Nanocatalyst Superior to Pt for Oxygen Reduction Reactions: The Case of Core/Shell Ag(Au)/CuPd Nanoparticles

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ABSTRACT: Controlling the electronic structure and surface strain of a nanoparticle catalyst has become an important strategy to tune and to optimize its catalytic efficiency for a chemical reaction. Using density functional theory (DFT) calculations, we predicted that core/shell M/CuPd (M = Ag, Au) NPs with a 0.8 or 1.2 nm CuPd, shell have similar but optimal surface strain and composition and may surpass Pt in catalyzing oxygen reduction reactions. We synthesized monodispersed M/CuPd NPs by the coreduction of palladium acetylacetonate and copper acetylacetone in the presence of Ag (or Au) nanoparticles with controlled shell thicknesses of 0.4, 0.75, and 1.1 nm and CuPd compositions and evaluated their catalysis for the oxygen reduction reaction in 0.1 M KOH solution. As predicted, our Ag/CuPd and Au/CuPd core/shell NPs with 0.75 and 1.1 nm shells were more efficient catalysts than the commercial Pt catalyst (Fuel Cells Store), with their mass activity reaching 0.20 A/mg of noble metal at 0.1 V vs Ag/AgCl (4 M KCl); this was over 3 times higher than that (0.06 A/mg Pt) from the commercial Pt. These Ag(Au)/CuPd nanoparticles are promising non-Pt catalysts for oxygen reduction reactions.

INTRODUCTION

Recent advances in energy research call for the rational design and synthesis of catalysts with unprecedented efficiency in catalyzing energy conversion reactions, especially the oxygen reduction reaction (ORR). Numerous studies on ORR have focused on catalysts with ultralow Pt contents, with both electronic and geometric effects being used to explain ORR catalysis. Electronic effects result in charge redistribution on the surface of the catalysts, making the catalytic sites “hotter,” while geometric effects often put shape and atom distance in consideration to tune the binding strength between Pt and O. Pt–O bonding on a perfect Pt(111) is calculated to be 0.2 eV stronger than the optimal level (∆E = -0.2 eV), and a compressed Pt strain on the catalyst surface may help to weaken the Pt–O bond and to enhance ORR catalysis. Experimentally, a variety of Pt-based alloy and core/shell nanoparticles (NPs) have been designed, synthesized, and tested to improve oxygen dissociative adsorption on Pt and Pt–O desorption for Pt surface regeneration. A more important aspect is to develop a non-Pt catalyst with catalytic power comparable to or even superior to that of Pt. Studies on energetics of oxygen dissociative adsorption on 1 nm Pd shells with a series of core metals have shown that tuning charge redistribution and surface strain can change the d-band center of the Pd shell and, thus, oxygen dissociative adsorption energy. For this reason, core/shell Cu/Pd, Co/Pd, and Mo/Pd systems may be similar to Pt in catalyzing ORRs. In contrast, the presence of a more electronegative Au core does not favor the increase in Pt activity for the ORR, but the Au core can help to enhance shell stability.

Considering Au (or Ag) core and Cu alloy effects on Pd ORR catalysis, we chose to study a ternary system based on core/shell Ag/CuPd or Au/CuPd NPs to understand how the Ag (or Au) core and CuPd alloy effects can be used to tune and optimize Pd catalysis for the ORR. Herein, we present our study on tuning M/CuPd (M = Ag, Au) into the active ORR catalyst in 0.1 M KOH solution. The unique aspect of the ternary core/shell M/CuPd for ORR is that it allows the dual tuning of both surface strain and composition to achieve more rational control on catalytic properties and to facilitate catalysis optimization. Our computational and experimental data both show that CuPd alloy composition and shell thickness are important to control the ORR activity of the Ag/CuPd NPs. The optimal Cu concentration and CuPd shell thickness are 37(±3)% and ~1 nm, respectively. Au as a core in the core/shell structure can further improve CuPd catalysis for the ORR. Among the different catalysts studied, including Ag, CuPd, Ag/CuPd, and Au/CuPd as well as commercial Pt, Ag/CuPd and Au/CuPd core/shell NPs under the optimal tuning show the
highest mass activity for the ORR at 0.18 and 0.20 A/mg of noble metal, respectively, at −0.1 V (vs Ag/AgCl) and retain 77.6% of this activity after 48000 s i−i test. As a comparison, the commercial Pt catalyst (Fuel Cells Store) has a mass activity of 0.06 A/mg of Pt and retains 62.9% activity after the same stability test. Our studies demonstrate an important route to the rational design and synthesis of highly active non-Pt catalysts for the ORR.

