alloy was obtained by dealloying Ni from high Ni content PtRuNi alloy precursors.[170] The as-prepared nanoporous PtRuNi catalyst with Ni in the core exhibited a peak current density of 1.9 times higher than that of the PtRu/C catalyst for MOR due to the electronic structure of the outer metal modified by the Ni core (Figure 9c). In addition, the methanol oxidation current on N-PtRuNi/C was much higher than that on PtRu/C after the CA test of 3000 s, demonstrating the high stability of N-PtRuNi/C catalyst. Surface oxygen-mediated ultrathin PtRuNi nanowires were synthesized by a general wet-chemical method combined with thermal annealing.[171] The oxidation state of nickel after thermal annealing can provide oxygen-containing species for the removal of CO adsorbed on Pt surface, and theoretical calculation confirmed that the addition of O can enhance the adsorption of methanol on the O-2p band and enhance the anti-CO poisoning ability. Thus the MOR performance of Pt$_{62}$Ru$_{18}$Ni$_{20}$O/C was improved by a mass activity of 5.1 and 9

times of Pt$_{65}$Ru$_{35}$/C and Pt/C, respectively (Figure 9d).

Compared with other alloying elements, Cu is more stable against electrochemical oxidation than other solute metals (such as Ni and Co), and the submonolayer amounts of Cu are preferentially stable in the second Pt layer which can effectively change the electronic structure of the Pt surface layer.[172] The hexapodal PtRuCu nanocrystalline alloy catalysts were prepared by a facile method based on Stranski-Krastanov growth and galvanic replacement.[173] The improved catalytic activity of PtRuCu/C catalyst was due to the presence of Cu in the system that can modify the d-band center of Pt and alleviate the dissolution of the Pt atom by sacrificing the Cu atom on the surface. A similar report was observed for PtRuCu$_6$-A/C catalyst with a Pt-Ru-Cu core and Pt-Ru shell with surface defects, which possessed a high density of surface defects at the nanoscale level prepared by selectively dissolving surface metal atoms in sulfuric acid solution (Figure 9e).[174] The composition of the ternary Pt-Ru-Cu system for MOR was optimized by combinatorial synthesis and high-throughput screening.[175] The Pt$_{66}$Ru$_{17}$Cu$_{17}$ composition showed the best MOR catalytic activity, which was 26% and 86% higher than that of the PtRu/C catalyst in cyclic voltammetry and chronoamperometry tests, respectively. In addition to Ni and Cu, the introduction of Fe, Sn and other metal elements can also improve the methanol oxidation capacity of PtRu-based alloy catalyst.[176,177] Quaternary PtRu alloys have also been developed to enhance electrocatalytic performance.[178-180] Benefiting from the synergistic effect of Co and W metals, PtRuCoW quaternary alloy system showed much better performance for methanol oxidation.[181] Mo and W provide more oxygen-containing substances to form quaternary PtRuMoW catalysts and effectively increase the catalytic activity in MOR.[182] The alloying strategy can effectively improve the mixing enthalpy

of the catalyst, and the strong interaction between PtRu and other metal atoms improves the structural stability of the catalyst. The enhanced activity and durability in MOR can be understood by the electronic effect and compression strain effect of the d center. However, there are still some problems in the alloy structure, such as easy aggregation of active sites, oxidation and dissolution of non-precious metals, which endangers the stability of the catalyst.

**Core-shell Structure.** The engineering of core-shell nanostructures can yield highly exposed active surfaces and accelerate charge transfer.[183,184] In a core-shell structure, the lattice mismatch between the core and shell creates lattice strain at the surface. By changing the internal and external geometries, the catalytic performance can be significantly improved through ligand and/or strain effects. The optimized surface of Pt could also effectively avoid the dissolution of Ru caused by the production of high-valence Ru oxide on the PtRu-based catalysts surface, and increase the density of surface active sites.[185,186] The rational design and construction of the PtRu core-shell structure are of great significance for enhancing the activity and stability of PtRu-based catalysts.

Ru@Pt core-shell catalysts with a clean surface and good dispersion were prepared by a capping agent-free polyol synthesis method.[187] The chemical composition of the shell was tuned by changing the pH value. It was found that the CO poisoning tolerance of the Ru@Pt core-shell system with an alloy shell was much better than that of Ru@Pt with a Pt-rich shell core-shell system. In addition, Ru@Pt core-shell nanoparticles with amorphous and highly crystalline Ru cores were synthesized using a sequential ethanol reduction method.[188] Among them, the ordered Ru core can produce clear heterostructures at the Ru-Pt interface, which reduced the adsorption energy of CO and enhanced the catalytic activity. Core-shell Ru@Pt catalysts with sub-nanoscale and ordered Pt shells were synthesized using a microwave heating solvent method.[185] Due to the strain effect and electronic interaction induced by the core-shell heterojunction, the core-shell Ru@Pt catalyst exhibited much stronger resistance to CO poisoning; Ru@Pt$_{0.5}$/C with an atomic ratio of Ru:Pt 1:0.5 exhibited significantly enhanced activity and durability for methanol oxidation compared with the commercial PtRu catalysts.

