Modulating Electronic Structure of an Au-Nanorod-Core–PdPt-Alloy-Shell Catalyst for Efficient Alcohol Electro-Oxidation

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Direct alcohol fuel cells (DAFCs) utilize alcohol electro-oxidation reactions (AORs) to provide electricity, where catalysts with optimal electronic structures are required to accelerate sluggish AORs. Herein, an electrocatalyst with an Au-nanorod core and a PdPt-alloy shell is designed. Its electronic structures are modulated through epitaxial growth of a PdPt-alloy shell on the Au-nanorod core, which exhibits a tensional strain effect and atomic steps. Three key problems of AORs are solved with this catalyst, including poor adsorption of alcohols on the catalyst, CO poisoning of the catalyst, and a high free energy barrier for the AORs. Taking methanol electro-oxidation reaction (MOR) as an example, this catalyst shows 9.4 times higher mass activity than the market-available Pt/C catalyst. Theoretic simulations prove that this catalyst has a low free energy barrier for the MOR, and strong adsorption of methanol but weaker adsorption of carbonaceous intermediates. The reasons behind this are the stretched geometric structure of the PdPt (100)-alloy shell and the optimized electronic structure of catalytic sites on the catalyst surface. Meanwhile, efficient electro-oxidation of ethanol, ethylene glycol, and glycerol is realized. This work paves the way to design and synthesize universal and efficient AOR catalysts for the construction of high-performance DAFCs.

1. Introduction

Direct alcohol fuel cells (DAFCs) utilize alcohol electro-oxidation reactions (AORs) to generate electricity.[1–6] Compared with hydrogen in proton-exchange membrane fuel cells, DAFCs are more convenient and secure to be transported and stored. However, the conversion efficiencies of these AORs are commonly inferior to hydrogen oxidation. This is partially due to the sluggish kinetics of multielectrons’ transferred processes inside alcohols (e.g., methanol, ethanol, ethylene glycol, and glycerol).[7–11] In this regard, various catalysts of both noble and non-noble metals have been designed and synthesized to boost such sluggish AORs. Although noble metal catalysts (e.g., Pd, Pt, and Rh) are more expensive than non-noble metals (e.g., Ni, Co, and Mn), their more negative AOR onset potentials make them superior for the construction of DAFCs[5,12,13] originating from their unique electronic structures. Among reported noble-based catalysts, those based on the Pt metal are regarded as the star electrocatalysts for the AORs in terms of their oxidation overpotentials and Tafel slopes.[12,13] Notably, their alloys with other metals (e.g., Ru, Ni, Co, Pd, Rh, and Au) exhibit strong adsorption capability toward OH species or a so-called bifunctional mechanism, leading to improved AOR performance.[14–17] On the other hand, the serious poisoning effect of the carbonaceous intermediates (especially CO) hinders dramatically the activity of the used catalysts (especially the Pt catalysts) and eventually leads to much reduced conversion efficiencies of these AORs.[18,19] In this context, the screw-like PdPt alloy nanowires[10] and PdPt alloy nanoparticles[20] have been employed to replace single metallic Pt catalysts for methanol electro-oxidation reaction (MOR). Originating from varied electronic structures that are induced by the addition of Pd atoms, these PdPt alloys have been confirmed as commendable MOR catalysts. Although the sizes and compositions of these catalysts have been tuned and the AOR performance on these catalysts has been explored, the performance of these bimetallic heterostructures/catalysts is still far away for their commercial applications. The catalysts featuring superior AOR performance over those reported are still highly demanded for the construction of high-performance DAFCs.

It has been well known that the optimization of these noble-metallic heterostructures/catalysts with respect to their morphologies and exposed facets is helpful to enhance their catalytic performance.[21–24] Among various heterostructures, a catalyst with a core–shell structure has been attracted special attention.[25–28] Its structure and its catalytic activity of the shell are revealed to be highly dependent on the used core.[23–24] This is because the strain effect (expansion or compression) can be
effectively controlled, up to the difference of intrinsic lattice parameters between the core and the shell.\[^{33-41}\] For example, an expanded strain increases the d-band center of the active shell, resulting in strengthened adsorption of ethanol and OH species, and eventually much facilitated ethanol electro-oxidation.\[^{33}\] Moreover, the exposed crystal plane on the shell is possible to be modified during an epitaxial growth process. For example, the exposed facets of an Ir shell have been derived from a Pd core in a Pd@Ir core–shell catalyst.\[^{41}\] The epitaxial growth of noble metals or alloys on an appropriate substrate has been already proved to be one of the most promising strategies to optimize the heterostructures in pursuit of their high catalytic activity.\[^{42}\] Such exposed facets played an important role in the AORs. For example, the highly exposed crystal facets of Pt (100), (310), and (410) exhibited better AOR performance in comparison with the Pt (111) facet,\[^{43}\] stemming from their stronger adsorption capability toward OH species.\[^{43,44}\] Last but not least, these core–shell catalysts accelerate electron transfer rates at their interfaces, which are again much benefit for the AORs.

