

## Supporting Information for

### Shell Structure-enhanced Electrocatalytic Performance of Au-Pt Core-shell Catalyst

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#### 1. Experimental Section

All the chemical reagents are reagent grade and used without further purification. Hydrogen tetrachloroaurate (III) hydrate ( $\text{HAuCl}_4$ ) and chloroplatinic acid ( $\text{H}_2\text{PtCl}_6$ ) are bought from Tianjin Jinbolan Noble Metal Limited Corporation (Tianjin, China). formic acid ( $\text{HCOOH}$ ), sulfuric acid ( $\text{H}_2\text{SO}_4$ ), absolute ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ), and L-ascorbic acid (AA) are purchased from Shanghai Reagents Limited Corporation (Shanghai, China), and polyvinylpyrrolidone (PVP,  $M_w = 360000$ ) is purchased from China Institute of New Chemical Reagents (Shanghai, China). Nafion (0.05 wt %) and commercial Pt/C catalyst (with Pt loading of 20%) are purchased from YiBang/RuiBang New Power Sources Technology Co. LTD.

##### 1-1. Synthesis of Au nanoparticles

0.4 g PVP was dissolved into 10 mL  $\text{H}_2\text{O}$ , and then 5 mL of 0.1 M L-ascorbic acid (AA) was added to the mixture. 1.8 mL of 9.7 mM  $\text{HAuCl}_4$  solution was added into the above solution. The mixture was stirred for 15 min. Subsequently, the obtained mixture slurries were centrifuged and the products were washed with distilled water and absolute ethanol. After this, the obtained products were dispersed in 10 mL  $\text{H}_2\text{O}$  for further usage.

##### 1-2. Synthesis of Au-Pt core-rods nanoparticles

1 ml Au nanoparticles solution was added into 2.5 ml deionized water and ultrasonic treated for 15 min to ensure Au nanoparticles evenly dispersed, then, 0.5 ml HCOOH and 1 ml of 9.8 mM H<sub>2</sub>PtCl<sub>6</sub> solution were added in sequence. And then the solution was deposited for 8 h. The obtained products were washed with deionized water and absolute ethanol and dissolved into 1 mL ethanol.

### 1-3. Characterizations

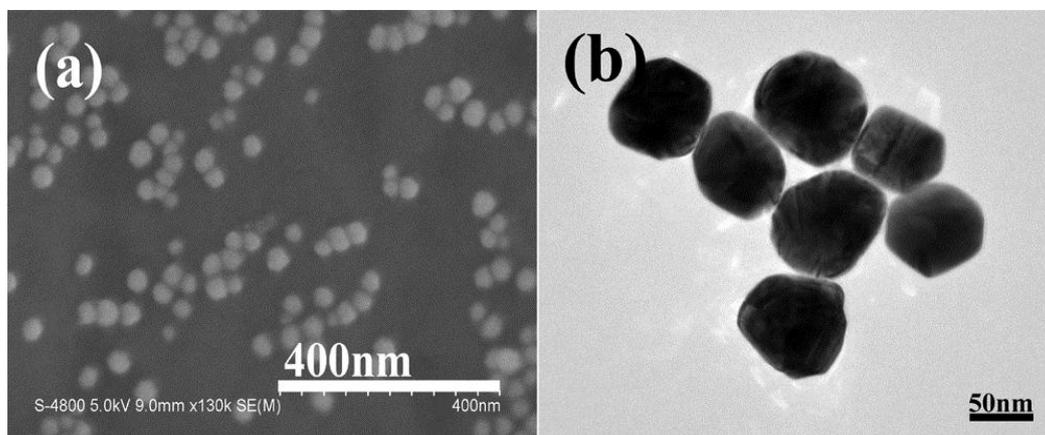
The samples are characterized by a scanning electron microscopy (SEM, Hitachi S-4800) and a transmission electron microscopy (TEM; Tecnai G2 20 S-TWIN, Holland). The samples for above characterizations are prepared by dropping their dilute solution on a carbon-coated copper grid and dried at room temperature. The room temperature UV-visible spectra of the samples are carried out by using a spectrophotometer (U-3010; 220 V, 50 Hz). The electrochemical characterization is carried out by using a CHI660C electrochemical workstation (Shanghai Chenhua apparatus corporation, China).