■ EXPERIMENTAL METHODS AND COMPUTATIONAL MODELS

Chemicals and Materials. Oleylamine (OAm, >70%), 1-octadecene (ODE), oleic acid (OA), palladium acetylacetonate (Pd(acac)2), copper acetylacetonate (Cu(acac)2), HAuCl4, H2O2 silver nitrate, 1,2-tetradeccanediol, hexane, isopropl alcohol, ethanol, and Naïon (5%) were all purchased from Sigma-Aldrich. The C–Pt (20%) mass loading, respectively, were performed on a potentiostat (Autolab). Measurements on a glassy-carbon (GC) electrode using Ag/AgCl (vs 4.0) to form a 4 mg/mL suspension.

Electrochemistry. Prior to the surface coating, the GC electrode (5 mm in diameter) was polished with 1.0 and 0.05 μm alumina powders, respectively, and rinsed with deionized water, followed by successive sonications in ethanol and doubly distilled water. The electrode was allowed to dry under nitrogen. A 5 μL portion of catalyst ink was cast on the GC electrode and dried. The counter electrode was Pt wire, and the reference electrode was Ag/AgCl (4 M KCl). The electrolyte was N2-saturated 0.1 M KOH solution. All of the catalyst electrodes were cleaned with a steady-state CV in the range of −0.8 to +0.1 V (vs Ag/AgCl) at 100 mV/s for 20 cycles. ORR measurements were conducted in O2-saturated 0.1 M KOH solution. The disk rotation rate was set at 1600 or 400 rpm. The potential scan rate was at 10 mV/s.

Calculations of ΔEF on Intermetallic CuPd Surface. The E0 value was determined by placing an O atom on the fcc hollow site following

\[ E_0 = E[\text{PdCu}+O] - E[\text{PdCu}] - E[O_2]/2 \]

where \( E[\text{PdCu}+O] \) and \( E[\text{PdCu}] \) are total energies of the PdCu alloy surface with and without O adsorbate, respectively. \( E[O_2] \) is the total energy of an oxygen molecule. For DFT calculations of total energies, we used \( 3 \times 3 \times 3 \sqrt{3}R30^\circ \) surface unit cells. A four-layer slab was used for these calculations with the top two layers fully relaxed. The optimal E0 value is 0.2 eV higher than that on a Pt(111) flat surface.17,18 The \( \Delta E_0 \) value was then calculated by shifting \( E_0 \) relative to this optimal value.

Calculation of Surface Strain on Core/Shell NPs. We construct the cuboctahedral models to represent core/shell NPs as shown in Figure 1b,d. To model the random alloy shell, 10 randomly generated atomic structures were examined to provide the strain distribution. All atoms were fully relaxed by the embedded atom method (EAM) interatomic potentials.38 There are eight (111) facets in the cuboctahedral NP, and for each (111) facet we selected three O-adsorbed sites (fcc hollow sites) to measure the local strain. Thus, for each NP model, 240 sites were included in the strain distribution.

Calculation of Interfacial Energy. Two 4 × 2 slabs with four atomic layers were used to calculate the interfacial energy (Figure 1f), with the bottom two layers being the core material M (M = Au, Ag). The left part of Figure 1f corresponds to the PdCu/CuM interface and the right part to the CuPd/CuM interface. The interfacial energy difference is defined as

\[ \Delta E[M] = E[\text{PdCuM}] - E[\text{CuPdM}] \]

where \( E[\text{PdCuM}] \) and \( E[\text{CuPdM}] \) are the total energies of the PdCuM and CuPdM interfaces, respectively.

