

Platinum-Gold Nanoparticles: A Highly Active Bifunctional Electrocatalyst for Rechargeable Lithium-Air Batteries

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Supporting Information

Synthesis of PtAu/C catalyst

Synthesis of PtAu nanoparticles

0.25 mmol HAuCl₄ (Sigma-Aldrich) and 0.25 mmol H₂PtCl₆ (Sigma-Aldrich) were dissolved in 20 mL oleylamine (Sigma-Aldrich) at 40 °C under an Ar blanket. The solution was then heated up to 160 °C and maintained at 160 °C for 2 h. PtAu particles were collected by adding 100 mL ethanol and following centrifugation. The as-prepared PtAu nanoparticles were dispersed then in non-polar solvents such as hexane and toluene.

Carbon loading and thermal treatment

150 mg Vulcan XC-72 (Premetek, USA) were pre-dispersed in 400 mL hexane (Sigma-Aldrich) by sonicating in ice bath for 5h. As-prepared PtAu nanoparticles (~100mg) were dissolved in hexane and then added dropwise into the Vulcan solution under sonication in ice bath. The solution was further sonicated for 2 h and stirred overnight. The catalyst powders were collected by purging Ar (evaporating hexane) at room temperature and dried in vacuum for 24 hours. The PtAu/C catalyst was finally treated at 250 °C in dry air for 30min to remove surfactant yielding 40 wt.% PtAu/C, which is determined by thermogravimetric analysis (TGA).

Preparation of Electrodes

Preparation of PtAu/C catalyst electrode for cyclic voltammogram

Electrodes with a Nafion[®]/carbon weight ratio of 0.5/1 were prepared by drop-casting ultrasonicated inks composed of carbon or catalyst, Nafion[®] dispersion (DE520, Ion-Power, USA), and 20 wt.% 2-propanol (Sigma-Aldrich) in de-ionized water (18.2 M Ω ·cm, Millipore) onto the glassy carbon disk, yielding a carbon loading of 0.2 mg/mL.

Preparation of air-electrode for Li-O₂ cell

Air-electrode with a Nafion[®]/carbon weight ratio of 0.5/1 were prepared by coating ultrasonicated inks composed of catalyst, lithium-ion-exchanged Nafion[®] dispersion (Ion-Power, USA), and 2-propanol (Sigma-Aldrich) onto the separator (Celgard C480). The electrodes were air-drying at 20°C for about 20 minutes and subsequent vacuum-drying for 3 hours.

Electrochemical Measurements

Cyclic voltammetry

As-prepared electrodes were then mounted to a rotator (Pine Instruments) and immersed into 0.5 M H₂SO₄ (Fluka). A spiral Pt wire was employed as the counter electrode, and a saturated calomel electrode (SCE, Analytical Sensor, Inc.) was used as the reference electrode. The potential of SCE with respect to the reversible hydrogen electrode (RHE) was calibrated from rotating disk electrode measurements of hydrogen oxidation. All the potential values reported in this paper refer to that of the RHE (V_{RHE}). After the electrolyte was bubbled with argon (Ar) for half an hour, the working electrodes were scanned between 0.02 and 1.7 V_{RHE} at a sweep rate of 50 mV/s for 3 times. Steady-state cyclic voltammograms were recorded at 50 mV/s in the same potential range at room temperature.

Determination of electrochemical surface area (ESA) of Pt and Au

The determination of Pt surface area was done as follows: 1) integrating the net (i.e., with double-layer capacitance subtraction) charge formation of hydrogen adsorption region (negative-going scan from 0.4 V_{RHE} – 0.02 V_{RHE}) and hydrogen desorption region (positive-going scan from 0.02 V_{RHE} – 0.4 V_{RHE}). Double-layer capacitance background was assumed by linear-extension from the double-layer region; 2) Average the net charge from hydrogen adsorption and

