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Pt skin coated hollow Ag-Pt bimetallic nanoparticles with high catalytic activity for oxygen reduction reaction



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HIGHLIGHTS

- Pt skin coated hollow Ag-Pt nanoparticle was prepared by a nonheating route.
- This Ag/Pt catalyst shows excellent ORR catalytic performances.
- The hollow structure raises the Pt utilization and thus the catalytic activity.
- The experimental results can be well supported by the DFT calculation results.

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G R A P H I C A L A B S T R A C T



ABSTRACT

The catalytic activity and stability of electrocatalyst is critical for the commercialization of fuel cells, and recent reports reveal the great potential of the hollow structures with Pt skin coat for developing high-powered electrocatalysts due to their highly efficient utilization of the Pt atoms. Here, we provide a novel strategy to prepare the Pt skin coated hollow Ag-Pt structure (Ag-Pt@Pt) of ~8 nm size at room temperature. As loaded on the graphene, the Ag-Pt@Pt exhibits a remarkable mass activity of 0.864 A/mg_{Pt} (at 0.9 V, vs. reversible hydrogen electrode (RHE)) towards oxygen reduction reaction (ORR), which is 5.30 times of the commercial Pt/C catalyst, and the Ag-Pt@Pt also shows a better stability during the ORR catalytic process. The mechanism of this significant enhancement can be attributed to the higher Pt utilization and the unique Pt on Ag-Pt surface structure, which is confirmed by the density functional theory (DFT) calculations and other characterization methods. In conclusion, this original work offers a low-cost and environment-friendly method to prepare a high active electrocatalyst with cheaper price, and this work also discloses the correlation between surface structures and ORR catalytic activity for the hollow structures with Pt skin coat, which can be instructive for designing novel advanced electrocatalysts for fuel cells.

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1. Introduction

Proton exchange membrane fuel cell (PEMFC) is regarded to be one of the most prospective energy conversion devices for various

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power supply applications because of their efficient and clean advantages. Although this technology is increasingly maturing and gradually improving, it still faces many problems and challenges, especially in the cost and durability [1,2]. One solution is to develop novel cathode electrocatalysts with better mass activity towards oxygen reduction reaction (ORR) and higher catalytic stability [3]. And the Pt-based metallic catalysts are promising candidates for replacing current pure platinum catalyst due to their good electroconductibility, superior catalytic activity [4], well controllability of their composition and structure [5], and wide practicability in low and high temperature fuel cells [6]. Therefore, although the advanced non-metallic catalysts show the excellent catalytic performance [7] nowadays, the Pt-based metallic catalysts are still worth being studied.

Up to now, many methods have been taken to improve the performance of Pt-based metallic catalysts. One successful research work is hollow structure or Pt skin coat deposited on non-noble metal substrate [8,9]. Compared to the pure Pt catalysts, the Pt-based bimetallic catalysts with Pt skin coated structure or hollow structure can utilize Pt atoms more efficiently and then lead to higher mass activity [10,11]. Moreover, by varying the surface atom arrangement of metal-Pt catalysts, the electronic structure of Pt can be regulated which is also helpful for improving the ORR catalytic activity of Pt [12–14].

In our previous work [15], we reported a ~20 nm Pt-coated hollow Ag-Pt bimetallic catalyst with higher ORR catalytic activity and better stability than that of the commercial Pt/C catalyst (from Johnson-Matthey) and the Ag@Pt core-shell structure. The enhancement was due to the successful elimination of the tensile effect between Ag and Pt, which would raise the d-band center of Pt and then reduce its activity towards ORR [16–18]. Therefore, the Pt on Ag-Pt structure is potential for catalyzing ORR.

Herein, we used a novel non-heating method modified from our reported method [15] to prepare much smaller Pt-skin-coated hollow Ag-Pt nanoparticle (Ag-Pt@Pt) (~7.5 nm). Then we compared its ORR catalytic performance with the hollow Ag-Pt nanoparticle (Ag-Pt only, without Pt skin) and commercial Pt catalyst (Pt/C). And to further investigate the Pt skin on Ag-Pt structure, the density functional theory (DFT) calculation was applied. We also tested the supporting effect of different carbon supports by loading the nanoparticles onto amorphous carbon (Vulcan XC-72R) and reduced graphene oxide (rGO).