Herein, a PdPt catalyst with a core–shell structure is designed and synthesized. The highly tensile PdPt-alloy shell is grown on an Au-nanorod core by means of an epitaxial growth method. On such an Au@PdPt core–shell catalyst, a stretched PdPt-alloy shell is expected. This is because the lattice parameters of face-centered cubic elements of Au, Pd, and Pt are slightly different. Moreover, the exposed facet of an Au-nanorod core is mainly (100). Other crystal facets of the PdPt-alloy shell such as (310) and (250) facets can be highly or efficiently exposed at the end of the Au-nanorod core. Furthermore, the strong interaction between the Au core and the PdPt-alloy shell prevents the dissolution of Pd or Pt atoms from the catalyst surface. In other words, the stability of such a core–shell catalyst is expected to be enhanced. Such an Au@PdPt core–shell catalyst is thus an ideal AOR catalyst. It has to point it out that the tensional strain of the Au@PdPt core–shell nano-octahedrons has been tuned through varying the thickness of the PdPt shell. On these catalysts, improved performance toward electro-oxidation of formic acid reaction (FOR), oxygen reduction reaction (ORR), and MOR has been realized.\[^{45}\] However, the reaction mechanisms of these catalytic reactions have not been fully understood and revealed, especially for different AORs. In this contribution, the AOR performance of different alcohols on this newly designed Au@PdPt catalyst is thus reported. The investigated alcohols include methanol, ethanol, ethylene glycol, and glycerol. As a case study, the MOR performance is examined in detail. Density functional theory (DFT) calculations were further conducted to reveal the influences of stretched geometric structure and optimized electronic structure of the Au@PdPt catalyst on the MOR performance and further to clarify the oxidation pathways of methanol (e.g., a CO pathway and a HCOOH pathway) on this catalyst.

2. Results and Discussion

2.1. Synthesis and Characterization of the Au@PdPt Core–Shell Catalyst

The Au@PdPt core–shell catalyst was synthesized according to the steps schematically described in Figure 1a. Briefly, the Au nanorods are first prepared by using a reported seed-growth method,\[^{46}\] followed by the co-reduction of Pt(II) and Pd(II) species into Pt and Pd metals with a reductant (e.g., ascorbic acid, AA). Note that the reduction potential of Pd(II) species into Pd metal is lower than that of Pt(II) species into Pt metal.\[^{47}\] To slow down the rates of two reduction reactions, especially for the reduction reaction of Pd(II) species into Pd metal, some Br\(^{-}\) ions were added. In this way, the co-reduction of Pd(II) and Pt(II) species into Pd and Pt metals was realized.\[^{47}\] Note that the lattice parameters of face-centered cubic Au, Pd, and Pt elements are 4.08, 3.89, and 3.92 Å, respectively. The co-reduced Pd and Pt metals are thus epitaxially grown on the surface of an Au-nanorod core. The phase composition of the Au@PdPt core–shell catalyst was first analyzed by means of X-ray diffraction (XRD). The diffraction peaks at 38.3°, 44.6°, 64.9°, and 78.0° (Figure S1a, Supporting Information) are attributed to the (111), (200), (220), and (311) facets of Au, respectively. When the Pd and Pt metals are grown on the surface of the Au-nanorod core, a new (111) peak appears at 39.80° (Figure S1b, Supporting Information). It is located between 39.86° for the Pd (111) facet and 39.74° for the Pt (111) facet, an indirect indication of the growth of a PdPt alloy on the surface of an Au-nanorod core. As control experiments, the catalysts of Pd/C, Pt/C, and PdPt/C alloy were also synthesized (Figure S2, Supporting Information). When compared with those for Pd nanoparticles, Pt nanoparticles, and the PdPt alloy (Figure S1c, Supporting Information), the positions of diffraction peaks in the Au@PdPt core–shell catalyst shift negatively. For example, the change of 2θ value (1.50°) from the PdPt (111) facet to the Au (111) facet for the Au@PdPt core–shell catalyst is smaller than that (1.58°) from the standard Pt (111) facet to the standard Au (111) facet, as well as that (1.93°) from the standard Pd (111) facet to the standard Au (111) facet. In this regard, the lattice parameter of the PdPt-alloy shell in the Au@PdPt core–shell catalyst is larger than that of Pt nanoparticles as well as that of Pd nanoparticles. The tensional strain in the Au@PdPt core–shell catalyst is thus produced.

