

Supporting Information

Highly Active Pt@Au Nanoparticles Encapsulated in Perfluorosulfonic Acid for the Reduction of Oxygen

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Experimental

Synthesis of Pt@Au Nanoparticle: The successive reduction (known as the seed-mediated growth method) was used to synthesize the Pt-Au nanoparticles with the core-shell structure. The perfluorosulfonic acid (Nafion) stabilized Au nanoparticles were synthesized using NaBH₄ as reduction agent. Briefly, 40 ml HAuCl₄ (1.5 mg ml⁻¹), 200 ml 5 wt.% Nafion (Dupont Co.) using as stabilizer and 200 ml ethanol/water (V/V = 2/3) were mixed. One milliliter of aqueous NaBH₄ (0.019 mol dm⁻³) solution was added dropwise to the mixed solution under vigorous stirring. The colour of mixed solution immediately changed to red, which indicates Au hydrosol(Au seed) were synthesized. The as-synthesized Au hydrosol was below 277K. aged for 24h to NaBH₄ decompose residual before it was used. Pt@Au nanoparticles were prepared as follows. The H₂PtCl₆•6H₂O (1.5 mg ml⁻¹) solution with different atomic ratio of Pt/Au was added to the Au seed solution and stirred for 30 mins. Then the aqueous NaBH₄ solution was added dropwise to the mixed solution under vigorous stirring. The red solution turned into dark indicating the formation of Pt@Au nanoparticles encapsulated in Nafion.

Preparation of carbon-supported Au/C, Pt/C and Pt@Au/C catalysts: The Vulcan XC-72 carbon black (Cabot corp., SBET = 250 m² g⁻¹) previously suspended in ethanol solution was added to the metal Nanoparticles (Au and Pt@Au hydrosol) prepared above coupled with agitation for 4 h. After filtration, washing, and drying at 373 K in a vacuum oven, carbon-supported Au/C, Pt/C and Pt@Au/C catalysts were prepared. For every catalyst, the metal loading on the Carbon is 20Wt.%.

Electrode preparation: To prepare an electrode, the uniform suspension was made by mixing 5 mg of catalyst with 100 ul of Nafion™ (5 wt%) and 1.0 ml of Deionized water by adopting ultrasonic for 1 hr. Then 5 ul of the catalyst suspension was placed on the well-polished carbon electrode with micropipette and the electrode dried in air. Transmission electron microscopy (TEM) images of catalysts were performed by JEOL 2010 high-resolution transmission electron microscopy (HRTEM). X-ray diffraction (XRD) patterns for the catalysts were obtained on a D/MAX-III A using Cu K radiation with a Ni filter. The UV/vis spectra of the Au and Pt@Au hydrosols were measured by a PE Lambda 35 spectrometer.

The electrochemical performance of the catalysts were carried out in a conventional three-electrode electrochemical cell in 0.1 mol dm⁻³ HClO₄ using AUTO LAB Electrochemical System (Eco Chemie Corp.). A Pt wire was used as the counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode. All potentials were converted to values with reference to a reversible hydrogen (RHE). In order to produce a clean electrode surface, several potential sweeps between -0.05 and 1.2 V versus RHE were applied to the electrode prior to the electrochemical measurement. The electrochemically active surface area (ECSA) was estimated based on the charge of hydrogen adsorption peak area in the CVs according to the following equation^[1]:

$$ECSA = \frac{Q_H}{0.21 * m}$$

Where m is the loading amount of metal (mg cm^{-2}) in the electrode, Q_H is the charge for hydrogen desorption (mC cm^{-2}) and 0.21 represents the charge required to oxidize a monolayer of H_2 on bright Pt.

The ORR measurements were performed in O_2 -saturated $0.1 \text{ mol dm}^{-3} \text{ HClO}_4$ solutions using the glassy carbon RDE at a rotation rate of 2500 rpm and a sweep rate of 5 mV s^{-1} . For the ORR at a RDE, the Koutecky–Levich equation is used to calculate the kinetic currents as follows^[2]:

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_d}$$

where i is the experimentally measured current, i_d is the diffusion-limiting current, and i_k is the kinetic current. Then the kinetic current was calculated according to the following equation:

$$i_k = \frac{i * i_d}{i_d - i}$$

The Pt shell thickness for Pt@Au nanoparticles were calculated according to the following formula^[3]:

$$D = D_{\text{core}} (1 + V_{\text{Pt}}[\text{Pt}] / V_{\text{Au}}[\text{Au}])^{1/3} \quad (1)$$

$$\text{Shell thickness} = (\text{calculated particle size} - \text{Au particle size}) / 2 \quad (2)$$