After loading the nanoparticles on carbon supports and measuring their ORR performance, we found that the Ag-Pt@Pt supported on carbon (Ag-Pt@Pt/C) showed better ORR performance than Ag-Pt nanoparticle on carbon (Ag-Pt/C, without Pt skin) and Pt/C, which demonstrated that the Pt skin on Ag-Pt structure possessed better ORR activity, and this conclusion could be supported by the DFT calculation results and other characterization results. The highest mass activity was procured from the Ag-Pt@Pt supported on rGO (Ag-Pt@Pt/rGO) sample, which showed an outstanding ORR catalytic activity of 0.864 A/mg_{Pt}, which was 5.30 times of the commercial Pt/C catalyst and brought a significant step forward for the field of ORR electrocatalysts. Meanwhile, the Ag-Pt@Pt/rGO was more stable than other samples during catalytic process, indicating that the performance of catalyst could be further improved if loaded on the support with better physical or chemical property.

2. Experimental

2.1. General materials

Sodium borohydride (NaBH₄, 98%) and Silver nitrate (AgNO₃, 99.8%) were obtained from Aladdin Industrial Co. Ltd. (Shanghai,

China). Potassium tetrachloroplatinate (K₂PtCl₄, 99.95%) was purchased from J&K Scientific Ltd. (Beijing, China). Ascorbic acid (analytical grade), polyvinylpyrrolidone (PVP, K-30), trisodium citrate dehydrate (sodium citrate, analytical grade), ammonia solution (25%) and perchloric acid (HClO₄, analytical grade) were bought from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Vulcan XC-72R carbon support (Cobalt Corp.), Nafion ionomer (5 wt %) and commercial 40 wt% Pt/C (Johnson Matthey, HiSPECTM 4000) were purchased from Shanghai Hesen Electrical Ltd. (Shanghai, China).

The purity of other reagents was analytical grade and used without any further purification.

2.2. Synthesis of Ag nanoparticles

We used a modified NaBH₄ reduction of AgNO₃ process to synthesize the Ag nanoparticles of ~5 nm size. 9.0 mg PVP, 8.0 mg sodium citrate and 3.0 mg AgNO₃ were dissolved into 10 mL deionized water in a round bottom flask. And then, with mighty stirring at room temperature, 0.4 mL NaBH₄ aqueous solution (100 mM) was added. Some gas would be produced and the color of the mixture quickly changed from colorless to dark brown after the addition of NaBH₄. The mixture was stirred for 24 h for the complete decomposition of NaBH₄. After that, an aqueous brownish red Ag nanoparticles dispersion was obtained.

2.3. Synthesis of hollow Ag-Pt bimetallic nanoparticles (Ag-Pt)

In a typical synthetic process, 6.0 mg ascorbic acid was added into previously-synthesized Ag nanoparticles dispersion. After being vigorous stirred for 30 min, 11.0 mg K₂PtCl₄ (The atomic ratio of Ag: Pt is 40: 60) dissolved in 0.5 mL deionized water was dropwise added. The color of the mixture would change from brownish red to black immediately. After constantly stirring for 3 h, the hollow Ag-Pt nanoparticles were precipitated with abundant acetone, and redisperse in 2 mL deionized water.

2.4. Synthesis of Pt skin coated hollow Ag-Pt nanoparticles (Ag-Pt@Pt)

3.0 mg ascorbic acid, 5.0 mg PVP and hollow Ag-Pt nanoparticles were stirred for 1 h at room temperature, and then 1.3 mL K₂PtCl₄ solution (10 mM) was added (the atomic ratio of Ag: Pt is ~30: 70). The solution was kept at room temperature for 2 h and the synthesized Ag-Pt@Pt nanoparticles were precipitated with abundant acetone for twice, and redispersed in 2 mL deionized water.

The Pt skin can be formed on the surface of hollow Ag-Pt nanoparticles without collecting and redispersing the hollow Ag-Pt nanoparticles, which makes the preparation of Pt skin coated hollow Ag-Pt nanoparticles a one-pot approach and it can produce the same product.

2.5. Synthesis of reduced graphene oxide (rGO)

To obtain reduced graphene oxide (rGO), a facile reduction process [19] was used on the graphene oxide (GO) obtained from modified Hummer method [20]. The prepared GO was dispersed in deionized water and the pH of this dispersion was adjusted to ~10 with ammonia solution. Then, calculated amount of ascorbic acid was added into the GO dispersion (the concentration of the ascorbic acid was 2 mM) and the whole mixture was heated to 95 °C and stirred for 30 min. Finally, the rGO was collected via precipitation and washed with deionized water thrice.