The Au@PdPt core–shell catalyst was then characterized using transmission electron microscopy (TEM) and high-resolution TEM (HRTEM). In its TEM image (Figure 1b), the uniform distribution of PdPt atoms on the Au-nanorod core is observed. The sizes of this Au@PdPt core–shell catalyst were further estimated. From the TEM (Figure S3a, Supporting Information) and HRTEM (Figure S3b, Supporting Information) images of the Au-nanorod cores, one can know that their average length and diameter are 29 nm (Figure S3c, Supporting Information) and 13 nm (Figure S3d, Supporting Information), respectively. Once Pd atoms are grown on the Au-nanorod cores, the obtained Au@Pd core–shell catalysts still maintain the same shape as the Au-nanorod cores (Figure S4a, Supporting Information). Their length (Figure S4b, Supporting Information) and width (Figure S4c, Supporting Information) are enlarged to 32 and 16 nm, respectively. The Au@Pt core–shell catalysts, obtained by the growth of Pt atoms on the Au-nanorod cores, are found to have identical shape (Figure S4d, Supporting Information), length (Figure S4e, Supporting Information), and width (Figure S4f, Supporting Information) with the Au@Pd core–shell catalysts. More interestingly, the Au@PdPt core–shell catalysts also have the same shape (Figure S4g, Supporting Information), length
(Figure S4h, Supporting Information), and width (Figure S4i, Supporting Information) as that of the Au@Pd core–shell catalysts. Consequently, the interaction of the Au-nanorod core with the shell of Pt atoms, Pd atoms, or a PdPt alloy is similar. For the Au@PdPt core–shell catalyst, such an interaction can be clearly seen from its TEM image, supported by the luminance contrast of the Au-nanorod core and the PdPt shell. From the analysis of the energy-dispersive X-ray spectroscopy (EDX) line profiles of the Au@PdPt catalyst (Figure 1c), its core–shell structure is further confirmed. Moreover, the uniform distribution of Pd (olive) and Pt (red) atoms on the surface of the Au-nanorod (yellow) core is proved in the elemental mapping of this Au@PdPt core–shell catalyst (Figure 1d). This PdPt-alloy shell is further confirmed to be grown along the (100) facet (Figure 1e; Figure S3b, Supporting Information), attributed to the support effect of the Au (100) facet of the Au-nanorod core during the reduction process.[48] Surprisingly, the PdPt-alloy shell exhibits a (100) interplanar spacing of 0.202 nm. Although it is much larger than the conventional Pd or Pt (100) interplanar spacing (0.194 nm), it is close to the interplanar spacing of the Au (001) facet (0.146 nm) of the Au (001) facet. In order to analyze better the strain effect in the Au@PdPt core–shell catalyst, its geometric phase analysis (GPA) was conducted (Figure S5, Supporting Information). Obvious distance changes of few atoms are observed along the (100) and (110) orientations. Those results indicate that the PdPt-alloy shell along the (100) orientation is consistent with the Au-nanorod core. The atomic distance of the PdPt-alloy shell along the (110) orientation is rarely affected by the Au-nanorod core. Furthermore, there is no lattice warp at the interface of this Au@PdPt core–shell catalyst, an indication of the epitaxial growth of the PdPt-alloy shell on the Au-nanorod core. Consequently, the top and bottom sides of this Au@PdPt core–shell catalyst (namely, the PdPt-alloy shell) appear not to be smooth. These atomic steps (Figure 1f) are exposed as the (311) facet, which can act as active sites for the AORs.