Computational Parameters. The DFT calculations were carried out using the VASP package59,60 with the projector augmented wave potentials (PAW)41 and Perdew–Burke–Ernzerhof generalized gradient approximation (PBE-GGA).42 An energy cutoff of 400 eV was used for the plane-wave basis set. The Brillouin zone was sampled on the basis of the Monkhorst–Pack scheme with a \( 3 \times 3 \times 1 \) k-point mesh.53

■ RESULTS AND DISCUSSION

Computational Studies of M/CuPd NPs. To understand the effects of alloy composition, shell thickness, and core material of M/CuPd NPs on Pd–O bonding and further on the
ORR activity, we employed density functional theory (DFT) to analyze the oxygen adsorption energy ($\Delta E_O$), a commonly used descriptor for ORR activity, on different kinds of NP surfaces. Since oxygen overbinds to Pd and Cu surfaces ($\Delta E_O$ is negative), the goal is to design CuPd alloys with less negative $\Delta E_O$ values to achieve higher ORR activities. First, we focus on the dependence of $\Delta E_O$ on the surface strain and chemical composition of intermetallic CuPd (the disordered CuPd alloys have similar dependence; see Figure S1 (Supporting Information)). Specifically, three chemical compositions with Cu/Pd atomic ratios of 2/7, 1/2, and 2/1, each under a compression from 0 to 5%, were examined. Figure 1a depicts $\Delta E_O$ as a function of the surface strain and chemical composition on the flat (111) surface of the CuPd alloys. We see a monotonic increase of $\Delta E_O$ with respect to the compression of the alloys. Since Cu has a smaller lattice constant than Pd, alloying more Cu would increase the compression and $\Delta E_O$ value. However, a large Cu concentration (green curves in Figure 1a) actually lowers $\Delta E_O$ which is consistent with the fact that oxygen binds too strongly on the Cu surface. Hence, there is a competition between the strain and chemical effects with respect to Cu concentration.

Three cuboctahedral NP models are constructed to represent Ag/Cu$_x$Pd, with $x/y = 2/7$, 1/2, and 2/1, and these core/shell NPs have the same core diameter of 3.2 nm (16 atomic layers) and shell thickness of 0.8 nm (4 atomic layers) (Figure 1b). All CuPd alloy shells are set to have a solid solution structure to estimate the strain distribution on the shells. As shown in Figure 1c, the higher the Cu concentration in the alloy, the greater the compressive strain on the NP surface. On the basis of the strain distributions and the alloy compositions, we estimated the $\Delta E_O$ distribution for each NP as indicated by the dashed boxes in Figure 1a. The horizontal and vertical positions of each box represent the range of the strain and $\Delta E_O$ for each NP, respectively. The ORR activity of the core/shell NPs is ranked as Ag/CuPd$_2$ > Ag/Cu$_2$Pd$_7$ > Ag/Cu$_2$Pd and the optimized Ag/CuPd NPs even surpass Pt for the ORR.

We chose Ag/CuPd$_2$ NPs to study the shell thickness effect on the ORR. Three different core/shell NPs with shell thicknesses of 0.4, 0.8, and 1.2 nm were examined, and their structures and surface strain distributions are shown in Figure 1d,e. We can see that the shell becomes more compressive as the thickness increases. The Ag/CuPd$_2$ NPs with 0.8 and 1.2 nm shell thicknesses show the strain distributions similar to but better than those with 0.4 nm shells for the ORR. Since the NPs have the same chemical composition and only the strain effect is at play, we conclude that for Ag/CuPd$_2$, either a 0.8 or a 1.2 nm CuPd shell would have a higher ORR activity.

