

## Supplementary Information

# Pt-Au Core/Shell Nanorods: Preparation and Applications as Electrocatalysts for Fuel Cells

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## Experimental section

### 1. Preparation of Catalysts

The 45 wt % of Pt-Au/C nanorods with the Pt/Au ratio of 3:1 were prepared via the formic acid reduction method. Two step of reduction routes were used to synthesized Pt-Au/C nanorods with core/shell structures. In briefly, aqueous solutions of  $\text{H}_2\text{PtCl}_6$  (Alfa Aesar) and  $\text{HAuCl}_4$  (Aldrich) with stoichiometric ratio of 3:1 were blended and deposited with different sequence at 340 K onto the commercial carbon black (Vulcan XC-72R). For instance, the solution of  $\text{H}_2\text{PtCl}_6$  and carbon were first mixed and reduced by formic acid for 72 hours, and then Au precursor was reduced by formic acid for another 48 hours. The as-deposited catalysts were subsequently dried at 330 K for 24 h, and stored as fresh PtAu shell nanorods. On the contrary, the Pt shell nanorods were prepared by the initial reduction of Au precursor and following deposition of Pt. For comparison, the commercial Pt/C (TKK) catalysts with 50 wt % Pt loading were used.

### 2. Characterization of Catalysts

The exact compositions of the Pt-Au nanorods were examined by inductively coupled plasma- atomic emission spectroscopy (ICP-AES, Jarrell-Ash , ICAP 9000).

The metal loadings of the Pt-Au nanorods were performed by thermal gravimetric analysis (TGA, Perkin Elmer TGA-7). Initially, a small amount of Pt-Au nanorods was placed into a Pt made basket and then transferred it into TGA measurement with a temperature range starting from 300 to 1173 K at a heating rate of  $7 \text{ K min}^{-1}$  under air atmosphere.

The phase structure of the nanorods have been characterized by a Shimadzu X-ray diffractometer with a  $\text{CuK}\alpha$  ( $\lambda = 0.15406 \text{ nm}$ ) radiation source generated at 40 kV and 25 mA and performed in a  $2\theta$  range of 20 and  $80^\circ$ . The XRD with a scan rate

of  $1^\circ\text{min}^{-1}$  was used to estimate the grain size of alloy nanoparticles by Scherrer's formula.

The morphologies of the Pt-Au nanorods were examined by a Jeol-2100 high resolution transmission electron microscope (HRTEM) with a  $\text{LaB}_6$  electron gun source operated at 200 KeV. The line-scan results with varying composition across the nanorods were obtained by the equipped EDX attachment (Oxford). Initially, the catalysts were ultrasonically suspended in 2-propanol which was placed into a vial. The uniform suspension was then immediately dried on a 200 mesh/inch copper grid.

The morphologies of the Pt-Au nanorods were characterized by a field emission scanning electron microscope (FEI Nova Nano 230).

Electrochemical measurements were performed by a glassy carbon rotating disk electrode (RDE), a MSR rotator (Pine Instrument) and a microcomputer-controlled electrochemical analyzer (CHI700a, CH Instrument). The ink was mixed of 5 mg alloy catalysts and diluted Nafion solution (5 wt %, DuPont) in 1 mL 2-propanol which was dispersed in ultrasonic bath, and then deposited onto the glassy carbon RDE ( $0.196\text{ cm}^2$  area). A Pt plate and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively.

For the ORR measurement, 20  $\mu\text{L}$  of the slurry was deposited on the GC electrode. The estimated Pt metal loading on the GC electrode was about 44 and 33  $\mu\text{g}$  for Pt/C and Pt-Au nanorods, respectively. The electrolyte was used as 0.5 M  $\text{H}_2\text{SO}_4$  (Panreac) aqueous solution, and then saturated with high-purified  $\text{O}_2$  (99.999 %) at room temperature. Linear sweep voltammetry (LSV) was conducted to study the activity of the ORR with a scan rate of  $5\text{ mVs}^{-1}$  and a rotation rate of 1600 rpm. Before each electrochemical measurement, the electrodes were cycled several times between -0.24 and 0.96 V (vs. SCE), to produce clean surfaces at a scan rate of 20  $\text{mVs}^{-1}$  and a rotation rate of 1600 rpm. All potentials in this study are given with

