

Supporting Information for

Gold-Platinum Yolk-Shell Structure: Facile Galvanic Displacement Synthesis and Highly Active Electrocatalytic Properties for Methanol Oxidation with Super CO-Tolerance

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1. Experimental Section

1-1. Chemicals: In this paper, hydrogen tetrachloroaurate (III) hydrate (HAuCl_4) and chloroplatinic acid (H_2PtCl_6) are bought from Tianjin Jinbolan Noble Metal Limited Corporation (Tianjin, China). Silver nitrate (AgNO_3), ethylene glycol (EG), ammonia ($\text{NH}_3\cdot\text{H}_2\text{O}$), sodium borohydride (NaBH_4), methanol (CH_3OH) and potassium hydroxide (KOH) 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). Commercial Pt/C electrocatalyst (the loading of Pt is about 40 % and Pt nanoparticles is about 2.8 nm) are purchased from YiBang/RuiBang New Power Sources Technology Co. LTD. All the reagents are analytical grade except that AgNO_3 is chemical grade. In addition, all the chemicals are used as received without any purification.

1-2. The preparation of Au nanoparticles (NPs): Typically, 0.4 g PVP is added into 10 mL of 0.7 mmol/L HAuCl_4 aqueous solution under vigorously stirring, and then 5 mL 2 % $\text{NH}_3\cdot\text{H}_2\text{O}$ is added into the above solution under continuously stirring. Next, the solution is transferred into a 25 mL stainless autoclave and kept at 120 °C for 2 h. When cooled down to room temperature, the product is centrifugated and washed with deionized water and absolute ethanol 2-3 times. The obtained Au NPs are dispersed in 25 mL EG and ready for use.

1-3. Preparation of Au@Ag core-shell (C-S) structure: The method is similar to that reported by Tsuji et al.¹ Typically, 0.1 g PVP and 15 mg AgNO₃ are added into above Au NPs solution (EG) under violently stirring, respectively. Several minutes later, the prepared solution is transferred into a 100 mL flask and kept at 140 °C in oil bath for 2 h. The color changes from red to orange-yellow. When cooled to room temperature, the product is centrifugated and washed with deionized water and absolute ethanol 2-3 times. The obtained product is dispersed in 20 mL deionized water in a glass tube and ready for use.

1-4. Preparation of Au-Pt yolk-shell (Y-S) structure: 0.6 mL of 19 mmol/L H₂PtCl₆ is added into the above 20 mL Au@Ag C-S structure aqueous solution and reversed for 10 seconds, and then left undisturbed under the black condition for 4 h. The color changes from orange-yellow to blue. The product is centrifugated and washed with NH₃•H₂O, deionized water and absolute ethanol 2-3 times in turn.

1-5. Preparation of Pt NPs: 5 mL of 0.01 mol/L fresh ice-cold NaBH₄ is added drop by drop into 10 mL of 1.9 mmol/L H₂PtCl₆ and stirred vigorously for 30 min. Finally, the product is centrifugated and washed with deionized water and absolute ethanol 2-3 times.

1-6. Preparation of Au@Pt C-S structure: The method is similar to that reported by Sun et al.² Typically, 0.5 mL HCOOH and 0.5 mL of 19 mmol/L H₂PtCl₆ are added into the 20 mL as-prepared Au NPs aqueous solution and reversed for 10 seconds, and then left undisturbed for 4 h. Finally, the product is centrifugated and washed with deionized water and absolute ethanol 2-3 times. The loading of Pt is about 50 %.

1-7. Preparation of silver NPs: Typically, 0.2 g PVP and 5 mL of 2 % NH₃•H₂O are added into 10 mL of 0.02 M AgNO₃ solution. The solution is transferred to a 25 mL autoclave for 12 h at 120 °C. When cooled to room temperature, the product is centrifugated and washed with deionized water and absolute ethanol 2-3 times.

1-8. Preparation of hollow Pt structure: 2 mL of 19 mmol/L H₂PtCl₆ are added into the Ag NPs aqueous solution reversed for 10 seconds, and then left undisturbed under the black condition for 4 h. The product is centrifugated and washed with NH₃•H₂O, deionized water and absolute ethanol 2-3 times in turn.