To study the core effect on CuPd shell strain, we replaced Ag with Au and calculated the surface strain distribution (Figure 1f). We can see that surface strain distributions are independent of the core materials. We calculated the interfacial energy between the PdCu shell and the core (Au or Ag). For simplicity, we modeled the shell by a bilayer PdCu (Pd on top of Cu) vs CuPd (Cu on top of Pd) (Figure 1f). When the core is Au, the PdCuAu interface is energetically more stable than the CuPd/Au interface with an energy difference of $-264$ mJ/m$^2$. If the core is Ag, the PdCuAg interface is energetically less stable than the CuPd/Ag interface with an energy difference of $+5$ mJ/m$^2$. Therefore, with Au as the core, it is energetically favorable for Pd to segregate at the NP surface, leading to higher ORR activity.

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**Figure 1.** (a) $\Delta E_O$ as a function of strain and composition. Black, red, and green curves represent Cu/Pd atomic ratios of 2/7, 1/2, and 2/1, respectively. Several curves in each color correspond to various fcc hollow sites for O adsorption. $\Delta E_O$ on the Pt(111) surface is indicated by the dashed horizontal line. Black, red, and green boxes outline the possible $\Delta E_O$ values on Ag/Cu$_x$Pd$_y$, Ag/Cu$_2$Pd$_y$, and Ag/Cu$_2$Pd NPs, respectively. (b, c) Models of core/shell NPs for various shell compositions with a shell thickness of 0.8 nm (b) and evaluated distribution of surface strain on these core/shell NPs (c). The dashed curve in (c) indicates Au/CuPd$_2$ NPs. (d, e) Models of core/shell NPs for various shell thickness with a composition of CuPd$_2$ (d) and evaluated distribution of surface strain on these core/shell NPs (e). (f) Slab models for calculation of PdCuM (left) and CuPdM (right) interfacial energies.
Synthesis of M/CuPd NPs. Our computational results indicate that Ag/CuPd 2 NPs with 0.8 and 1.2 nm shell thicknesses may surpass Pt on catalysis for the ORR and replacing Ag with Au can further optimize the ORR catalysis. To confirm these predictions, we developed a seed-mediated growth method to prepare monodisperse core/shell M/CuPd NPs for electrocatalytic studies of ORR. In the synthesis of Ag-based core/shell NPs, we first prepared monodisperse Ag NPs by reacting 380 mg of silver nitrate with 20 mL of OAm in the presence of 0.4 mL of OA at 120 °C for 18 h (see Experimental Methods and Computational Models). Figure 2a shows the typical TEM image of the Ag NPs. The Ag NPs have an average size of 3.1 ± 0.2 nm. To synthesize Ag/CuPd NPs, 30 mg of Pd(acac) 2 and 26 mg of Cu(acac) 2 were added to a solution of 10 mL of ODE, 1.0 mL of OAm, 1.0 mL of OA, and 0.2 g of 1,2-tetradodecanediol, and the solution was heated to 80 °C. A 30 mg portion of Ag seeds dispersed in 2 mL of ODE was added to the above mixture, and the solution was further heated to 200 °C for 25 min. The product was precipitated out by adding isopropyl alcohol and washed with isopropyl alcohol and ethanol, respectively, before it was dispersed in hexane. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was used to measure the composition of the as-prepared Ag/CuPd NPs. The synthesis yielded Ag/Cu37Pd63 with a 0.75 ± 0.05 nm shell, denoted as Ag/Cu37Pd63-0.75 (Figure 2b). With the amount of Ag NPs and Pd(acac) 2 fixed, the composition of the CuPd shell could be tuned by controlling the molar ratio of Pd(acac) 2 to Cu(acac) 2. Under the same reaction conditions as in the synthesis of Ag/Cu37Pd63 NPs, 30 mg of Pd(acac) 2 + 26 mg of Cu(acac) 2 and 30 mg of Pd(acac) 2 + 52 mg of Cu(acac) 2 resulted in Ag/Cu20Pd80 (Figure S2a, Supporting Information) and Ag/Cu55Pd45 (Figure S2b, Supporting Information), respectively. Furthermore, with the amount of Ag NPs and the molar ratio of Pd(acac) 2 to Cu(acac) 2 fixed, the shell thickness of CuPd could be tuned from 0.4 ± 0.05 nm (denoted as Ag/Cu37Pd63-0.4; Figure S3a, Supporting Information) to 1.1 ± 0.10 nm (denoted as Ag/Cu37Pd43-1.1; Figure S3b, Supporting Information) when 15 mg of Pd(acac) 2 and 13 mg of Cu(acac) 2 and when 60 mg of Pd(acac) 2 and 52 mg of Cu(acac) 2 were added, respectively. Similarly, when 3.1 nm Au NPs (Figure S4a, Supporting Information) or 5 nm Au NPs (Figure S4b, Supporting Information) (see Experimental Methods and Computational Models) were used as seeding NPs, 4.6 ± 0.3 nm Au/CuPd NPs (Figure 2c) or 7.0 ± 0.4 nm Au/CuPd NPs (Figure S4c, Supporting Information) with a 0.8 ± 0.05 nm shell were also prepared. Figure S5 (Supporting Information) shows the XRD patterns of the face-centered cubic (fcc) Ag, Ag/Cu20Pd80, Ag/Cu37Pd63, and Cu40Pd60 NPs. The diffraction peaks from the Ag/CuPd core/shell NPs are between those from Ag and CuPd NPs, indicating that the formation of the core/shell structure leads to the expansion of CuPd lattice spacing. High-resolution TEM (HRTEM) was used to analyze the detailed structure of a single Ag/CuPd NP, as shown in Figure 2d. The CuPd lattice fringes have a 0.224 nm spacing, close to {111} interplanar distance of fcc-CuPd (0.223 nm) but shorter than that of fcc-Ag (0.238 nm). The elemental distribution within the core/shell structure was characterized by aberration-corrected STEM-EELS (Figure 2e,f), showing that NPs contain Pd in the outside shell and Ag (or Au) in the core. It should be noted that, from the CuPd and CuAg phase diagram (Figure S6, Supporting Information), Cu forms an alloy much easier with Pd than with Ag. Therefore, Cu would stay in the shell of Ag/CuPd core/shell NPs but it cannot be detected easily by STEM-EELS in the thin CuPd shell.