respect to the reference electrode, which is +0.241 V vs. NHE. For the comparison of ORR activity on all catalysts, the current density is calculated from the experimental data based on the mass-transfer correction for RDE by the following equation:<sup>S1</sup>

$$I_k = \frac{I_d I}{I_d - I} \quad (1)$$

where  $I$  is the experimentally measured current density during the ORR,  $I_k$  is the mass transport free kinetic current density and  $I_d$  is the diffusion-limited current density. Moreover, the mass activity is obtained by the normalization of kinetic current to the weight of Pt. All of the  $I_k$  reported in this study is compared within the mixed kinetic-diffusion region at  $E = 0.85$  V.

The stability of the Pt-Au nanorods was conducted via cyclic voltammograms (CV) characterization on an identical three electrode system. A similar preparation method of catalyst inks was also used as described above. The CV plots were recorded at a scan rate of  $20 \text{ mVs}^{-1}$  in the  $\text{N}_2$ -saturated  $0.5 \text{ M H}_2\text{SO}_4$  aqueous solution between  $-0.24$  and  $1.36$  V (vs. SCE). Furthermore, the potential cycling experiments of accelerated durability test (ADT) were used to characterize the electrochemical stability and performance of the Pt-Au nanorods and Pt/C catalyst.<sup>21, S2</sup> The ADT was conducted by continuously potential cycling between  $0.6$  and  $1.2$  V with periodic measurements of electrochemical surface area (ECSA) and ORR activity after every 400 scans. Moreover, each ECSA value is normalized to the original active surface area (calculate from the  $\text{H}_{\text{ads/des}}$  region in 1<sup>st</sup> scan) in order to compare the degradation rate of ECSA. The ECSA was performed by the integration of the charges associated with hydrogen adsorption/desorption region and by the use of assumed value for desorption of monolayer  $\text{H}_{\text{ads}}$  on Pt of near  $210 \mu\text{Ccm}^{-2}$ .<sup>S3</sup>

CO stripping measurement: CO was pre-adsorbed onto the electrode surface at  $0.1$  V (vs. NHE) by purging the high purity CO gas through  $0.5 \text{ M H}_2\text{SO}_4$  for 30 mins.

Finally, N<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> was used for the CO stripping study. Two CVs were collected between -0.35 and 1.2 V (vs. SCE) at a scan rate of 50 mVs<sup>-1</sup>. The first potential sweep was conducted to electro-oxidize the adsorbed CO species.

Formic acid oxidation measurement: N<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> and 2 M HCOOH were used for the FAO. CV scans were conducted to study the activity of the FAO with a scan rate of 20 mVs<sup>-1</sup>. The CV profiles were recorded in the 31<sup>th</sup> cycle.

Table S1 EDS, ICP-AES, TGA, and electrochemical characterization of PtAu shell and Pt shell nanorods.

Catalyst	Metal composition		Metal loading (wt %) <sup>[c]</sup>	I <sub>08</sub> (mAcm <sup>-2</sup> ) <sup>[d]</sup>
	Pt : Au <sup>[a]</sup>	Pt : Au <sup>[b]</sup>		
PtAu shell	71.0 : 29.0	74.3:25.7	46.0	2.6
Pt shell	78.0 : 22.0	74.1:25.9	45.0	3.0

<sup>a</sup> The metal composition of Pt-Au nanorods estimated by energy dispersive spectroscopy (EDS) (shown in Figure S1).

<sup>b</sup> The exact metal composition of Pt-Au nanorods examined by ICP-AES.

<sup>c</sup> The exact metal loading of Pt-Au nanorods examined by TGA.

<sup>d</sup> The current density at 0.8 V determined from rotating-disk voltammograms (shown in Figure 2 (a)).