2.6. Loading the nanoparticles onto support material

Specific amount of the support material (Vulcan XC-72R carbon support or rGO) was sonicated for 5 h in 1 mL H₂O. After that, the Ag-Pt or Ag-Pt@Pt nanoparticles dispersion was added into the sonicated support material dispersion. The Pt loading amount was fixed at 40 wt% in all the catalysts. After constantly stirring for 24 h, the Ag-Pt on carbon support (Ag-Pt/C, 40 wt% Pt), Ag-Pt@Pt on carbon support (Ag-Pt@Pt/C, 40 wt% Pt) or Ag-Pt@Pt on rGO (Ag-Pt@Pt/rGO, 40 wt% Pt) were collected by precipitation. The samples were dried at room temperature in vacuum after being washed twice with ethanol.

2.7. Characterization

The transmission electron microscopy (TEM) images and electron energy dispersive X-ray (EDX) analysis of the samples were obtained by FEI Tecnai G2 F30. The elemental contents were measured by inductively coupled plasma (ICP, NCS Testing Technology, Plasma1000) technique. Their X-ray diffraction (XRD) patterns were characterized with a Mini Flex 600X-ray diffractometer (Rigaku) using Cu K α radiation at the scan rate of 2.0°/min. X-ray photoelectron spectroscopy (XPS) was carried out via a PHI QUANTUM 2000 using Al Ka radiation. The samples were dropped on small Si slice for XPS measurement. And the binding energy was referenced to the C1s spectrum at 284.6 eV.

2.8. Electrochemical measurements

A CHI 730E dual channel electrochemical workstation (CH Instruments, Inc.) with a three-electrode cell was applied to carry out the electrochemical measurements. The reference electrode was a KCI-saturated leak-free Ag/AgCl electrode and the counter electrode was a graphite electrode. All the potentials were recorded with respect to a reversible hydrogen electrode (RHE).

Dried samples (1.5 mg catalyst), ethanol (980 μ L) and Nafion ionomer (5 wt%; 20 μ L) were sonicating for 3 h to prepare catalyst ink. After that, 5 μ L ink was moved onto the freshly polished glassy carbon of a rotating disk working electrode (RDE, 0.247 cm² in surface area, PINE Instrument Co. Ltd) and left to dry. The Pt loading on all working electrode is 3 μ g (12.15 μ g/cm²).

Cyclic voltammetry (CV) curves were recorded in N₂-saturated 0.1 M HClO₄ at the scan rate of 50 mV/s. The CO stripping curves were obtained by CV scanning of the working electrode kept at 0.05 V in CO (>99.9%, Xinhang)-saturated 0.1 M HClO₄ for 20 min. The solution was purged with N₂ for 25 min before the -0.05-1.30 V scanning with the scan rate of 50 mV/s. The linear scanning voltammetry (LSV) were recorded in O₂-saturated 0.1 M HClO₄ solution at the scan rate of 10 mV/s and the rotating speed of 1600 rpm. And the accelerated durability test (ADT) was carried out by cycling between 0.6 and 1.0 V for 15000 cycles in the O₂-saturated 0.1 M HClO₄ solution at a scan rate of 50 mV/s. The process of ADT - 80 °C was the same as the ADT, but the cycling number is 4000 and the operation temperature is 80 °C.

The tests were performed at room temperature unless otherwise stated.

2.9. Density function theory (DFT) calculation

Two slabs were built to model the adsorption of oxygen on fcc sites of different surfaces. For both slabs, the three bottom layers were set to be fixed, and the Pt on Ag-Pt was modeled by placing two and three Pt layers on the Pt₃Ag substrate. All slabs are constructed from (2×2) unit cells to make sure that the coverage of oxygen is 0.25. The vacuum layer of our calculated slabs was set to

12 Å.

Oxygen adsorption energy was calculated by the following equation:

$$\Delta E_{O} = E(slab + O) - E(slab) - 1/2E(O_{2})$$

Calculations of oxygen adsorption energy of Ag-Pt, Pt on Ag-Pt and Pt (111) surface were performed by Vienna *ab initio* simulation package (VASP) [21]. We chose the projector augmented-wave (PAW) approach [22]. To describe the exchange-correlation functional, the generalized gradient approximation (GGA) was selected as the parameter of Perdew, Bruke, and Ernzerhof (PBE) [23]. For all calculations, we set the energy cutoffs to 550 eV, which was chosen by our convergence test. The Kohn-Sham equations were solved for the following valence states: O(2s2p), Pt(6s5d), and Ag(5s4d).