Table S1. Properties of nanoparticles prepared with different Pt/Au mole ratios

Pt/Au mole ratio	Measured particle size(nm) (By TEM analysis)	Calculated particle size (nm)	Calculated Pt shell thickness (nm)
0	4.4	—	—
0.5	4.9	5.02	0.31
1	5.6	5.5	0.57
2	6.5	6.34	0.98
4	7.7	7.52	1.58

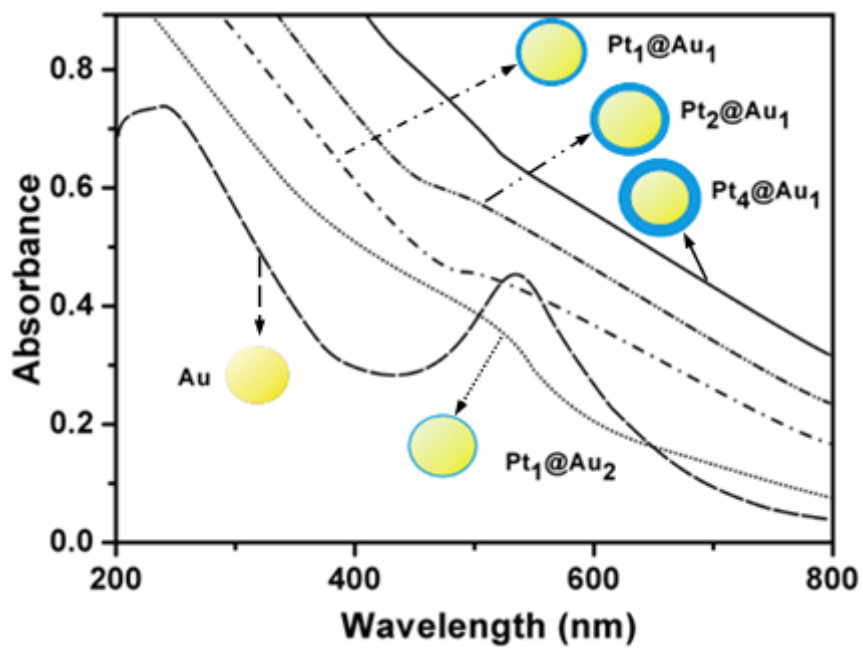


Fig. S1 UV-Vis spectra of aqueous suspension of Au hydrosol and Pt@Au hydrosol with different ratio of Pt/Au