**Table S2** Results of ECSA and ORR activities for various catalysts.

Samples	ECSA <sup>a</sup> (m <sup>2</sup> /g)	ORR activity (at E = 0.80 V)	
		I <sub>k</sub> <sup>b</sup> (mAcm <sup>-2</sup> )	MA <sup>c</sup> (Ag <sub>Pt</sub> <sup>-1</sup> )
Pt/C	69	2.5	11.4
PtAu shell	29	5.0	29.7
Pt shell	35	7.0	41.3

<sup>a</sup> Electrochemical surface area (ECSA): the ECSA is estimated by integrating the charges associated with electro-oxidation of H<sub>ads</sub> species.

<sup>b</sup> Kinetic current density (I<sub>k</sub>): the kinetic current at E = 0.80 V.

<sup>c</sup> Mass activity (MA): the mass activity is obtained by the normalization of kinetic current to the weight of Pt.

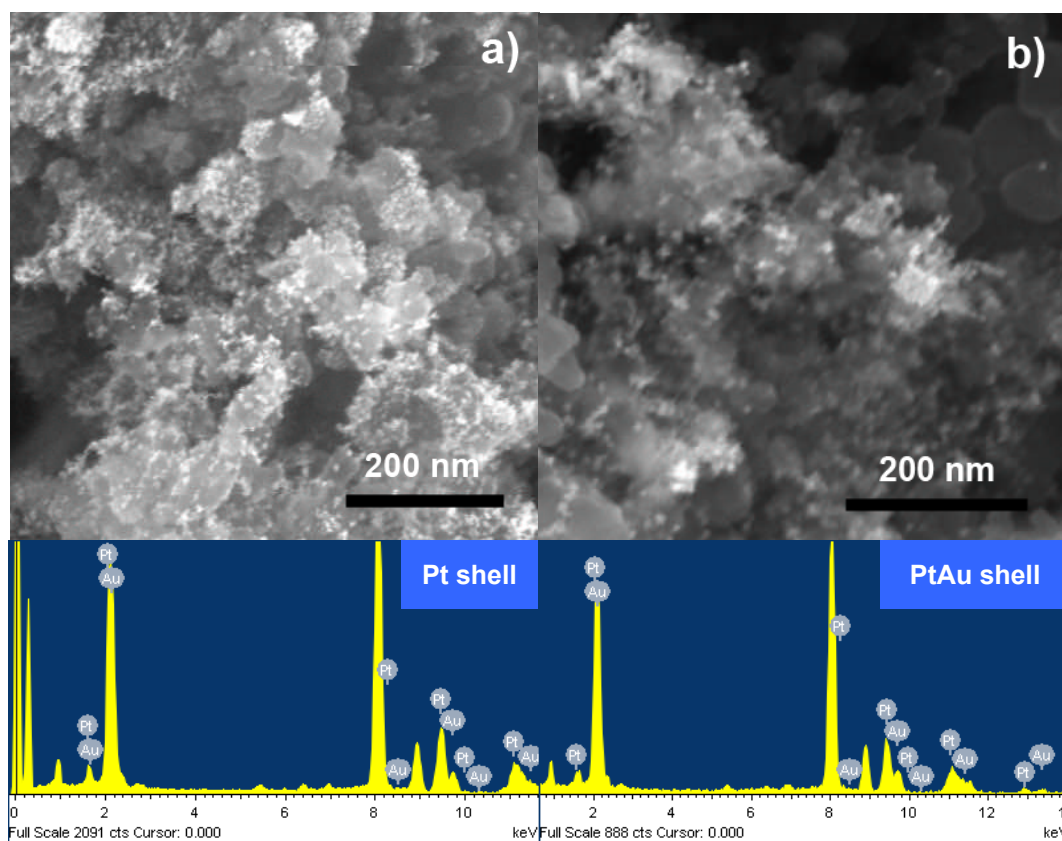


Figure S1 UHR-SEM images of Pt shell (a) and PtAu shell (b) nanorods. The chemical composition of Pt-Au nanorods examined by energy dispersive spectroscopy (EDS).