The shell thickness of the core-shell structure catalyst will affect the catalytic performance. For example, Ru-Pt core-shell nanoparticles with different numbers of Pt atomic layers were prepared and investigated for MOR.[189] Ru-Pt core-shell catalyst with 1.5 atomic layers as shell showed the best MOR performance probably due to the combined effect of lattice strain and the interaction of heteroatomic electron orbitals at the core-shell interface to achieve the best valence electron transition degree from Pt to Ru. In another study, Wang et al. reported an egg yolk-shell nanostructured catalyst consisting of a Pt core and a mesoporous bimetallic PtRushell (Pt@mPtRu).[190] The mesoporous PtRu shell prevented the aggregation of Pt nuclei, effectively increasing the specific surface area and providing largely exposed active sites from both internal and external surfaces. Benefiting from these advantages of the mesoporous yolk-shell

nanostructures, the Pt@mPtRu showed excellent catalytic activity for MOR, and the mass activities were 1.36 and 2.95 times that of mPtRu NCs and Pt/C, respectively (Figure 9f). Through accelerated durability test, the mass activity of Pt@mPtRu YSs was decreased by 16.1% compared to the initial value after 1000 cycles, superior to 27.6% of Pt/C catalyst. Besides, the catalytic activity of methanol electrooxidation can be improved using the transition metal as the core and PtRu as the shell catalyst.[191,192] Core-shelled Fe@(PtRu) nanocatalyst with Fe core and PtRu alloy shell showed 2.0-2.5 times higher MOR activity than that of PtRu catalyst.[193] A core-shell structured PtRuCo$_x$ electrocatalyst was developed by a sequential dealloying and annealing approach.[194] Compared with the conventional PtRu/C electrocatalyst, the presence of a PtRu-rich surface layer and a Co-rich core made the PtRuCo$_x$ core-shell catalyst exhibit remarkably high activity and stability for MOR.

## �■ CONCLUSION AND FUTURE PERSPECTIVES

The recent advances in PtRu-based catalyst for MOR were overviewed, and the largely improved catalytic performance of PtRu catalyst system compared to Pt could be attributed to the role of Ru in the system. Based on the bi-functional catalytic mechanism and the electronic effect, the synergistic effect in Pt-Ru-based catalyst effectively improves the anti-CO poisoning ability. The oxophilic Ru can increase the electron density around Pt and weaken the adsorption ability between Pt and adsorbed CO, and Ru can promote H$_2$O dissociation at lower potentials to form hydroxyl groups that assist the oxidation of CO adsorbed on the Pt sites nearby. The surface reactivity descriptors of CO binding energy ($\Delta G_{CO}$) and OH binding energy ($\Delta G_{OH}$) can be employed for novel catalyst design and catalytic performance prediction. The regulation strategies to improve the electrocatalytic activity of PtRu were concluded for the recent work, including support engineering, morphology design, and surface/interface regulation.

Although PtRu-based electrocatalysts have achieved some significant results, there is still a lot of room for the development of more efficient and stable PtRu-based catalysts. (1) The catalytic performance improvement of PtRu-based catalyst is still highly necessary because of the high cost and rareness of Pt and Ru. To realize the practical application, the PtRu nanoparticles can be dispersed into the carbon-based support that has a high surface area to increase the exposure of the active site and reduce the metal loading. Besides, the ternary or quaternary alloy based on PtRu might be an effective way to increase the catalytic performance and the noble metal utilization efficiency. (2) The stability of PtRu catalyst is closely related to practical application and it is necessary to establish a reasonable and orderly monitoring system for the structure and composition of catalysts to comprehensively understand electrocatalysts. For the supported PtRu-based catalyst, increasing the anchoring ability of PtRu over the carbon support should be paid more attention to in future studies. The leaching of other elements from the PtRu-based alloy should be carefully probed, which is seldom reported in the current reports. (3) Transfering the novel nano-structured catalyst from the fundamental study to the practical application is

still required for some advanced nanostructured catalysts. Some advanced nanostructured catalysts have been developed and only reported for potential application in the electrochemical measurements, but the practical measurements based on the critical criteria, especially following the fuel cell application, were rarely done. Besides, the large-scale fabrication of this catalyst is still full of challenges as these catalysts were obtained with the help of templates or capping agents.

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## n   COMPETING INTERESTS

The authors declare no competing interests.

## n   ADDITIONAL INFORMATION

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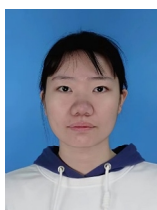
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