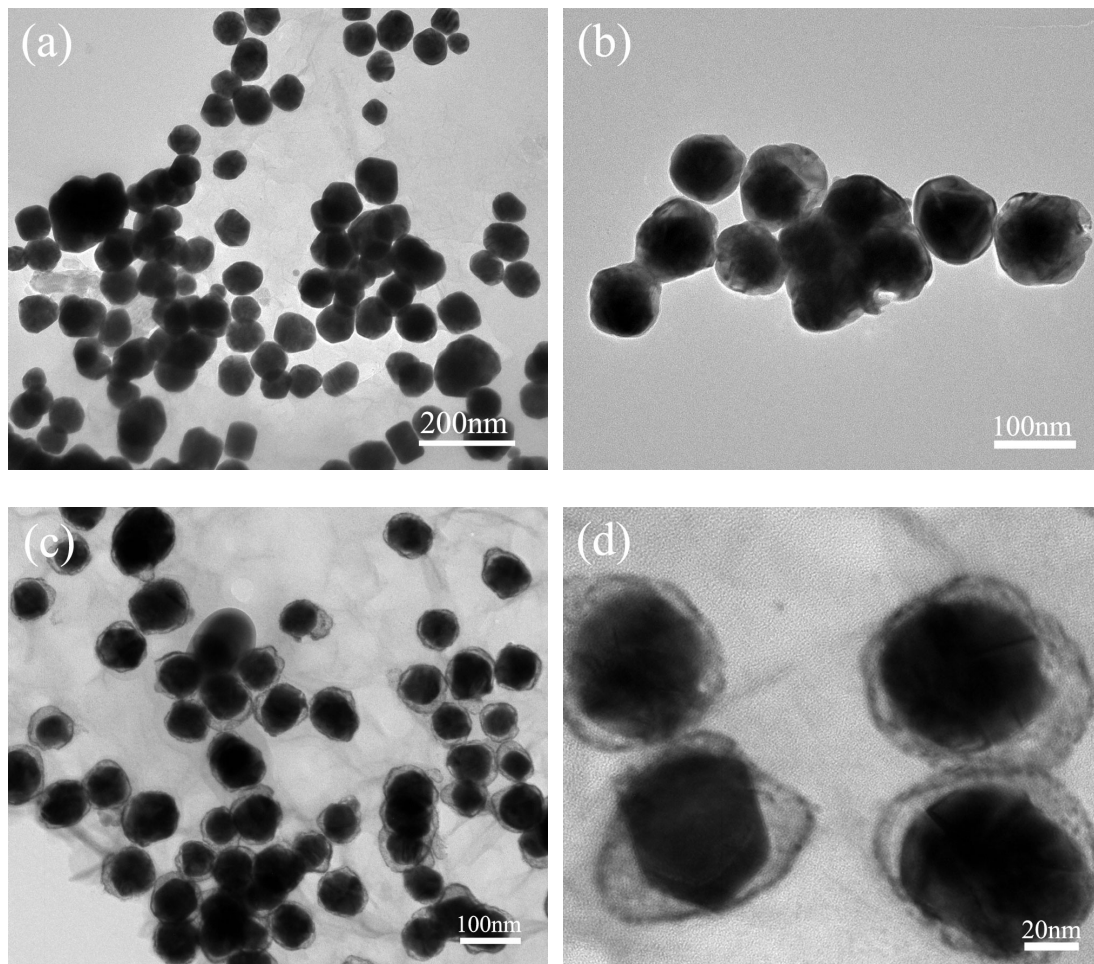
1-9. Characterizations: The samples are characterized by a transmission electron microscopy (TEM; Tecnai G2 20 S-TWIN, Holland). The elemental mappings and cross-sectional compositional line profiles are performed by using a JEM-2100F (JEOL, Japan) equipped with energy dispersive spectrometer (EDS) analyses. 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 absorption 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).