Subsequently, the electronic states of the elements of Au, Pd, and Pt in the catalysts of Au@Pd, Au@Pt, Au@PdPt, and Au nanorods were analyzed by X-ray photoelectron spectroscopy (XPS). Their XPS Au 4f spectra (Figure 2a) confirm the presence of a large amount of Au(0) species and a tiny amount

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Figure 1. a) Synthetic steps, b) TEM image, c) EDX line profiles of different elements in the Au@PdPt core–shell catalyst. d) EDX elemental mapping of the Au@PdPt core–shell catalyst. e) HRTEM image of the interface between the PdPt-alloy shell and the Au-nanorod core. f) HRTEM image of the atomic steps of the PdPt-alloy shell. In panel (c), the elements of Au, Pd, and Pt are in the colors of yellow, olive, and red, respectively.
of Au(II) species in these catalysts. The electronic states of Au in these catalysts are consistent in that the binding energy of Au(0) 4f7/2 of the Au nanorods (83.88 eV) is close to that of the catalysts of Au@Pd (83.86 eV), Au@PdPt (83.87 eV), and Au@Pt (83.89 eV). On the other side, both Pt(0) and Pt(II) species are observed in the related XPS Pt 4f spectra (Figure 2b). The Pt(II) species results from surface oxidation of Pt atoms in these catalysts. However, the binding energy of Pt(0) 4f7/2 in the Au@Pt core–shell catalyst is 71.28 eV, which is 0.05 eV more negative than that (71.33 eV) of the Pt catalyst, but 0.30 eV more positive than that (70.98 eV) of the Au@PdPt core–shell catalyst. Consequently, no obvious electron transfer occurs from the Au-nanorod core to the PdPt-alloy shell, while the electron transfer from Pd to Pt in the shell does happen. In the XPS Pd 3d spectra of the core–shell catalysts of Au@Pd and Au@PdPt (Figure 2c), a small amount of Pd(II) species is seen. The XPS Pd 3d spectrum of the Au@Pd core–shell catalyst shows a Pd(0) 3d5/2 peak. The binding energy of this peak (336.18 eV) is nearly same to that of the Pd catalyst, but 0.2 eV more negative than that of the Au@PdPt core–shell catalyst. These results are in line with those in the XPS Pt 4f spectra (Figure 2b). Again, remarkable electron transfer between Pd and Pt in the PdPt-alloy shell happens, although the obvious occurrence of electron transfer between the Au-nanorod core to the PdPt-alloy shell has not been noticed. A synergy effect from Pd and Pt in the alloy shell thus benefits much for the AORs.

The electronic states of Au, Pd, and Pt elements in the Au@PdPt core–shell catalyst were further examined by means of X-ray absorption near edge structure (XANES). It is worth mentioning that the XANES spectrum of the Au-L3 coincides with the Pt-L3 extended X-ray absorption fine structure (EXAFS) spectrum (Figure S6, Supporting Information).[49] The XANES spectra of the Pt L3 edge (Figure 2d) indicate a slight oxidation state of Pt atoms in the core–shell catalysts of Au@Pt and Au@PdPt. There is an obvious pre-edge absorption peak of Pt atoms (around 11 540 eV) for the Au@PdPt core–shell catalyst, which originates probably from the alloying effect of the PdPt shell. Meanwhile, the intensities of the Pd XANES spectra help to identify the surface oxidation states of Pd species (Figure 2e). The EXAFS spectra of Pd species in the R space show a Pd–Pd path distance of 2.57 Å in the Au@Pd core–shell catalyst, which is larger than that (2.51 Å) in a Pd foil (Figure 2f). As for the Au@PdPt core–shell catalyst, the path distance of Pd–Pd or Pd–Pt is 2.60 Å, which is close to the path distance of Pd–Pd in the Au@Pd core–shell catalyst, although it is still larger than that of a Pd foil. The Wavelet transform diagrams exhibit a K position of 6.4 Å−1 for the Au@PdPt core–shell catalyst, which is smaller than that of the Au@Pd core–shell catalyst (8.4 Å−1) or
a Pd foil (8.5 Å−1) (Figure 2g). These results prove again the existence of a Pd–Pt bond or the alloy effect of the PdPt-alloy shell in the Au@PdPt core–shell catalyst. A tensional strain is thus confirmed in the PdPt-alloy shell. The calculated value is about 3.5% (= 2.6/2.51). Note that the lattice parameter of Au (4.08 Å) is slightly (4%) higher than that of Pd (3.89 Å) and Pt (3.92 Å). This 3.5% stretched value in the Au@PdPt core–shell catalyst suggests that the strain is weakened when the layer number of the shell is increased, in line with previous reports.[51]