More details can be found in the supplementary material.

3. Results and discussion

3.1. Synthetic process of Ag-Pt/C, Ag-Pt@Pt/C and Ag-Pt@Pt/rGO

There are two factors that favor this non-heating synthesis route. First one is the small size of the Ag nanoparticle. The Ag nanoparticle with a smaller size has higher surface energy which could facilitate the galvanic replacement reaction between Ag nanoparticle and $PtCl_4^{2-}$. So, to reduce the diameter of the Ag nanoparticle, PVP was added in the preparing process to limit the growth of Ag nanoparticles. As a result, the diameter of the Ag nanoparticles is 3–5 nm (as shown in Fig. S1) and ~10 nm [15], with and without PVP, respectively. Therefore, in this work, the galvanic replacement can be carried out at room temperature, while ~10 nm Ag nanoparticle has to be heated to 80 °C to react with $PtCl_4^2$. And the other key factor is that the Pt complex can be reduced by ascorbic acid at low temperature, which was reported by several literature recently [24,25]. The decrease of the reaction temperature results in energy efficiency and environmental protection benefits.

The $PtCl_4^{2-}$ can be reduced by ascorbic acid (reduction reaction) or Ag atoms of Ag nanoparticles (galvanic replacement reaction), and the change of the reaction rate of these two competing reaction could result in different structure [26]. As shown in Scheme 1, under the experimental condition reported in this work, a well-controlled hollow Ag-Pt bimetallic shell with uniform shell thickness can be obtained. And then, the second time reduction of $PtCl_4^{2-}$ would epitaxially deposit Pt atom on hollow Ag-Pt shell and form a thin Pt outer shell, which is called Pt skin. Finally, a Pt skin coated hollow Ag-Pt structure (Ag-Pt@Pt) is built.

The nanoparticles were loaded on carbon support for better dispersion (Ag-Pt/C and Ag-Pt@Pt/C as the abbreviation), and to compare the effect of different carbon support, Ag-Pt@Pt was also loaded on reduced graphene oxide (shorten as Ag-Pt@Pt/rGO).

3.2. Characterization of Ag-Pt/C, Ag-Pt@Pt/C and Ag-Pt@Pt/rGO

TEM images of Ag-Pt/C, Ag-Pt@Pt/C and Ag-Pt@Pt/rGO are presented in Fig. 1 and Fig. S2. The nanoparticles disperse well on the support and their hollow structure can be confirmed. The hollow Ag-Pt nanoparticles have the diameter of ca. 6.34 nm and the thickness of ca. 1.20 nm, and the lattice spacing of 0.230 nm are found in the inner part and the surface of Ag-Pt nanoparticle. The 0.230 nm spacing is located between the Ag (111) planes (0.2359 nm, JCPDS no. 04-0783) and Pt (111) planes (0.2265 nm, JCPDS no. 04-0802) and can be ascribed to Ag-alloyed-Pt. The average size of Ag-Pt@Pt nanoparticles is 7.52 nm and the shell enlarges to ca. 1.80 nm due to the coating of Pt skin. The spacing of



Scheme 1. The synthesis of hollow Ag-Pt nanoparticle and hollow Ag-Pt@Pt nanoparticle.

lattice fringes in the inner part of Ag-Pt@Pt is 0.230-0.231 nm, and different from Ag-Pt nanoparticle, the lattice fringes in the skin part of Ag-Pt@Pt show a 0.227 nm spacing, which is corresponding to the pure Pt skin.

Fig. 2 shows the XRD patterns, which are applied to further characterize the structure of synthesized samples. The three Ag/Pt samples have similar XRD patterns that all their diffraction peaks are located between the diffraction peaks of pure Ag (JCPDS No.04-0783) and pure Pt (JCPDS No.04-0802), which is due to the alloying of Ag and Pt, and this result indicates that the main structure of the samples is Ag-alloyed-Pt. In the pattern of Ag-Pt/C, the peak of plane (111) is near $2\theta = 38.7^{\circ}$, and in the patterns of Ag-Pt@Pt/C and Ag-Pt@Pt/rGO, the peak of plane (111) move to $2\theta = 39.2^{\circ}$, which is more close to the pure Pt. So the XRD measurement also confirms the difference of structure between the hollow Ag-Pt and the hollow Ag-Pt@Pt. The XRD patterns of as-prepared graphene oxide (GO) and reduced graphene oxide (rGO) are presented in Fig. S3. In the pattern of rGO, the characteristic diffraction peak of GO $(2\theta = 9.6^{\circ})$ [27] disappears in consequence of the successful reduction process of GO.