1-10. Electrochemical measurements: To prepare the working electrodes, 1 mg as-prepared catalysts are dispersed into 2 mL absolute ethanol, and then 15 μL of as-prepared catalyst is dropped onto a glass carbon electrode (3 mm diameter) which is polished with 0.3 μm and 0.05 μm $\gamma\text{-Al}_2\text{O}_3$ in turn before using, dried at room temperature. Finally, a 10 μL Nafion (0.05 wt %) solution is pipetted onto the catalyst film, and then dried before electrochemical measurements. The total loading of the catalysts is about 8 μg .

All the electrochemical measurements of the catalysts 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 0.5 M N_2 -saturated KOH aqueous solution. The CVs for CH_3OH electrooxidation measurements are carried out in 0.5 M KOH aqueous solution with 0.5 M CH_3OH at air atmosphere. Chronoamperometric curves for CH_3OH electrooxidation are investigated in 0.5 M KOH aqueous solution with 0.5 M CH_3OH for 3600 s, recorded at -0.3 V. All the measurements are performed at room temperature, and the CVs experiments are carried out at a scan rate of 50 mV s^{-1} . Besides, current densities are normalized in reference to the loading of Pt.

2. Additional Figures and Figure Captions

Figure S1



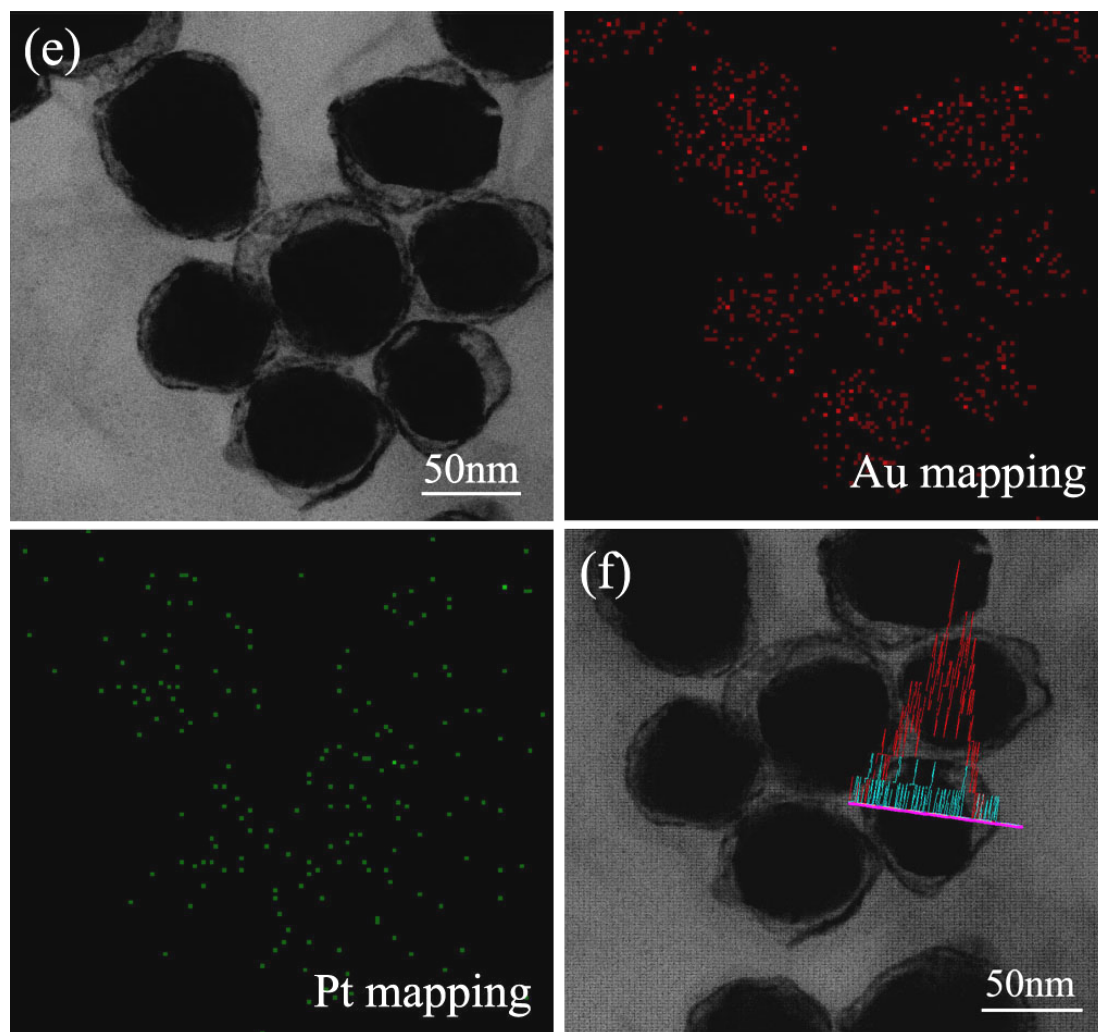


Figure S1. TEM images of Au (a), Au@Ag core-shell structure (b), Au-Pt yolk-shell structure (c), and (d) is the high-magnification TEM of Au-Pt yolk-shell structure. Elemental mapping images of Au and Pt (e) and cross-sectional compositional line profiles of the marked area (f).

Explanation of Figure S1

As is vividly depicted in Figure S1a to d, a series of chemical varieties from Au nanoparticles to the Au-Pt Y-S structure all take place successfully as designed orders. The procedures can be suggested by the following equations:

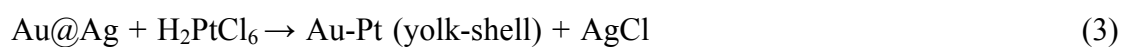
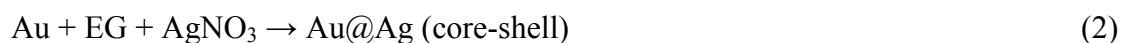