desorption; 3) the averaged net charge (μC) was then divided by the most accepted converting factor for Pt surface,¹ $210 \mu\text{C}/\text{cm}^2$, and yield the ESA of Pt. The determination of Au surface area was done as follows: 1) integrating the net (i.e., with double-layer capacitance subtraction) charge formation of AuO or Au(OH)₂ (negative-going scan from $1.34 V_{\text{RHE}} - 0.92 V_{\text{RHE}}$). Double-layer capacitance background was assumed by linear-extension from the double-layer region; 2) the net charge (μC) was then divided by the reported converting factor (i.e., $350 \mu\text{C}/\text{cm}^2$ for the potential window being $1.7 V_{\text{RHE}}$)² yielding the ESA of Au. Two experiments were conducted and the results show that ESA for Pt is $(23 \pm 4) \text{ m}^2/\text{g}_{\text{PtAu}}$ and for Au is $(15 \pm 1) \text{ m}^2/\text{g}_{\text{PtAu}}$. The specific ESA of PtAu/C is $(38 \pm 4) \text{ m}^2/\text{g}_{\text{PtAu}}$. The surface atomic ratio of Pt/Au is $(60 \pm 2\%)/(40 \pm 2\%)$.

Li-O₂ cell assembling configurations and testing conditions

Li-O₂ cell tests were conducted at room temperature in 1 M LiClO₄ in PC:DME (1:2 v/v) electrolyte, prepared from LiClO₄, propylene carbonate (PC), and 1,2-dimethoxyethane (DME) from Sigma-Aldrich (all <30 ppm H₂O). The Li-O₂ battery configuration used in this study consists of a lithium foil (15 mm diameter), two pieces of Celgard separator (C480) (17 mm diameter) and a Nafion[®]-bonded cathode (12.7 mm diameter) coated on a Celgard C480 using either pure Vulcan XC-72 carbon, 40%wt. PtAu/C (Vulcan), 40%wt. Au/C (Vulcan) (Premetek, USA), or 40%wt. Pt/C (Vulcan) (Premetek, USA). Li-O₂ cells were assembled in the following order: 1) placing a lithium foil onto the cell's stainless steel current collector, 2) adding 10 μL electrolyte, 3) placing two pieces of the separator onto the lithium foil, 4) adding 10 μL electrolyte, 5) placing the cathode-coated separator onto the separator, 6) adding on top a cathode current collector (316 stainless steel mesh and spring), and, 7) purging the cell with PC/DME-saturated oxygen for 10 minutes. Afterwards, cells were sealed and tested galvanostatically (Solartron 1470) at various rate ($50 \text{ mA}/\text{g}_{\text{carbon}} - 250 \text{ mA}/\text{g}_{\text{carbon}}$) with a low voltage limit of $2.0 V_{\text{Li}}$ and upper limits of $4.5 V_{\text{Li}}$ (pure carbon, subsequently hold at $4.5 V_{\text{Li}}$ for 5 hours before the next discharge), $4.4 V_{\text{Li}}$ (Au/C, no holding) and $4.0 V_{\text{Li}}$ (PtAu/C and Pt/C, no holding) to avoid electrolyte decomposition. In addition, the charging step in cycling testing at $100 \text{ mA}/\text{g}_{\text{carbon}}$ was designed to be terminated when the high cut-off voltage was reached or after a maximum of 20 hours ($=2000 \text{ mAh}/\text{g}_{\text{carbon}}$).

Characterization of PtAu nanoparticles

A TEM image of as-prepared PtAu nanoparticles

Figure S1 shows the TEM image of as-prepared PtAu nanoparticles before loading onto carbon support and heat treatment.

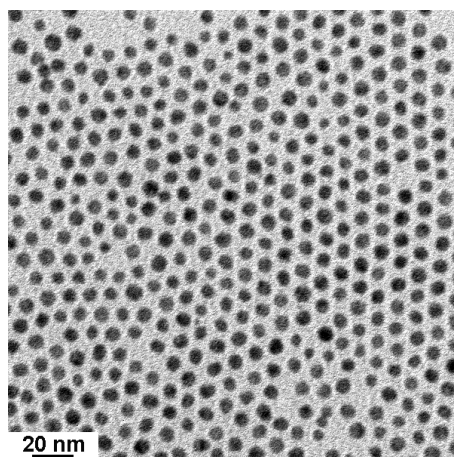


Figure S1. A representative TEM image of as-prepared PtAu nanoparticles.