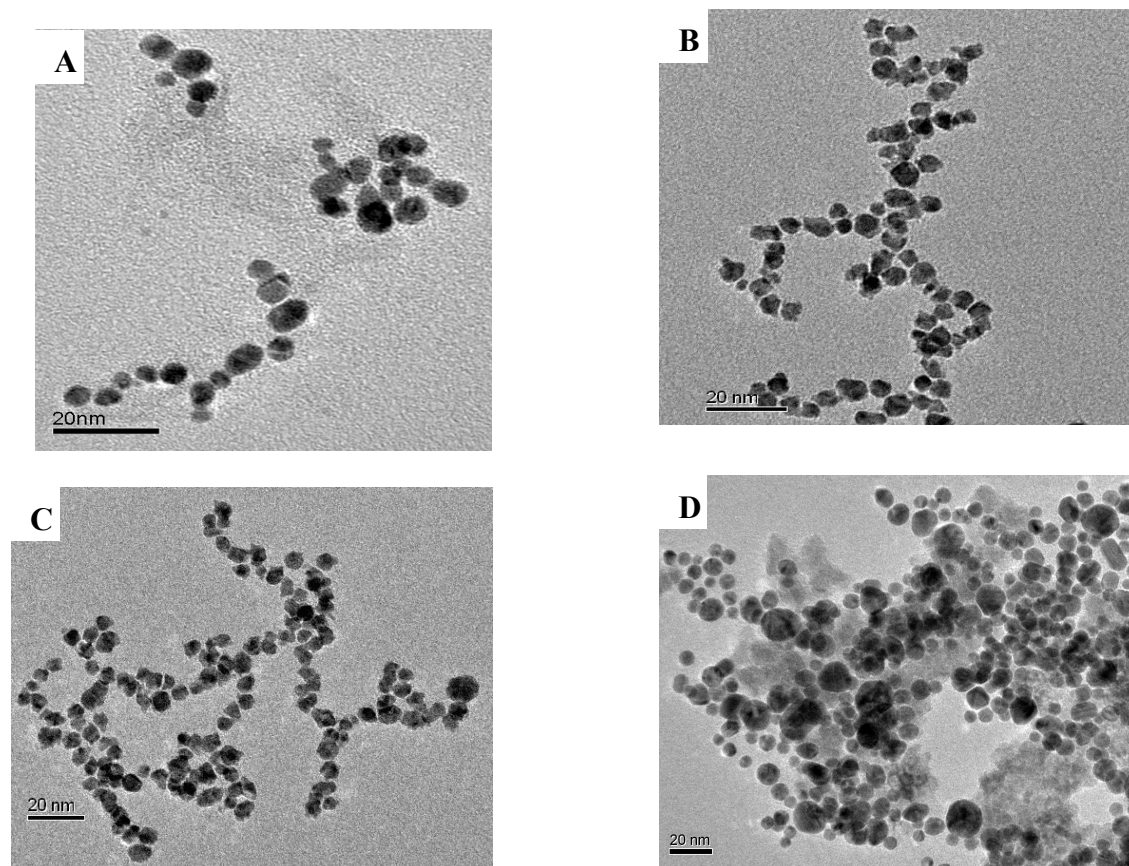


Fig. S2 TEM image of Pt@Au nanoparticles with different ration of Pt/Au : (A) Pt/Au=1:2, (B) Pt:Au=1:1, (C) Pt:Au=2:1 and (D) Pt:Au=4:1