Electrocatalysis of M/CuPd NPs. The electrocatalytic performance of the as-synthesized M/CuPd NPs were studied by cyclic voltammetry, the rotating disk electrode technique, and the current (i)−time (t) technique. To perform these tests, the as-prepared NPs were first deposited on the Ketjen carbon support (EC-300J) via sonicating two constituents (the
Figure 3. (a, b) Mass activity comparison at $-0.2$ V of Ag/CuPd NPs with different shell composition (a) and thickness (b) in O₂-saturated 0.1 M KOH solution at a scan rate of 10 mV/s. Rotation rate: 1600 rpm. (c) ORR polarization curves of Ag/Cu₃₇Pd₆₃ NPs at different rotation rates; (d) K-L plots of the ORR from Ag/Cu₃₇Pd₆₃ NPs. (e, f) ORR polarization curves (e) and ORR mass activity summaries (f) at $-0.1$ V of Ag/Cu₃₇Pd₆₃, Cu₄₀Pd₆₀, and Ag NPs in O₂-saturated 0.1 M KOH solution at 293 K. Scan rate: 10 mV/s. Rotation rate: 1600 rpm.

Figure 4. (a, b) ORR polarization curves (a) and ORR mass activity summaries (b) at $-0.1$ V of Ag/Cu₃₇Pd₆₃ and Au/Cu₄₀Pd₆₀ in O₂-saturated 0.1 M KOH solution at 293 K. Scan rate: 10 mV/s. Rotation rate: 1600 rpm. (c) ORR polarization curves of Au/Cu₄₀Pd₆₀ NPs at different rotation rates. (d) K-L plots of the ORR from Au/Cu₄₀Pd₆₀ NPs.
mass ratio of NP to C is 1/2) in hexane and then heated to 150 °C overnight to remove the surfactant according to the previous method. These M/CuPd NPs were uniformly distributed on a carbon support, as shown in Figure S7 (Supporting Information) (denoted as C-M/CuPd). The treated C-NP catalysts were redispersed in deionized water/isopropyl alcohol/5% NaBr (4/1/0.05 v/v/v) to reach a concentration of 4 mg/mL. A 5 μL portion of the catalyst ink was casted on the surface of the GC electrode and dried under ambient conditions. Figure S8a (Supporting Information) and Figure 3a show typical ORR polarization curves (Figure S8a) and mass activity comparisons (Figure 3a) of the Ag/CuPd NPs with different shell compositions obtained at room temperature in O2-saturated 0.1 M KOH. From Figure 3a, we can see that Ag/Cu37Pd63 NPs have the highest ORR activity among all Ag/CuPd NPs studied. The effect of the shell thickness of CuPd on the ORR activity of Ag/CuPd NPs was also investigated, as shown in Figure S8b (Supporting Information) and Figure 3b. The NPs with 0.75 nm shells have ORR activities similar to those with ∼1.1 nm shell but activities higher than those with 0.4 nm shells, which is consistent with our computational prediction.

Rotating disk electrode (RDE) measurements were used to study the ORR kinetics of the Ag/Cu37Pd63 NPs in 0.1 M KOH (Figure 3c). The number of electrons involved in the reduction of one O2 molecule on the Ag/Cu37Pd63 NPs was determined via a combination of RDE techniques and the Koutecky–Levich (K-L) equation. The corresponding K-L plots (Figure 3d) give n = 4.0 from −0.2 to −0.4 V, revealing that the Ag/CuPd NPs still favor a 4e oxygen reduction process.

The ORR catalytic activity of the optimized Ag(Au)/CuPd NPs was further compared with that of the commercial Pt catalyst in the O2-saturated 0.1 M KOH solution (Figure 5a). Both Au/Cu40Pd60 and Ag/Cu37Pd63 NPs have half-wave potentials more positive than that of the commercial Pt catalyst. In order to give quantitative information on the ORR activity of different catalysts, the corresponding Tafel plots (Figure 5b) and ORR mass activities at −0.1 V (normalized against all noble metals present in the catalyst) were
To summarize, our DFT calculations predict that M/CuPd (M = Ag, Au) NPs with 0.8 and 1.2 nm CuPd$_x$ shells have the optimal surface strain and composition to catalyze ORR. We prepared monodisperse M/CuPd NPs experimentally by co-precipitation of Pd(acac)$_2$ and Cu(acac)$_2$ in the presence of 3.1 nm Ag or Au seeds with shell thicknesses controlled at 0.4, 0.75, and 1.1 nm and compositions at Cu$_{25}$Pd$_{75}$, Cu$_{50}$Pd$_{50}$, and Cu$_{75}$Pd$_{25}$. These controls allow us to tune both shell electronic structure and surface strain to maximize ORR performance. In 0.1 M KOH solution, the Au/Cu$_{50}$Pd$_{50}$ and Ag/Cu$_{50}$Pd$_{50}$ catalysts with 0.75 and 1.1 nm shell coatings are more efficient for ORR than any other M/CuPd catalysts with different Cu/Pd compositions, CuPd NPs, and Ag studied in this paper. They have a mass activity of about 0.20 A/mg of noble metal that is over 3 times higher than that from the commercial Pt (0.06 A/mg of Pt). They also exhibit higher durability than the Pt catalyst, retaining 77.6% of their activity after 48000 s $i-t$ test (62.9% for the Pt catalyst). Our study highlights the important aspect of tuning surface strain and composition in the core/shell structure to maximize its ORR performance and to develop more advanced NP catalysts with ORR catalysis superior to that of Pt. The strategy demonstrated here can be extended to other core/shell systems, making it possible to design and tune NP catalysis for other important chemical reactions.

**ASSOCIATED CONTENT**

1. Supporting Information
   Figure S1–S9, giving additional structures, TEM images, and plots. This material is available free of charge via the Internet at http://pubs.acs.org.

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