The elemental distributions of Ag-Pt nanoparticle and Ag-Pt@Pt nanoparticle were characterized by line scan EDX. The line scan results of Ag and Pt of samples are shown in Fig. 3. For Ag-Pt sample, both Ag and Pt show curves like trapezoid with a concave upper side, which is typical for hollow particle. The curves of Ag-Pt@Pt sample is also typical for hollow structure, but the

distribution range of Pt is obviously large than Ag. This result strongly proves the Pt skin on Ag-Pt hollow structure, and the thickness of the Pt skin can be estimated from the gap between the distribution range of Ag and Pt (labeled by the dashed lines), which is 0.76 nm and corresponding to 2-3 Pt monolayers (the radius of Pt is 0.1385 nm [28]).

Table 1 lists the elemental composition of the Ag-Pt/C, Ag-Pt@Pt/C and Ag-Pt@Pt/rGO samples, measured by EDS, ICP and XPS. The atomic Ag: Pt ratio for the reactants of Ag-Pt nanoparticles is 40: 60 and 30: 70 for Ag-Pt@Pt. Similar results are obtained from EDS and ICP measurements that the Ag-to-Pt ratio is about 1: 3 for



Fig. 2. XRD patterns of Ag-Pt/C, Ag-Pt@Pt/C and Ag-Pt@Pt/rGO samples.



Fig. 1. Typical TEM images of Ag-Pt/C (a, e), Ag-Pt@Pt/C (b, f) and Ag-Pt@Pt/rGO (c, g). Red cycles indicate the hollow cavities of the nanoparticles. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Ag-Pt/C and about 1: 4 for both Ag-Pt@Pt/C and Ag-Pt@Pt/rGO. The samples all exhibit lower Ag atomic ratio than the starting precursors because of the losing of Ag during the galvanic replacement reaction. But for Ag-Pt@Pt/C and Ag-Pt@Pt/rGO, the results of XPS, which only analyze the surface of the material, show lower Ag ratios compared to EDS and ICP results. This comparison demonstrates that the surface of Ag-Pt@Pt nanoparticles is Pt-rich, which confirms the Pt skin on Ag-Pt structure.

XPS results are summarized in Fig. S5, Tables S2 and S3 for evaluating the surface composition and valence state of the samples. Fig. 4 shows the regional Pt_{4f} spectra of all samples. Compared to the spectra of Pt/C, the Pt_{4f} peaks of Ag-Pt/C (ca. 71.2 and 74.7 eV) shift positively by ca. 0.1 eV, and for the Ag-Pt@Pt/C and Ag-Pt@Pt/ rGO, the Pt_{4f} peaks (ca. 71.3 and 74.8 eV) shift positively by ca. 0.2 eV. It indicates that the electronic structure of the surface Pt atoms in the obtained materials has been manipulated by the electronic interaction between Ag and Pt [29,30]. The XPS binding energy of Pt atom is strongly related to its d-band center, which is critical for balancing the adsorption and desorption of oxygenated intermediates during the ORR catalyzing procedure. A higher dband center would make the Pt bind oxygen too strongly and thus break the balance [31]. For the prepared samples, the positive shift of binding energy suggests that the d-band center of Pt moves downwards, which will reduce the binding strength of oxygenated species on the Pt of the material surface and may lead to the increase of ORR activity.

3.3. Electrocatalytic performance of hollow Ag-Pt/C, hollow Ag-Pt@Pt/C and hollow Ag-Pt@Pt/rGO towards oxygen reduction reaction (ORR)

To measure the electrocatalytic performance of the nanostructure, the nanoparticles were supported by Vulcan XC-72R carbon or reduced graphene oxide (rGO) with the 40 wt% Pt loading amount (confirmed by ICP, Table S1). Commercial Pt/C catalyst from Johnson Matthey (HiSPECTM 4000, 40 wt% Pt) was selected to be the comparison baseline.