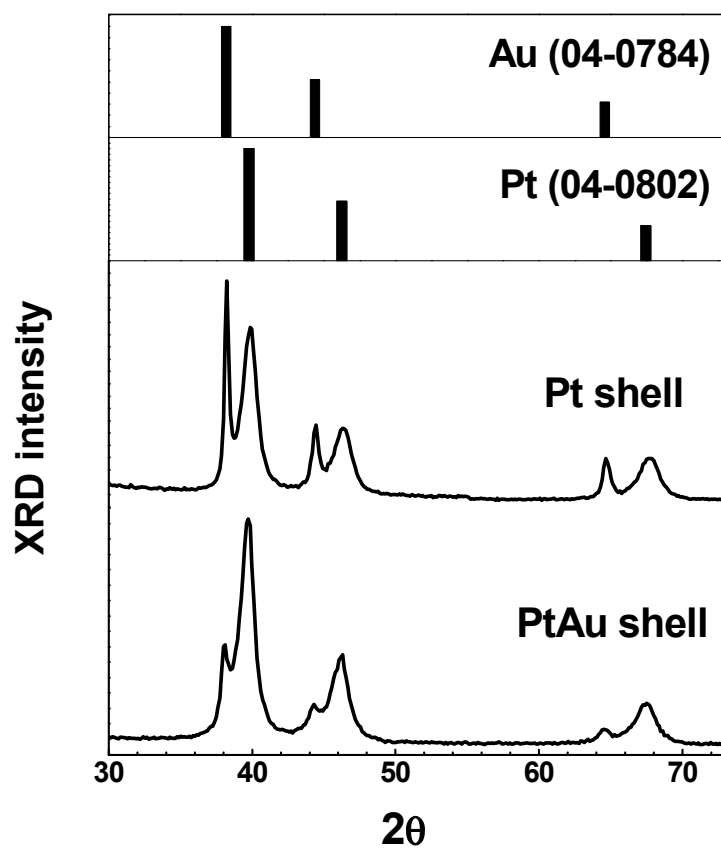


Figure S2 XRD patterns of the Pt shell and PtAu shell nanorods.

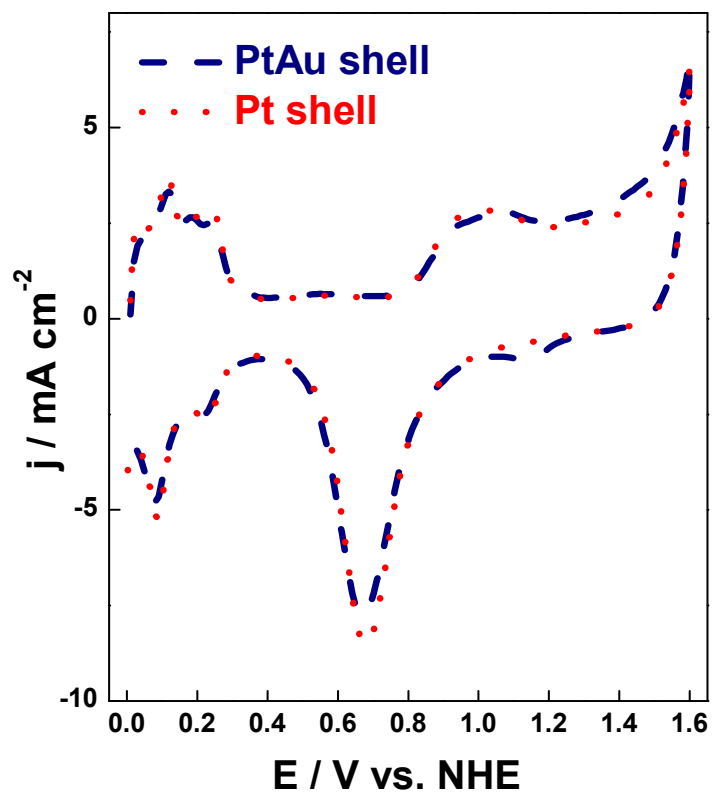


Figure S3 CV measurements of Pt shell and PtAu shell nanorods in 0.5 M H<sub>2</sub>SO<sub>4</sub>.