Figure S2

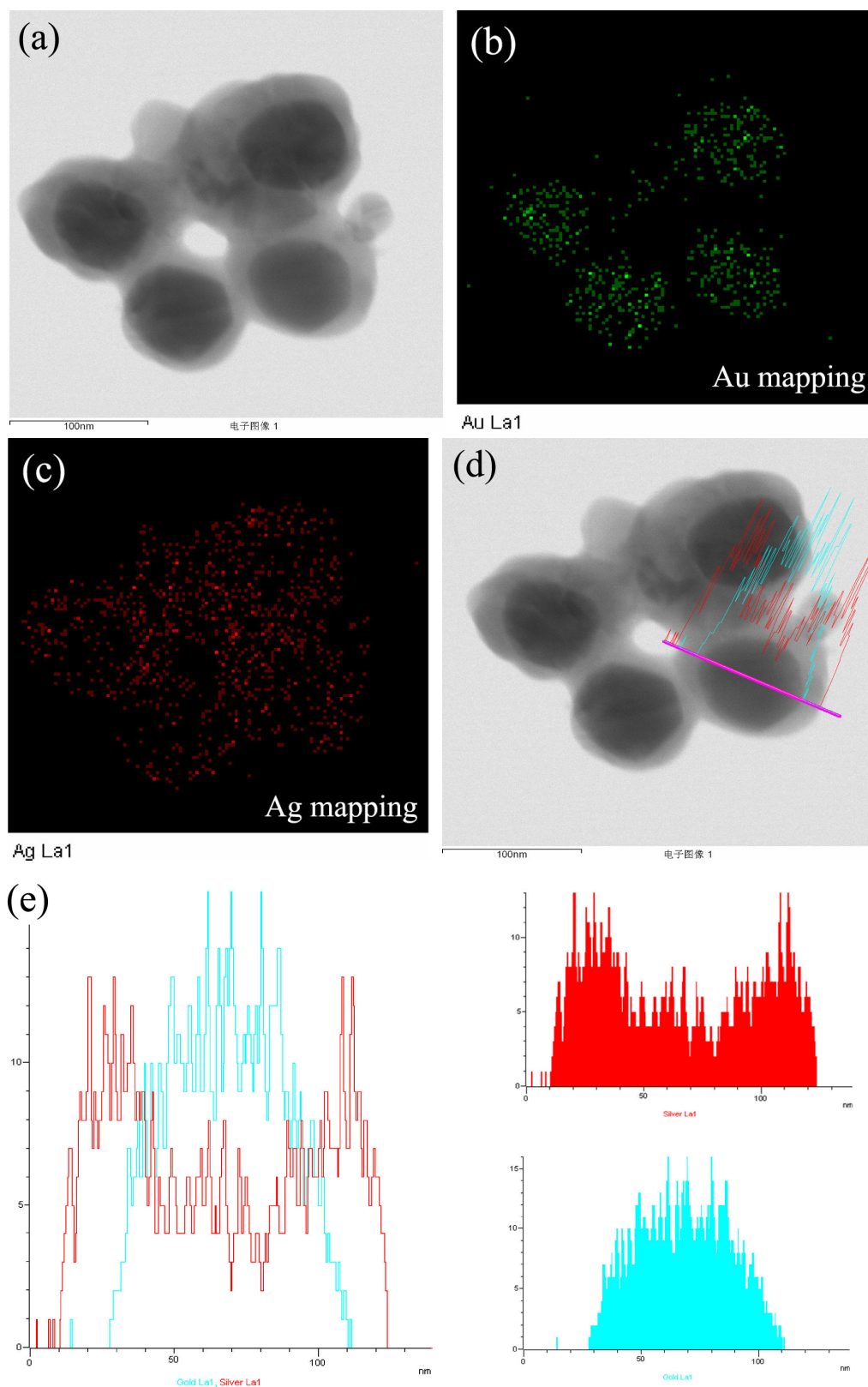


Figure S2. STEM-EDS mapping images of the Au@Ag core-shell structure (a), (b) and (c). Cross-sectional compositional line profiles (d) and (e) of the square area of Figure S2d.

Figure S3

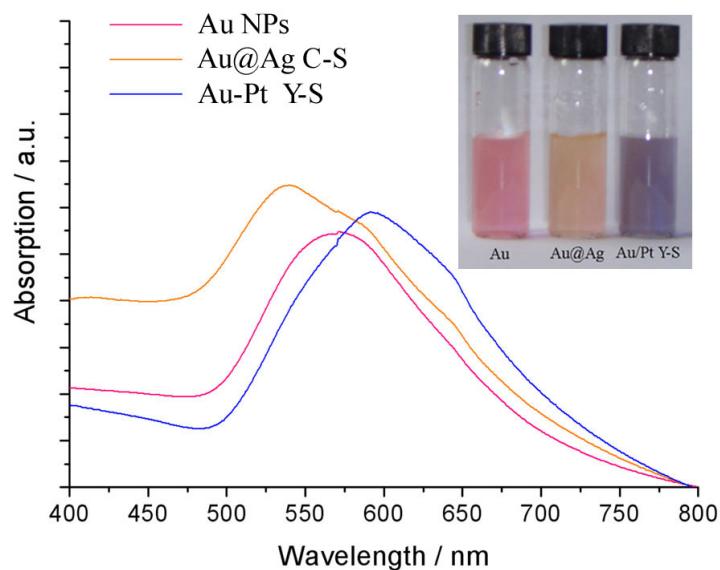


Figure S3. UV-vis spectra of Au NPs (red line), Au@Ag core-shell structure (yellow line) and Au-Pt yolk-shell structure (blue line). The inset is the photos of corresponding products in water.

Explanation of Figure S3

The optical properties of the Au-Pt Y-S structure are investigated with the help of UV-vis spectrophotometer. Figure S3 displays their typical UV-vis spectra in water, and the inset is their corresponding photos. As for Au NPs, the surface plasmon resonance (SPR) absorption peak is centered at 570 nm (red line), while that of Au@Ag C-S structure is located at 532 nm (yellow line) which is blue-shifted by 38 nm. On the contrary, the SPR absorption peak of Au-Pt Y-S structure, with a SPR absorption peak centered at 591 nm (red line), is red-shifted by 21 nm as compared with that of Au NPs. Herein, Pt shell and the space between the Au core and Pt shell should be responsible to the red-shift.