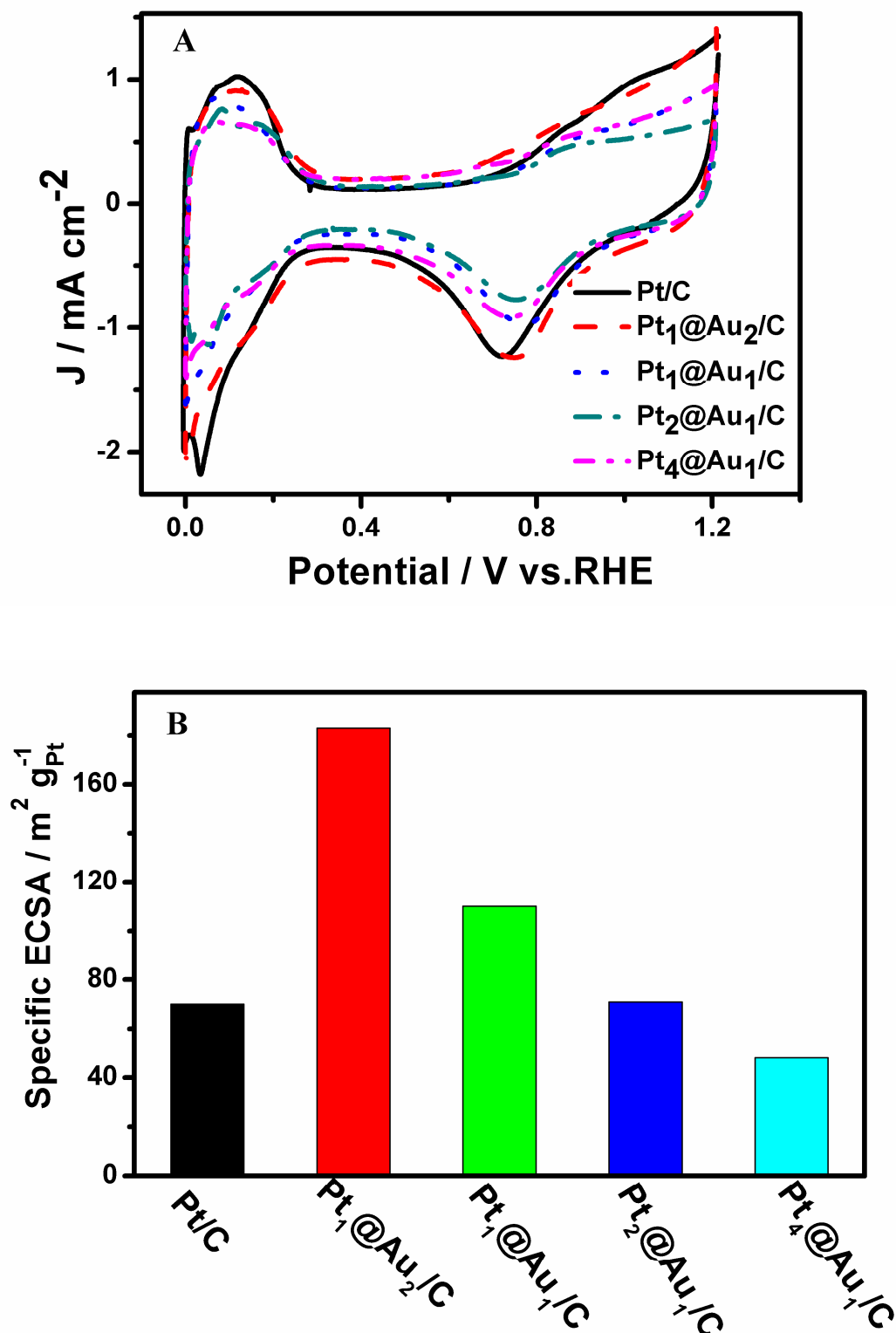


Fig. S3 (A) Cyclic voltammogram curves for the commercial Pt/C and Pt@Au/C catalysts with different ratios of Pt to Au in 0.1 mol dm⁻³ HClO₄ at a scan rate of 50 mV s⁻¹. (B) Comparison of ECSAs for the commercial Pt/C and Pt@Au/C catalysts with different ratios of Pt to Au.

The XRD patterns of Pt/C, Au/C and Pt@Au/C

From the XRD datas of catalysts, there are some negative shift for Pt@Au/C catalysts in comparison with the Pt/C catalysts, which prove the structure effect of Au core to Pt shell.

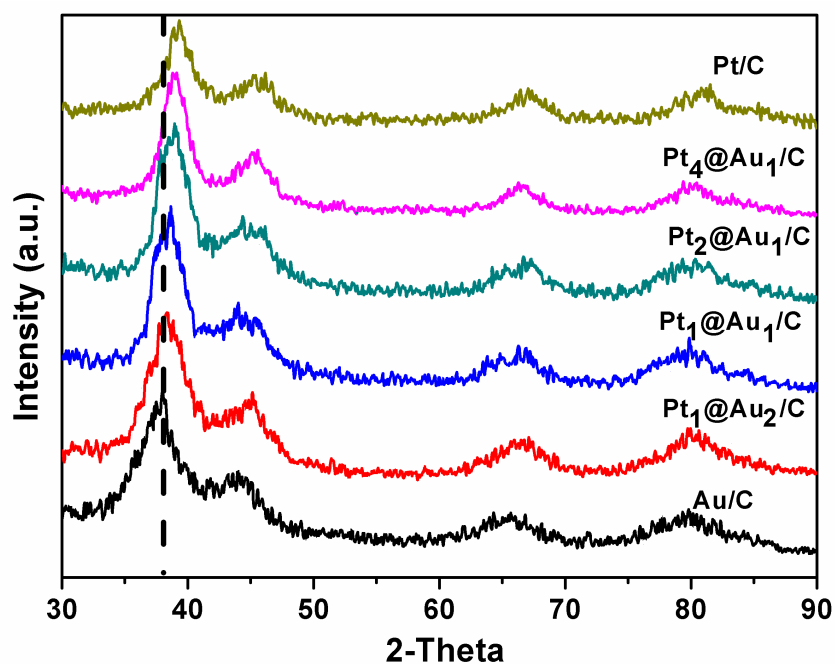


Fig. S4 The XRD patterns of Pt/C, Au/C and Pt@Au/C

The effect of Nafion encapsulated on Pt@Au for oxygen reduction

Fig.S5 shows that the Pt@Au/C encapsulated in Nafion have better ORR than the Pt@Au/C. The increase in activity is attributed to the introduction of Nafion with SO_3^- end groups on the surface of Pt@Au nanoparticle, which can enhance and facilitate the reaction species transfer process for ORR.