2.2. AOR Performance on the Au@PdPt Core–Shell Catalyst

Prior to the investigation of the AOR performance of the Au@PdPt core–shell catalyst, the CO-stripping experiments were conducted on the Au@PdPt core–shell catalyst and its counterparts in 1 M KOH solution. During such a CO-stripping process, CO* species is supposed to be transformed into COOH* species after its combination with OH* species. Subsequently, the generated COOH* species decomposes into CO2.[7,11] On the Au@PdPt core–shell catalyst, the onset potential for the CO oxidation (right side of the dash line, black curve of Figure 3a) is 0.37 V (vs reversible hydrogen electrode (RHE)) and the peak position is located at 0.64 V (vs RHE). These potentials are more negative than those on the Pd nanoparticles (0.79 and 0.68 V vs RHE), the Pt nanoparticles (0.66 and 0.51 V vs RHE), and the PdPt alloy (0.70 and 0.51 V vs RHE). This is because the tensional PdPt-shell has better adsorption ability toward OH* species. Namely, the formation of OH* species is easier on the Au@PdPt core–shell catalyst than on the catalysts of the Pd nanoparticles, Pt nanoparticles, the PdPt alloy. In this context, the Au@PdPt core–shell catalyst exhibits better CO resistance than other catalysts. On the Au@PdPt core–shell catalyst, an obvious preoxidation process of CO is observed within the potential range from 0.35 to 0.6 V (vs RHE), which is fully different from that on other catalysts. The

**Figure 3.** Electrochemical performance of the catalysts of Pd nanoparticles, Pt nanoparticles, the PdPt alloy, and Au@PdPt. a) CO-stripping tests, where the first and second cycles are marked with the black and red lines, respectively, b) MOR performance. c) The normalized mass activity and specific activity. d) Tafel analysis. e) Nyquist plots. f) Cycling stability. The scan rate in panels (a) and (b) is 50 mV s−1.
difference of this oxidation process on these catalysts confirms varied adsorption capability of CO on these catalysts.[52] Such a statement is further supported by the adsorption/desorption behavior of hydrogen on these catalysts. No clear waves are seen with respect to hydrogen adsorption/desorption once the surfaces of the Pt nanoparticles, the PdPt alloy, and the Au@PdPt core–shell catalyst are saturated with CO. Once the CO-stripping experiment is conducted, the waves of hydrogen adsorption/desorption (left side of the dash lines, red curves in Figure 3a) are clearly seen on these catalysts. Based on the areas of these CO-stripping peaks, the calculated electrochemical active surface areas (ECSAs) of the catalysts of Au@PdPt, Pd nanoparticles, Pt nanoparticles, and the PdPt alloy (Table S1, Supporting Information) are 70.3, 22.4, 35.3, and 35.8 m² g⁻¹, respectively.[33] The Au@PdPt core–shell catalyst exhibits the biggest ECSA, namely more active sites. Hence, this Au@PdPt core–shell catalyst is expected to be a promising catalyst for the AORs.

The MOR was then taken as a case study to examine the AOR performance of the Au@PdPt core–shell catalyst. The cyclic voltammograms (CVs) were recorded in 1 M CH₃OH + 1 M KOH solution (Figure 3b). As control experiments, the CVs of the catalysts of Pd nanoparticles, Pt nanoparticles, and the PdPt alloy were also recorded under identical conditions. On the Au@PdPt core–shell catalyst, a typical methanol oxidation peak is seen in the forward scan with a peak current density of 4830 mA mg⁻¹. It is much higher than that obtained on the catalysts of Pd nanoparticles (394 mA mg⁻¹), Pt nanoparticles (516 mA mg⁻¹), and the PdPt alloy (898 mA mg⁻¹). Moreover, the Au@PdPt core–shell catalyst (Figure 3c) shows better specific activity than the catalysts of Pd nanoparticles, Pt nanoparticles, and the PdPt alloy. In other words, the intrinsic activity of the Au@PdPt core–shell catalyst is enhanced. Such high mass activity and specific activity of this Au@PdPt core–shell catalyst are superior to other reported Pt- and Pd-based MOR catalysts (Table S2, Supporting Information). The Tafel analysis of the MOR on these catalysts was further conducted (Figure 3d). The Tafel slope on the Au@PdPt core–shell catalyst is 93 mV dec⁻¹, smaller than that of the catalysts of Pd nanoparticles (143 mV dec⁻¹), Pt nanoparticles (121 mV dec⁻¹), and the PdPt alloy (118 mV dec⁻¹). Consequently, the Au@PdPt core–shell catalyst has a better ability to adsorb CH₃OH and OH⁻.[33]