### 1-4. Electrochemical measurements

To prepare the working electrodes, 1 mg as-prepared catalysts are dispersed into 1 mL absolute ethanol, then 10 μL of as-prepared catalyst is dropped onto a glassy carbon electrode (3 mm diameter) which has been polished with γ-Al<sub>2</sub>O<sub>3</sub>, dried at room temperature. Finally, 5 μL Nafion solution is pipetted onto the catalyst film, and then dried before electrochemical measurements. The total loading of the catalysts is about 10 μg. All the electrochemical measurements are performed by using a CHI660C electrochemical workstation. A standard three-electrode cell is used, including an Ag/AgCl (saturated KCl) electrode as reference electrode, a Pt wire electrode as counter electrode and a working electrode. The cyclic voltammograms (CVs) experiments for hydrogen absorption and desorption are performed in 1 M Ar-saturated H<sub>2</sub>SO<sub>4</sub> solution. The CVs for CH<sub>3</sub>OH electrooxidation measurements are carried out in 0.5 M H<sub>2</sub>SO<sub>4</sub> with 0.5 M CH<sub>3</sub>OH solution. Chronoamperometric curves for CH<sub>3</sub>OH electrooxidation are recorded at 0.7 V 3600 s. All the measurements are performed at room temperature with a scan rate of 50 mV s<sup>-1</sup>. The current densities are normalized by the area of electrode (0.07 cm<sup>2</sup>).

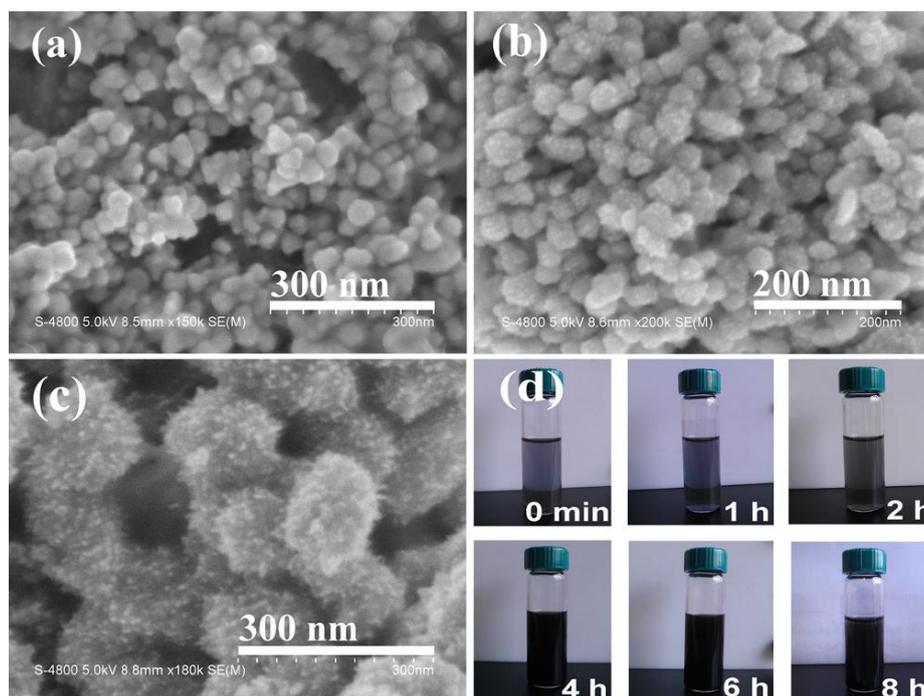
## 2. Additional Figures and Figure Captions