Particle size distribution of carbon supported PtAu nanoparticles

The particle size distribution of PtAu nanoparticles was examined in a JEOL 2010F TEM operated at 200 kV with a point-to-point resolution of 0.19 nm. Nanoparticles were first immersed in ethanol and subsequently dispersed on a lacey carbon grid and dried in air for TEM observations. One hundred and thirty-six randomly selected nanoparticles from HRTEM images were used to produce particle size distributions of PtAu/C as shown in Figure S2. For each

distribution, the number-averaged diameter d_n was determined by $d_n = \frac{\sum_{i=1}^n d_i}{n}$ while the volume-surface-area-averaged diameter was calculated by $d_{v/a} = \frac{\sum_{i=1}^n d_i^3}{\sum_{i=1}^n d_i^2}$ where d_i is the diameter of individual

particles. The specific surface area of nanoparticles based on the volume-surface-area-averaged diameter from TEM measurements was determined by $6(1000/(\rho_{\text{Pt}} d_{v/a}))$.

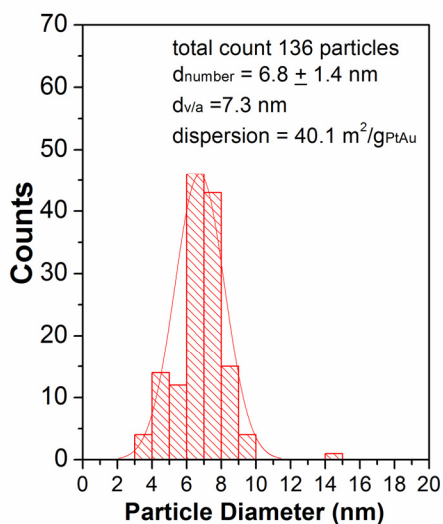


Figure S2. Particle size histogram of carbon supported PtAu nanoparticles obtained from HRTEM images (shown in Figure 1).

Scanning transmission electron microscope (STEM) images of carbon supported PtAu nanoparticles

The compositional distributions of Pt and Au of individual PtAu nanoparticles were examined by X-ray energy dispersive spectroscopy (EDS) in a JEOL 2010F TEM at room temperature using a beam voltage of 200 kV and INCA control software (Version 4.08, Oxford Instruments Analytical Limited). Pt $L_{\alpha 1}$ (~ 9.442 keV) and Au $L_{\alpha 1}$ (~ 9.674 keV) signals were used for composition quantification. The chemical compositions of individual PtAu nanoparticles were determined from signals collected for 275 s with a scanning beam of 2 nm in diameter, which provided sufficient signal-noise ratios for quantification of Pt and Au atomic fractions. Errors in the Pt and Au atomic fractions in the analysis of each spectrum were generated by INCA, which were related to the standard deviation of X-ray signal counting.