The Ag-Pt/C, Ag-Pt@Pt/C, Ag-Pt@Pt/rGO and Pt/C show similar CV curves (Figs. S6a–d) with typical hydrogen adsorption/desorption peaks of Pt in acidic electrolytes [32]. The Ag-Pt/C catalyst exhibits a typical Ag oxidation peak at ca. 0.56 V (vs. RHE, in the forward sweep) in acid solution, and the Ag peak does not appear in the CV curve of Ag-Pt@Pt/C and Ag-Pt@Pt/rGO, which demonstrates the full coating of the Pt skin on the hollow Ag-Pt nanoparticle in



Fig. 3. Elemental line scan results of nanoparticle on Ag-Pt/C (left) and Ag-Pt@Pt/rGO (right). The scale bar of the high angle annular dark-field scanning TEM images is 2 nm.

Table 1

The atomic Ag: Pt ratios measured by various methods.

Sample	atomic ratios ^a	atomic ratios ^b	atomic ratios ^c
Ag-Pt/C	26: 74	27: 73	28: 72
Ag-Pt@Pt/C	21: 79	22: 78	17: 83
Ag-Pt@Pt/rGO	20: 80	22: 78	16: 84

^a EDS analysis results (Fig. S4).

^b ICP analysis results (Table S1).

^c XPS analysis results (Fig. S5, Table S2).



Fig. 4. High-resolution Pt 4f spectra of Ag-Pt/C, Ag-Pt@Pt/C, Ag-Pt@Pt/rGO and Pt/C.

the two samples.

The CO stripping curves (Fig. 5a) are used to measure the specific electrochemical surface area (ECSA_{CO}), which is obtained from the charge in the subtracted CO oxidation region to the specific charge of monolayer CO adsorption with a ratio of 420 mC/cm² based on Pt mass [33]. The Ag-Pt/C shows the highest ECSA_{CO} of 119.43 m^2/g_{Pt} , and the ECSA_{CO} of Ag-Pr@Pt/C (109.51 m^2/g_{Pt}) and Ag-Pt@Pt/rGO (112.89 m^2/g_{Pt}) are also higher than that of Pt/C $(73.20 \text{ m}^2/\text{g}_{Pt})$. The experimental data are summarized in Fig. 5b. The enhancement in the ECSA is mainly due to the special hollow structure of the Ag/Pt nanoparticles. In the hollow structure, there are less inner Pt atoms which cannot involve the catalytic reaction on the surface compared to solid structure, by improving the utilization of the Pt atom, the ECSA is increased. It is worth mentioning that the peak of absorbed hydroxyl species (ca. 0.65 V of backward sweep) of Ag-Pt@Pt/rGO (44 mV), Ag-Pt@Pt/C (23 mV) and Ag-Pt/C (12 mV) shifts positively compared to the Pt/C. This result implies the faster desorption of OH_{ad} species from the surface of the samples [34,35]. As the OH_{ad} on Pt surface would block O₂ adsorption and the subsequent steps of ORR [36], the ORR catalytic activity of the Ag-Pt@Pt/rGO, Ag-Pt@Pt/C and Ag-Pt/C would be higher than that of Pt/C.

Fig. 5c displays the linear scanning voltammetry curves of the four samples to compare their ORR catalytic activities. The half-wave potentials of Ag-Pt/C, Ag-Pt@Pt/C, Ag-Pt@Pt/rGO and Pt/C are 875 mV, 908 mV, 920 mV and 847 mV, respectively. The calculated kinetic current densities (ik) results were summarized in Table S4. The mass activities (at 0.90 V vs. RHE) of the samples are shown in Fig. 5d. At 0.90 V (vs. RHE), the mass activities of Ag-Pt/C, Ag-Pt@Pt/C, Ag-Pt@Pt/C, Ag-Pt@Pt/rGO and commercial Pt/C are 0.243, 0.611, 0.864 and 0.163 A/mg_{Pt}, respectively. The Ag-Pt@Pt/rGO possesses the highest mass activity which is 5.30 times higher than that of commercial Pt/C, and the Ag-Pt@Pt/C also has a very excellent mass



Fig. 5. (a) CO stripping voltammograms. (b) The electrochemical surface area before and after the accelerated durability test (ADT). (c) Linear scan voltammograms. (d) Kinetic mass activities of the ORR at 0.90 V (vs. RHE) of the fresh and cycled samples.