**Figure S1**



**Figure S1.** SEM (a) and TEM (b) images of Au nanoparticles.

**Figure S2**

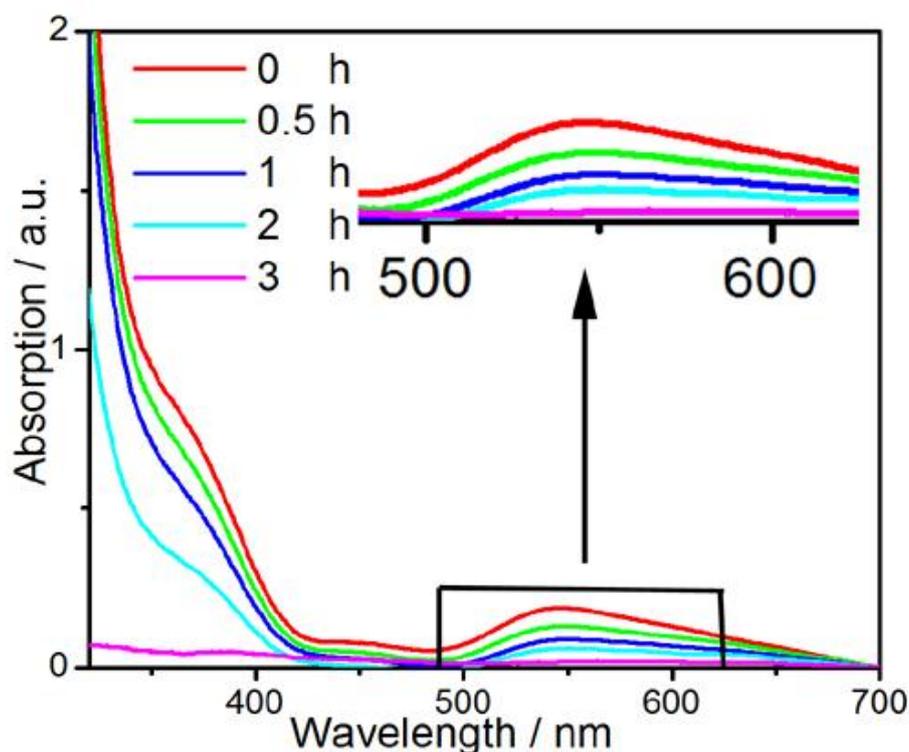


**Figure S2.** SEM images of different reaction time of Au-Pt core-rods catalyst: (a) 1 h, (b) 2 h, (c) 4 h. (d) is the corresponding photographs of colloidal suspensions.

### **Explanation of Figure S2**

To elucidate the growth progress, different stages of the formation of Au-Pt core-rods nanostructure are observed by SEM (**Figure S2a to c**). **Figure S2d** is the photo image of the solution at corresponding reaction time. With the reaction going, the color is change from light purple to black (about 2 h), then it keeps black when the time is further prolonged. As shown in **Figure S2a**, spherical Au nanoparticles nearly keep its original state. When the reaction time comes to 2 h, Pt nanoparticles are obviously provided on the surface of Au NPs via the reduction of hexachloroplatinic acid ( $\text{H}_2\text{PtCl}_6$ ) by formic acid ( $\text{HCOOH}$ ), as shown in **Figure S2b**. Gradual reduction of the  $\text{PtCl}_6^{2-}$  led to the continuous nucleation and growth of Pt nanorods on the Au NPs and the color of solution is increasingly light. Based on **Figure S2c**, the Pt nanorods have grown very well after 4 h's reaction. After a period of 8 h, the solution is completely colorless and the growth of the Pt nanorods was terminated, the product morphology and size are not changed anymore and it can be found that Pt nanorods are distributed uniformly on the surface of Au nanoparticles.

**Figure S3**

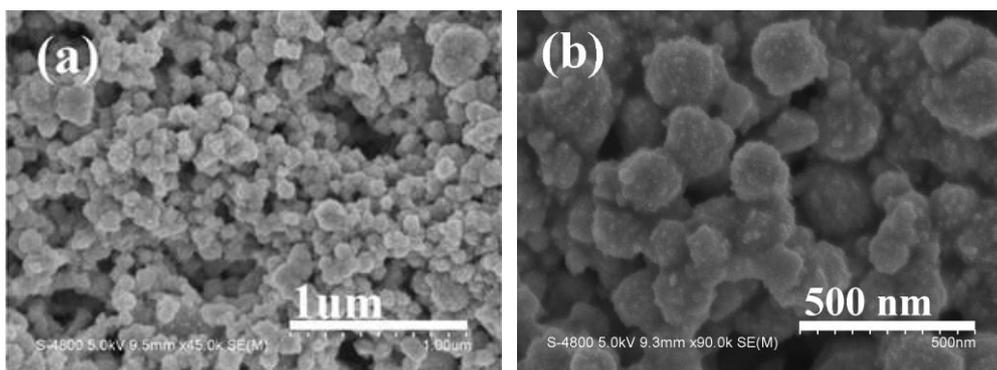


**Figure S3.** UV-vis spectra of Au-Pt core-rods at different reaction time.

#### **Explanation of Figure S3**

The synthesis progress is also monitored with the help of UV-vis spectrophotometer at different reaction time, as shown in **Figure S3**. The red line shows us the UV-vis spectra of Au NPs in water solution, and an obvious peak centered at 540 nm is found, which is belonged to their surface plasmon resonance (SPR) absorption. As we see, with the reaction time increasing, the absorption peak intensity of Au NPs decreases, which is accompanied by the suppression of the absorption peak due to the formation of the Pt nanorods on Au NPs. These results reveal a continuous overgrowth of the Pt nanorods on the surface of Au seed, which is well consistent with SEM analysis. After the reaction for 3 h, the SPR adsorption peak nearly disappears, indicating that the surface of Au is completely covered by Pt nanorods.