In addition, the Au@PdPt core–shell catalyst has the lowest charge-transfer resistance (Rct = 2.3 KΩ), as calculated from the Nyquist plots of these catalysts (Figure 3e). It is thus beneficial for the charge transfer of the MOR. Note that the stability of the Au@PdPt core–shell catalyst is superior to that of the catalysts of Pt nanoparticles, Pd nanoparticles, and the PdPt alloy. For example, the Au@PdPt core–shell catalyst remains 36% of its initial activity (Figure 3f), much higher than that for the catalysts of Pt nanoparticles (2%), Pd nanoparticles (3%), and the PdPt alloy (19%) even after 1000 cycles. Notice that the shape of recorded CVs on the utilized catalysts is found to be slightly changed during this stability test. During the course of the forward scanning, the peak potential on the Au@PdPt core–shell catalyst shifts from 0.822 to 0.786 V. Differently, this peak is found to be positively shifted on the catalysts of Pt nanoparticles, Pd nanoparticles, and the PdPt alloy (Figure S7, Supporting Information). The negative shift of this peak potential on the Au@PdPt core–shell catalyst thus proves enhanced stability and better application potential of the Au@PdPt core–shell catalyst for the construction of direct methanol fuel cells (DMFCs). Such enhanced stability is attributed to the interaction between the Au-nanorod core with the PdPt-alloy shell.[31] The MOR performance of the Au@PdPt core–shell catalyst was also tested using a rotating disk electrode at a rotating speed of 1600 rad min⁻¹. The obtained steady-state current density is much smaller than that without rotating (Figure S8a, Supporting Information). In contrast, no obvious decrease of the current density is observed on the Pt nanoparticles (Figure S8b, Supporting Information). This decrease of the current on the Au@PdPt core–shell catalyst is assumably due to the loss of generated HCOOH intermediate[53] from the surface of the rotating electrode, which does not occur on a still electrode.

As control experiments, the MOR activity on the Au@PdPt core–shell catalysts (Figure S9, Supporting Information) that own varied atomic ratios of Pd to Pt but a fixed atomic ratio of the Au-nanorod core to the PdPt-alloy shell (here 3:1) was studied. Among the core–shell catalysts of Au@Pd₄Pt (Figure S9a–c, Supporting Information), Au@Pd₄Pt₄ (Figure S9d–f, Supporting Information), and Au@PdPt, the Au@PdPt core–shell catalyst exhibits the highest MOR activity (Figure S9g, Supporting Information). A volcanic curve (Figure S9h, Supporting Information) is drawn to express the MOR activity of these catalysts, where suggests a synergistic effect between the Au-nanorod core and the PdPt-alloy shell for the MOR.

More importantly, the Au@PdPt core–shell catalyst can be applied as a universal electrocatalyst for other AORs (Figure S10, Supporting Information), such as for ethanol electro-oxidation reaction (EOR), glycerol electro-oxidation reaction (GOR), and ethylene glycol electro-oxidation reaction (EGOR). For the EOR, GOR, and EGOR, the mass activities of the Au@PdPt core–shell catalyst are 3893, 2990, and 3018 mA mg⁻¹, respectively. They are 3.3-, 3-, and 3.8 times higher than those (1193, 988, and 788 mA mg⁻¹) on the Pt nanoparticles, respectively. In short, the Au@PdPt core–shell catalyst features superior AOR performance over the market-available Pt catalyst.