activity (3.75 times of commercial Pt/C). The mass activities of both Ag-Pt@Pt/C and Ag-Pt@Pt/rGO significantly surpass the 2017 target of U.S Department of Energy (DOE), a mass activity of 0.440 A/mg_{Pt} at 0.90 V at 80 °C under IR-free conditions. Moreover, the comparison of ORR performance of the obtained catalyst and the similar materials reported previously is provided in Table S5, which illustrates that the Ag-Pt@Pt/rGO prepared in this work shows one of the best ORR activities among the similar Ag/Pt materials. The Ag-Pt/C is 1.49 times of Pt/C as mass activity but only 0.91 times of Pt/C as specific activity. This comparison demonstrates that although the ECSA_{CO} of Ag-Pt/C is much higher than that of commercial Pt/C, but the Ag-Pt surface is not suitable for catalyzing ORR because the Ag atoms of Ag-Pt surface cannot adsorb oxygen, which limits the specific activity of Ag-Pt/C in some degree [16].

The ORR activities of Ag-Pt@Pt/C and Ag-Pt/C are much higher than that of Pt/C, which demonstrate the enhanced activity of Pt skin on Ag-Pt substrate. Obviously, one of the reasons is the higher ECSA of Ag-Pt and Ag-Pt@Pt. However, although both of the Ag-Pt and Ag-Pt@Pt samples possess higher ECSAs than that of Pt/C, they show very different ORR activities, which indicate that the hollow structure is not the predominant factor for the enhancement in ORR activities. To further investigate this enhancement, the DFT calculations were employed. And the oxygen adsorption energy (ΔE_0) was chosen as the criterion for its well correlation to the ORR activity of Pt-based material [37–40]. As shown in Fig. 6, the oxygen adsorption energy of Ag-Pt (111) (1.73 eV), 2-layer Pt on Ag-Pt (1.66 eV) and 3-layer Pt on Ag-Pt (1.71 eV) are all lower than that of bulk Pt (111) surface (1.74 eV), revealing a faster desorption of OH_{ad} species which is also observed from CO stripping. According to the Sabatiter volcano [41–44], the predictive optimal shift value is about 0.20 eV lower than the value of bulk Pt (111) surface, where a surface may shows the best ORR performance [45]. The shift value

of 2-layer Pt on Ag-Pt (0.08 eV) and 3-layer Pt on Ag-Pt (0.03 eV) are closer to the optimal shift value than Ag-Pt (111), indicating the higher ORR catalytic activity of Ag-Pt@Pt surface. Although the theoretical calculations are based on ideal and close-packed single crystal surfaces, which may not exactly represent the real structure of surface, that still offer useful information for the design of surface structure.

Both samples with two or three layers of Pt on Ag-Pt substrate exhibit better ORR activity than the bulk Pt sample. On the contrary, the activity of the sample with Ag-Pt surface is no match for the sample with Pt on Ag-Pt surface due to the stronger oxygen affinity. Hence, the calculation results give a reliable explanation for different activity of the Ag-Pt@Pt/C, Pt/C and Ag-Pt/C. The variety of ΔE_0 may arise from their different surface structure and charge transfer which has been observed from the XPS measurement



Fig. 6. Calculated oxygen adsorption energy (ΔE_0) for different surface structure. The vertical views of the oxygen-adsorpted models are shown in Fig. S7.

(Fig. 4). As for the enhancement of Ag-Pt@Pt/rGO compared to Ag-Pt@Pt/C, it could be mainly attributed to the better electrical conductivity of the rGO support [46–48]. And the rGO shows a weak ORR catalytic activity (Fig. S8), suggesting that rGO not only acts as support but also improves the catalytic activity synergistically [49,50].

Furthermore, the accelerated durability test (ADT) is used to examine the electrochemical stability of the samples. The

calculated results from the CO stripping curves (Fig. S6) of the aged samples demonstrate that the Ag-Pt/C, Ag-Pt@Pt/C and Ag-Pt@Pt/ rGO retain 70%, 64% and 69% of ECSA_{CO}, respectively, but the Pt/C only retains 49%. And the comparisons of the LSV between the fresh samples and the aged samples (Fig. 7) also show that the commercial Pt/C is more unstable than three other samples under same condition, since the Ag-Pt/C, Ag-Pt@Pt/C and Ag-Pt@Pt/rGO lose 36%, 38% and 32% of the mass activity, respectively, but the Pt/C