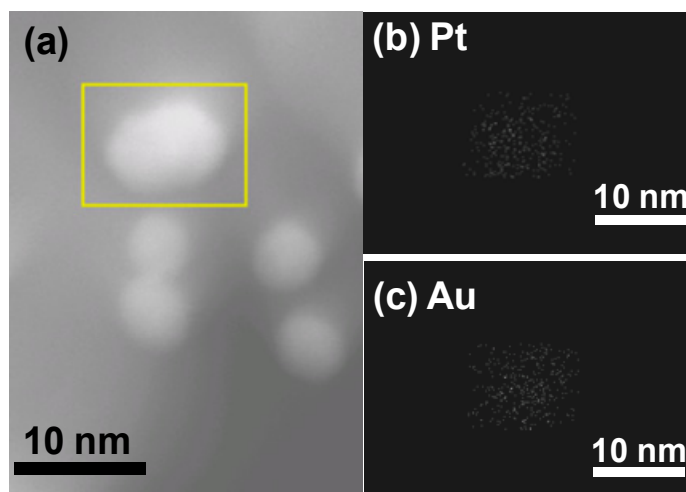


Figure S3. (a) High-angle annular dark-field (HAADF) image of PtAu nanoparticles. The image was taken with JEOL 2010F TEM in STEM mode. (b) and (c) Energy-dispersive X-ray (EDX) mapping of the region in yellow rectangular of (a), where (b) is Pt distribution quantified from Pt $L_{\alpha 1}$ -line, and (c) is Au distribution quantified from Au $L_{\alpha 1}$ -line.

The discharge/charge comparison of Pt/C and PtAu/C at 100 mA/g_{carbon}

Figure S4 shows that the charging voltage profile of PtAu/C became lower than Pt/C in the subsequent cycles.

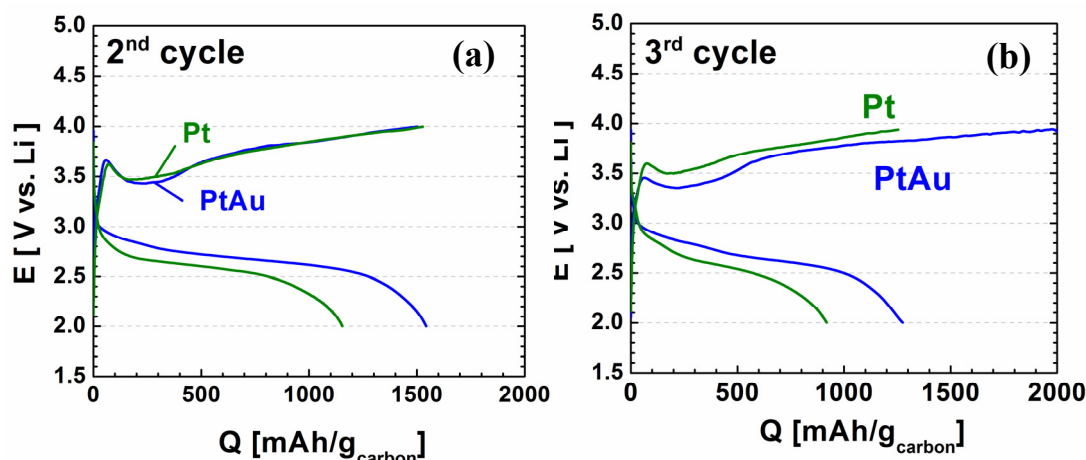


Figure S4. Li-O₂ cell (a) 2nd and (b) 3rd discharge/charge profiles of Pt/C, and PtAu/C at 100 mA/g_{carbon}.

Charging background measurements for PtAu/C at 50 mA/g_{carbon}

Figure S5 shows the charging background measurement of PtAu/C cells under Ar and O₂-filled environment at 50 mA/g_{carbon}. The results reveal that the charge associated with electrolyte decomposition on PtAu/C became significant at voltages ≈ 4.0 V_{Li} at 50 mA/g_{carbon}. The background measurements confirm the high charging activity of PtAu/C toward the decomposition of lithium (per)oxide discharge products at shown in Figure 3b.

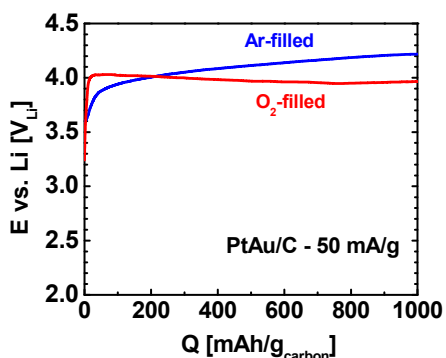


Figure S5. Background measurements during charging at 50 mA/g_{carbon} of an Ar and O₂-filled cell (charging first) for PtAu/C.

References

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