2.3. MOR Mechanism on the Au@PdPt Core–Shell Catalyst

To interpret the superior MOR performance of the Au@PdPt core–shell catalyst, the DFT calculations were carried out. Taking the tensional strain of the (100) PdPt-alloy shell into account, the model catalysts of PdPt (100)-0% (Figure 4a), PdPt (100)-2% (Figure S11, Supporting Information), and PdPt (100)-4% (Figure 4b) were constructed with the lattice constants of 0%, 2%, and 4%, respectively. The highest strain state of 4% in this work was based on the lattice constant of Au (4.08 Å), slightly larger than that of Pd (3.89 Å) and that of Pt (3.92 Å). For comparison, a contrastive Pt (111) model catalyst (Figure S11, Supporting Information) was also constructed. In the case of the PdPt (100)-0% model catalyst, one surface Pt atom is coordinated with four Pd atoms in the first layer. It is further coordinated with two Pt atoms and two Pd atoms in the second layer. The average length of these coordination bands was calculated to about 2.89 nm. When the PdPt (100)-0% model catalyst is
stretched to 2% and 4%, the average band lengths are elongated to 2.92 and 2.95 nm, respectively. In other words, the tensional strain decreases the coordination degree of surface Pt atoms in the PdPt (100)-0% model catalyst. A similar tendency was found for the surface Pd atoms in the PdPt (100)-0% model catalyst. The increase of the tensional strain state leads to the decrease of coordination degree and hence results in a continuous change of the d-band electron-projected density of states (PDOSs) of Pt (Figure 4c) and Pd atoms (Figure 4d) on the surface of the PdPt (100) model catalyst as well as the shift of the d-band centers of those Pt (Figure S12a, Supporting Information) and Pd atoms (Figure S12b, Supporting Information) to their Fermi levels. These more positive d-band centers indicate stronger adsorption natures of Pt and Pd atoms/sites on the PdPt (100)-4% model catalyst toward target molecules. In more detail, the Gibbs energy of CH$_3$OH absorbed on the PdPt (100)-4% model catalyst is $-0.351$ eV (Figure 4e), much higher than that ($-0.051$ eV) on the PdPt (100)-0% model catalyst (Figure 4f). The corresponding images on the PdPt (100)-0% model catalyst (Figure 4g) and on the PdPt (100)-4% model catalyst (Figure 4h) clearly show the difference of the charge densities, where electron transform from the O atom of CH$_3$OH to Pt site is quite obvious. This is in line with the stronger adsorption of CH$_3$OH on the PdPt (100)-4% model catalyst. With respect to the PDOSs of the O atom in free CH$_3$OH (Figure 4i), it can be divided into s, p$_x$, p$_y$, and p$_z$ bands. Note that the energy ranges of the p$_z$ band are close and overlapped with those of the d band of Pt sites. The energy changes of p bands are thus utilized to explain the difference of these adsorbed energies. After the adsorption of CH$_3$OH on the PdPt (100)-0% model catalyst and on the PdPt (100)-4% model catalyst, the energies of those p bands are reduced (Figure 4j). The energy changes of p$_x$-0% and p$_y$-0% are very similar with those of p$_x$-4% and p$_y$-4%, respectively. However, the p$_z$-4% exhibits more obvious decrease of this energy than the p$_z$-0%. Therefore, the interaction of the p$_z$-band of O atom in CH$_3$OH with the d band of Pt atoms is increased when the PdPt (100) model catalyst is stretched, leading to stronger adsorption of CH$_3$OH on the PdPt (100)-4% model catalyst. This stronger adsorption behavior was further confirmed by the temperature-programmed desorption (TPD) experiments of CH$_3$OH (Figure S13, Supporting Information). The Au@PdPt core–shell catalyst shows the highest desorption temperature for CH$_3$OH among three catalysts (namely Pt nanoparticles, the PdPt alloy, and the Au@PdPt core–shell catalyst). Consequently, the advantages of the designed catalysts in this study are well illustrated when compared with non-noble metal catalysts in terms of their performance and electronic structures.