Fig. 7. Linear scan voltammograms of fresh and cycled samples (a–d). Representative TEM images of fresh and cycled Ag-Pt/C (e, g) and Ag-Pt@Pt/rGO (f, g). In the element line scan, grey line represents Pt and the blue line represents Ag, and the scale bar in the dark-field photos is 2 nm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

loses 51% of its mass activity after the ADT (summarized in Table S6). The mass activity of the aged Ag-Pt@Pt/rGO is as high as 0.589 A/mg_{Pt}, which still surpass the DOE 2017 target. The ADT at 80 °C was also performed to test the stability of the samples near PEFC operation temperature. As shown in Fig. S9, the catalytic stability of Ag-Pt@Pt/rGO is also better than that of commercial Pt/C at higher temperature.

These results reveal that all the three Ag/Pt samples possess better electrochemical stability than the commercial Pt/C. As shown in the TEM images and the elemental line scan results of cycled catalysts (Fig. 7 and Fig. S10), the morphology and particle size of Ag-Pt and Ag-Pt@Pt nanoparticles is well-maintained after ADT process, and the thickness of Pt skin of cycled Ag-Pt@Pt sample is about 0.72 nm and very close to the fresh sample (0.76 nm), demonstrating the excellent stability of the structure of the Ag-Pt bimetallic nanoparticle. Furthermore, the EDS (Fig. S4) and ICP (Table S1) results of the aged samples show that the atomic ratio of Ag raises after ADT, but it only raises ~1.4% for Ag-Pt/C sample and ~0.7% for Ag-Pt@Pt/rGO samples, which illustrates that the two samples both lost some Pt atoms during the ADT in some degree, but not much. The above results are consistent with previous report by Ramirez-Caballero et al. Their DFT calculation results indicated that the Ag-Pt structure would bind Pt atom more strongly than pure Pt because of the different radii, cohesive energy and surface energy of Ag and Pt [51]. Therefore, the Ag-Pt and Ag-Pt@Pt would be more stable than pure Pt under the ORR catalyzing conditions.

According to the ICP results of the aged samples, the Ag-Pt/C sample lost 37% of the whole Pt amount and the Ag-Pt@Pt/rGO lost 34% during ADT. As the structure and the atomic ratio of nanoparticles retained well during ADT, the major loss of Pt atoms should come from the detachment of the catalyst nanoparticles from the carbon supports, which could be the main reason for the decrease of ECSAs and mass activities after ADT. And for Ag-Pt@Pt/ rGO, the higher stability than Ag-Pt@Pt/C may be contributed to the stronger binding between Pt and graphene than Pt and XC-72R carbon support due to the π bonding strength of graphene [52,53], and higher corrosion resistance of rGO compared with other carbon support [54–56].

4. Conclusion

Pt skin coated hollow Ag-Pt bimetallic nanoparticles were synthesized via a novel environment-friendly method. And TEM, EDS XPS, and XRD measurements were used to verify the structure of the samples. The comparison of the ORR activity among the Ag-Pt@Pt/C, Ag-Pt/C and Pt/C indicates that the hollow structure can remarkably enlarge the Pt utilization and then lead to a higher mass activity. Meanwhile the control of the material surface structure is also critical for improving the ORR activity of catalyst. According to the measured ORR activity, the surface with Pt on Ag-Pt structure is more suitable for catalyzing ORR than pure Pt surface, and the Ag-Pt surface is not as good as pure Pt surface, which is also confirmed by the DFT calculation. After being loaded on graphene, the Ag-Pt@Pt/ rGO sample exhibits a highest ORR mass activity of 0.864 A/mg_{Pt}, 5.30 times of the commercial Pt/C catalyst, which was one of the highest values among the state of art of Ag/Pt bimetallic catalysts. And the Ag-Pt@Pt/rGO remains most mass activity than other samples after ADT process, suggesting that graphene support can enhance the ORR performance of Ag-Pt@Pt nanoparticles.

This research work provides a facile method to build hollow Ag-Pt@Pt nanoparticles with higher ORR catalytic activity and longer durability, which might be referable in preparation of novel Ptbased catalysts. And the DFT calculation of different Pt-based surfaces for investigating the relationship between ORR activity and material surface structure would be helpful for designing the surface structure of novel catalyst.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http:// dx.doi.org/10.1016/j.jpowsour.2017.08.066.

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