**Figure S4**

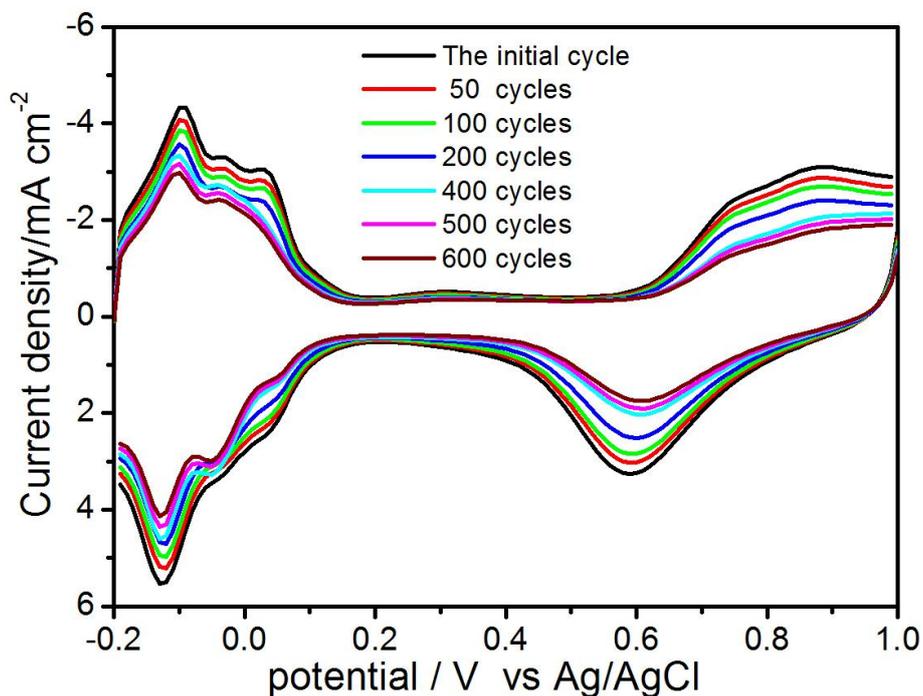


**Figure S4.** Low (a) and high (b) magnification SEM images of Au-Pt core-shell composite catalyst.

#### **Explanation of Figure S4**

**Figure S4** shows the low (a) and high (b) magnification SEM images of Au-Pt core-shell composite catalyst. This Au-Pt core-shell composite catalyst is obtained nearly the same as the synthesis of Au-Pt core-rods catalyst except with the low concentration of  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ . Reaction concentration is supposed to be an important effect factor on the growth of nanostructures. In general, as we see in **Figure S4**, the concentration of  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  decide the morphology of Pt on Au nanoparticles. When we use  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  in low concentration, we cannot get the Au-Pt composite catalyst with Pt nanowire morphology. Simultaneously, the electrocatalytic performance is also much worse than that of Au-Pt core-rods composite catalyst.

**Figure S5**



**Figure S5.** The stability of the Au-Pt core-rods catalyst in 1 M H<sub>2</sub>SO<sub>4</sub>. Sweep rate: 50 mV s<sup>-1</sup>.

#### **Explanation of Figure S5**

Figure S5 shows the stability of the Au-Pt core-rods catalyst. The experiment is operated in 1 M H<sub>2</sub>SO<sub>4</sub>, at the scan rate of 0.05 V s<sup>-1</sup> and cycled for 600 cycles. It was found that the hydrogen adsorption/desorption peaks (between -0.20 and 0.2 V) reduced slowly and orderly among the 200 cycles, with increasing the cycles of CV curves, especially the CV curves of 400 cycles are very close to that of 500 cycles and 600 cycles, which indicates that the stability of this catalyst could be stable when the reaction response to a certain period of time.