A completed MOR process is then proposed (Figure S14, Supporting Information) after taking the optimized structures of adsorbates generated during the MOR on the model catalysts of PdPt (100)-0% (Figure S15, Supporting Information), PdPt (100)-2% (Figure S16, Supporting Information), PdPt (100)-4% (Figure S17, Supporting Information), and Pt (111) (Figure S18, Supporting Information) into account. It consists of two thermodynamics processes: the adsorption of CH$_3$OH at the beginning of the MOR and the desorption of CO$_2$ at the...
end of the MOR. The former seems much more crucial than the latter for the MOR; in that the excitation of CH$_3$OH is the precondition for the MOR. Hence, the stronger adsorption of CH$_3$OH on the PdPt (100)-4% model catalyst than that on the model catalysts of PdPt (100)-2%, PdPt (100)-0%, and Pt (111) makes the PdPt (100)-4% model catalyst a perfect catalyst for the MOR (Table S3, Supporting Information). Besides two thermodynamics processes, several complicated electrochemical processes occur to oxidize CH$_3$OH* species into CO$_2$* species, in which many intermediates are formed and six electrons might be released. For example, there are two possible reaction pathways: a CO pathway and a HCOOH pathway. On the Pt (111) model catalyst, the energy barrier of a HCOOH pathway is 0.708 eV (Figure 5a), close to that (0.799 eV) of a CO pathway (Table S4, Supporting Information). However, CO* species is easy to be formed since the energy barrier for the formation of CO* species is only 0.574 eV. On the other hand, the energy barrier of the conversion of CO* species to COOH* species is as high as 0.799 eV. In this context, the formed CO* species strongly adsorbs on the Pt sites. For the Pt nanoparticles, the Gibbs free energy barrier (0.708 eV) is too high for a HCOOH pathway during the MOR. Consequently, CO* intermediate seriously poisons the Pt sites and is difficult to be removed. In this case, the MOR is hindered. Compared with the model catalysts of PdPt (100)-0% (Figure 5b), PdPt (100)-2% (Figure 5c), and Pt (111), those energy barriers on the PdPt (100)-4% model catalyst (Figure 5d) are effectively reduced. For example, the adsorbed CO intermediate can be removed with an energy barrier of 0.423 eV, which is smaller than that on the model catalysts of PdPt (100)-0% (0.738 eV), PdPt (100)-2% (0.566 eV), and Pt (111) (0.799 eV) (Table S4, Supporting Information). Such a decreased energy barrier is in line with the CO-stripping results (Figure 3a); in that, the Au@PdPt core–shell catalyst exhibits the most negative onset potential among the used catalysts. Meanwhile, the energy barrier of a HCOOH pathway on the model catalysts of PdPt (100)-0% (0.261 eV), PdPt (100)-2% (0.350 eV), and PdPt (100)-4% (0.305 eV) is also much smaller than on that (0.708 eV) of a Pt (111) model catalyst (Table S4, Supporting Information). The lower energy barrier (0.305 eV) of a HCOOH pathway than that (0.423 eV) of a CO pathway on the PdPt (100)-4% model catalyst confirms again the easier formation of HCOOH intermediate, in line with other experiment results (Figure S6, Supporting Information). In conclusion, the tensional PdPt (100) model catalyst has a much lower MOR energy barrier than the Pt (111) model catalyst. The PdPt (100)-4% model catalyst exhibits stronger adsorption of CH$_3$OH and a lower free energy barrier for MORs, which are modulated by the geometric stretch and electronic structure change of the Au@PdPt core–shell catalyst. This explains well the superior MOR performance of the Au@PdPt catalyst.

3. Conclusion

The PdPt alloy has been epitaxially grown on the (100) facet of the Au nanorods, resulting in a highly tensional PdPt layer. Thanks to this strong interaction between the Au-nanorod core to the PdPt-alloy shell, this Au@PdPt core–shell catalyst exhibits excellent alcohol electro-oxidation performance, such as high mass activity and long-term stability. Theoretic calculations prove that a HCOOH pathway with low reaction free energy barriers occurs on the tensional PdPt (100) alloy surface during the methanol electro-oxidation process. Meanwhile, the CO adsorb energy is optimized on the tensional PdPt (100) alloy surface. In summary, this study demonstrates that the surface states of the active sites on the core–shell catalysts are possible to be engineered and modulated by lattice confinement. Although the employment of such a strategy to design and synthesize other similar core–shell electrocatalysts as well as the utilization of these catalysts for more alcohol electro-oxidation reactions needs to be conducted, this work provides the possibility of developing universal and efficient AOR catalysts for the construction of high-performance DAFCs at an industrial scale.
Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Research data are not shared.

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