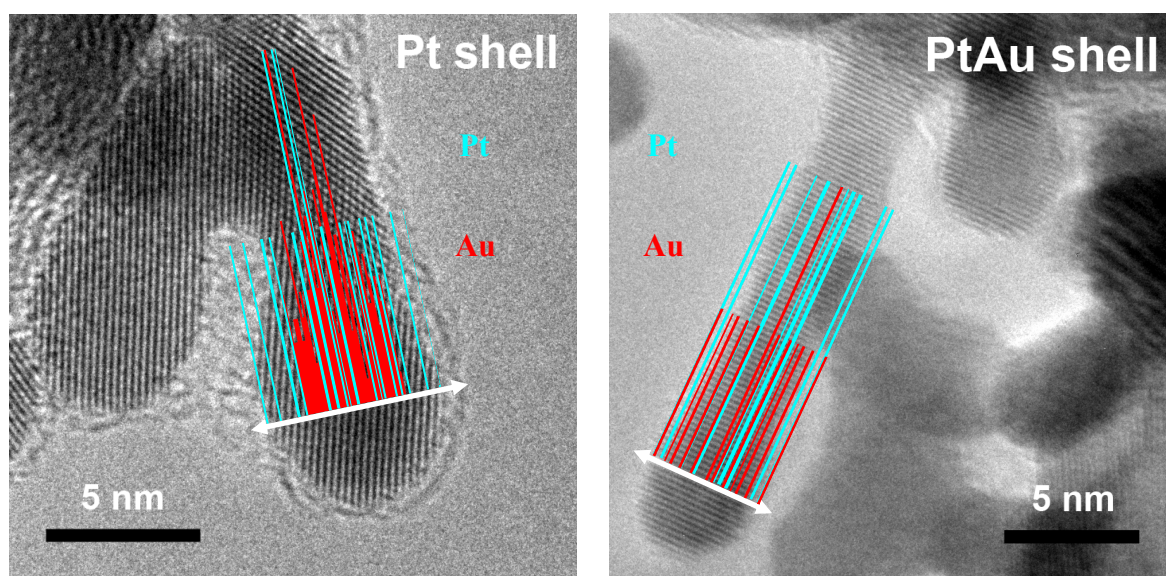


Figure S4 The line-scan results of Pt shell and PtAu shell nanorods.

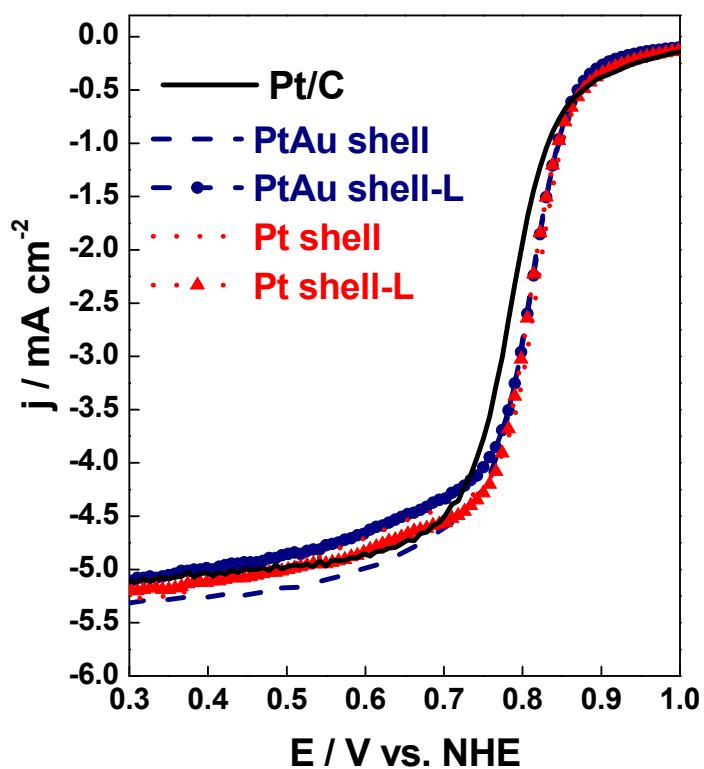


Figure S5 Comparison of the LSV results with a potential range of 0.3 – 1.0 V in 0.5 M H<sub>2</sub>SO<sub>4</sub> saturated with O<sub>2</sub> for Pt-Au nanorods and Pt/C catalyst.

## References

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