# Supporting Information

## Synthesis of Hollow Pt-Ag Nanoparticles by Oxygen-Assisted Acid Etching as

## **Electrocatalysts for the Oxygen Reduction Reaction**

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Figure S1. EDX line-scan analysis of different sized Ag@Pt core@shell NPs



**Figure S2.** STEM and EDX mapping images of different sized Ag@Pt core@shell NPs. Shell thickness was measured from the EDX mapping images.



Figure S3. EDX analysis of different sized Ag@Pt core@shell NPs.



**Figure S4.** TEM image of 12.5 nm Ag@Pt core@shell NPs soaked in acetic acid solution under Ar flow for 4 h.



**Figure S5.** TEM images of (A) Ag@Pt core@shell NPs with 9.1 nm Pt shell, and (B) Ag@Pt core@shell NPs with 9.1 nm Pt shell soaked in acetic acid under air for 4 h. The insets are the corresponding mixed mapping images, Pt is red and Ag is green.



Figure S6. EDX analysis of different sized Pt-Ag hollow NPs.



**Figure S7.** EDX line-scan analysis of the shell of 12.5 nm core@shell (A) and hollow NPs (B), (C) EDX analysis of the shell of 12.5 nm core@shell NPs.



**Figure S8.** XPS spectra of (A) N 1s from hexadecylamine (HDA) capped Ag@Pt core@shell NPs, (B) O 1s from acetic acid capped Pt-Ag hollow NPs.



**Figure S9.** TEM images of Pt-Ag hollow nanocatalysts loaded on carbon black, (A) 22.4 nm, (B) 12.5 nm, and (C) 5.8 nm. Scare bar = 20 nm.



Figure S10. Cyclic voltammogram of commercial Pt NP/C.

#### Further Insights into the Polarization Curves:

The diffusion limited region of the polarization curve is observed at currents below 0.6 V where the overpotential for ORR is high and the kinetics are predominantly controlled by diffusion of oxygen to the catalyst. In this case, the limiting current for the 22.4 nm Pt-Ag hollow NPs particles was approximately  $4.3 \text{ mA cm}^{-2}$ , which was lower than the value of ~5 mA cm<sup>-2</sup> of the 5.8 nm and 12.5 nm particles. We attribute the lower limiting current to the relative size of the hollow NPs relative to the size of the carbon support particles. The 22.4 nm particles were close to the size of the carbon particles (50 – 100 nm) and were therefore not as well dispersed on the surface of the electrode as the smaller 5.8 and 12.5 nm. This is expected to produce a lower limiting current than is predicted theoretically.<sup>1</sup> In this case, the effect is relatively negligible representing a difference of only about 10% of the diffusion limited current of the more dispersed particles. Since the activity is measured in the kinetically controlled region of the polarization curve at relatively low overpotentials, the difference in limiting current should have a negligible effect on the measured activity to the one calculated directly from the polarization curve. This further confirmed the fact that the difference in the diffusion limited current has a negligible impact on the measured activity at 0.9 V.



**Figure S11.** Polarization curves (bottom) obtained from a rotating ring-disk electrode for oxygen reduction on 5.8 nm Pt-Ag hollow NPs in 0.1 M HClO<sub>4</sub> solution with a sweep rate of 20 mV s<sup>-1</sup>. The rotation rates are indicated on the graph. The ring current (top) was collected with a potential of 1.27 V.



Figure S12. Koutecky-Levich plots at different potentials obtained from the data in Figure S11.

**Rotating Ring-Disk Electrode (RRDE) Measurements:** 

$$I = \frac{1}{I_K} + \frac{1}{I_D} = \frac{1}{I_K} + \frac{1}{B\omega^{1/2}}$$
(1)

$$B = 0.62nFAD_{O_2}^{2/3} v^{-1/6} C_{O_2}$$
<sup>(2)</sup>

Koutecky-Levich plots (Figure S12) were created from the data in the kinetically controlled region of the polarization curves shown in Figure S11. According to Equation 1, the measured disk current (I) can be calculated from the kinetic current  $(I_K)$ , the rotation rate  $(\omega)$ , and the constant 'B'. The experimental values for IK and B for a given potential can be extracted from the Koutecky-Levich plot from the yintercept and slope, respectively of linear fit of the data. In this case, the experimental value of the constant 'B' for the plot at 0.9 V was determined to be 0.0955 mA s<sup>-1/2</sup>. The theoretical value for B can be calculated according to Equation 2 where n is the number of electrons, F is Faraday's constant, A is the geometric area of disk electrode,  $D_{O_2}$  is the published value of the diffusion coefficient of O<sub>2</sub> (1.93 × 10<sup>-5</sup>) cm<sup>2</sup> s<sup>-1</sup>), v is the published value of the kinetic viscosity of the solution ( $1.009 \times 10^{-2}$  cm<sup>-2</sup> s<sup>-1</sup>), and  $C_{O_2}$  is the concentration of dissolved O<sub>2</sub> in solution  $(1.26 \times 10^{-3} \text{ mol } \text{L}^{-1})$ .<sup>2</sup> From Equation 2, the theoretical values of B calculated for the four-electron reduction of oxygen to water and the two-electron reduction of oxygen to peroxide were 0.0914 mA s<sup>-1/2</sup> and 0.0457 mA s<sup>-1/2</sup>, respectively. The experimental value for B  $(0.0955 \text{ mA s}^{1/2})$  is in excellent agreement with the theoretical value calculated for the four electron process, suggesting that the ORR at the hollow Pt-Ag catalysts follows a four electron process. The ring current data (Figure S11) revealed that no peroxide was detected in the kinetically controlled region of the polarization curve. This is further evidence that the process largely follows a four-electron process.



**Figure S13.** Cyclic voltammograms of the 5.8 nm Pt-Ag hollow NPs obtained over the course of a 20,000 cycle accelerated durability test.



**Figure S14.** Polarization curves obtained commercial Pt NP/C over the course of a 20,000 cycle accelerated durability test. The electrochemical surface area (ESA) and specific activity of the catalyst (inset) are shown as a function of the number of cycles.



**Figure S15.** (A) TEM image, (B) HAADF-STEM image, (C-E) their corresponding EDX elemental mapping images, and EDS of 5.8 nm hollow Pt-Ag nanocatalysts after 20000 cycles. The molar ratio of Pt:Ag is 94:6 after 20000 cycles, showing the slight dissolution loss of surface Ag atoms in acidic media.

#### References

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