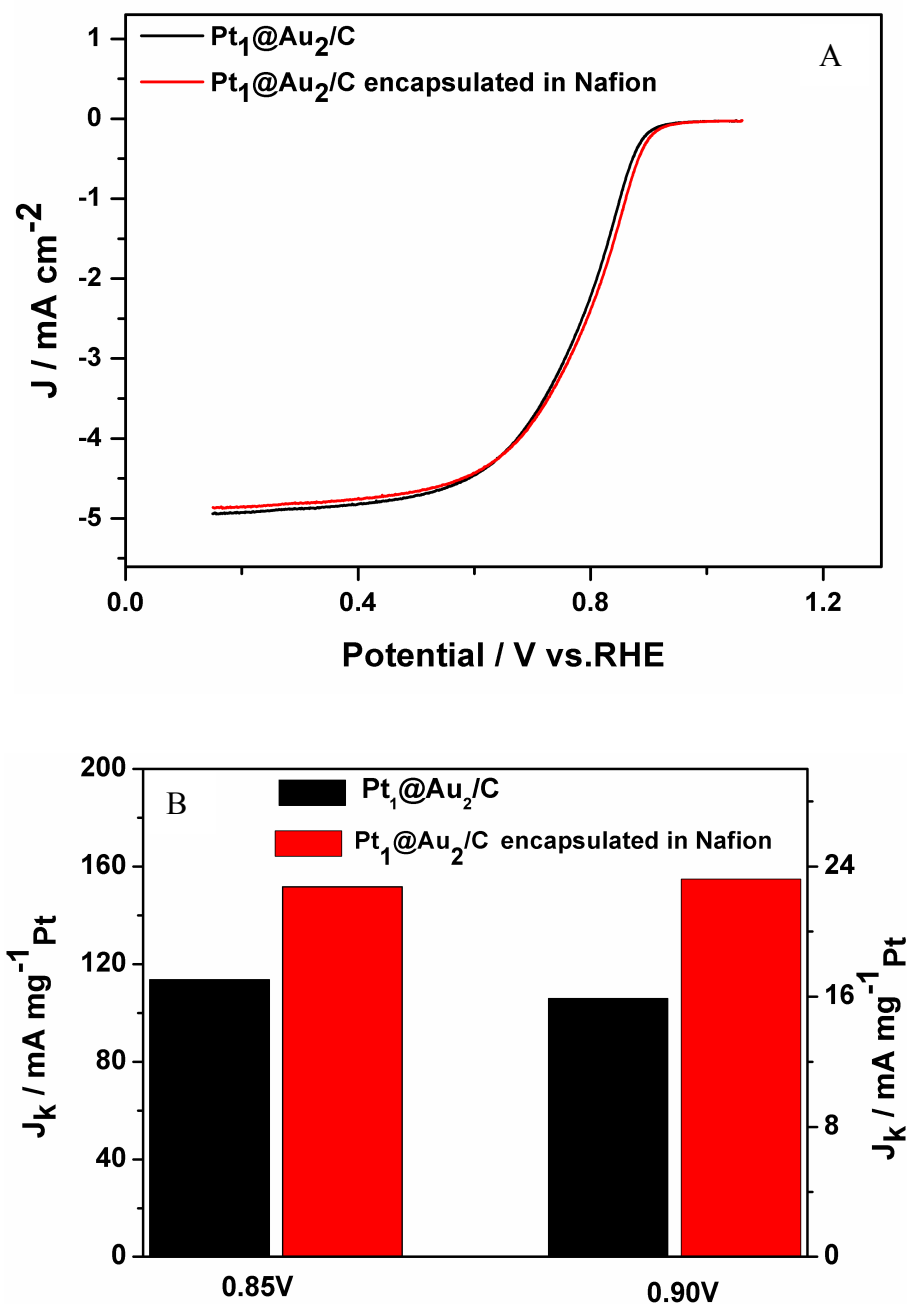


Fig. S5 (A) Comparison of ORR (oxygen reduction reaction) activities of the Pt@Au/C encapsulated in Nafion and Pt@Au/C catalysts in $0.1 \text{ mol dm}^{-3} \text{ HClO}_4$ for ORR reduction at 2500 rpm, sweep rate of 5 mV s^{-1} with scanning the potential in the negative direction and at room temperature. (B) Pt mass activity of the Pt@Au/C encapsulated in Nafion and Pt@Au/C catalysts at 0.85 V and 0.90 V vs. RHE.

References

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