Figure S4

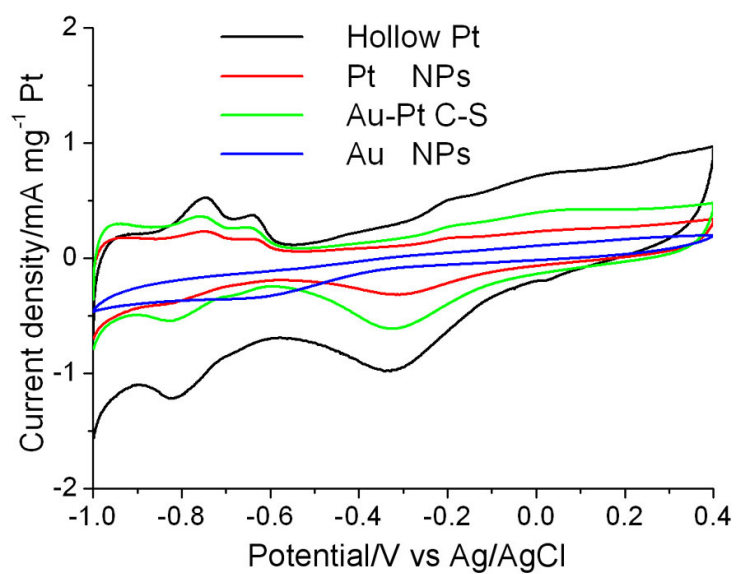


Figure S4. Cyclic voltammograms of the hollow Pt (black line), Au@Pt core-shell (green line), Pt NPs (red line) and Au NPs (blue line) catalysts, measured at a scan rate of 50 mV s⁻¹ in 0.5 M N₂-saturated KOH aqueous solution at room temperature.

Figure S5

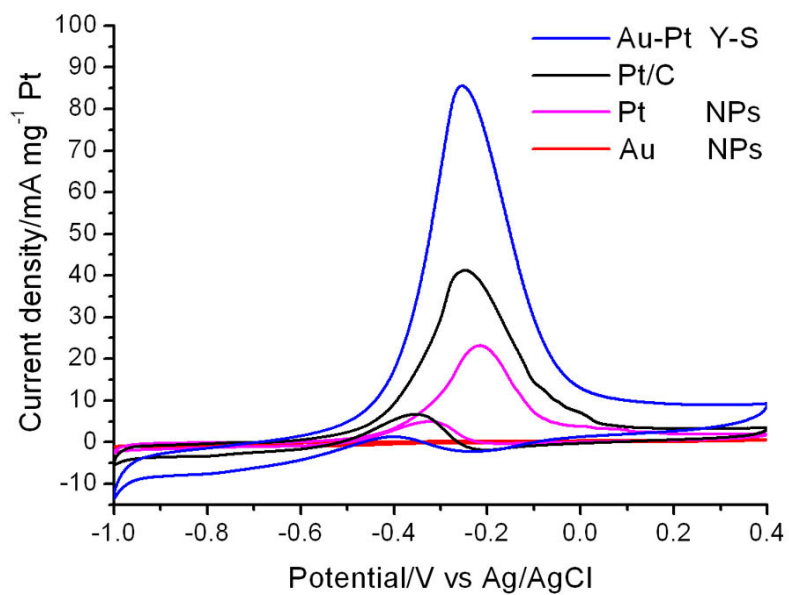


Figure S5. Cyclic voltammograms for CH₃OH oxidation reaction catalyzed by Au-Pt yolk-shell (blue line), commercial Pt/C (black line), Pt NPs (pink line) and Au NPs (red line) catalysts respectively, measured at a scan rate of 50 mV s⁻¹ in 0.5 M KOH aqueous solution with 0.5 M CH₃OH at room temperature and air atmosphere.

Figure S6

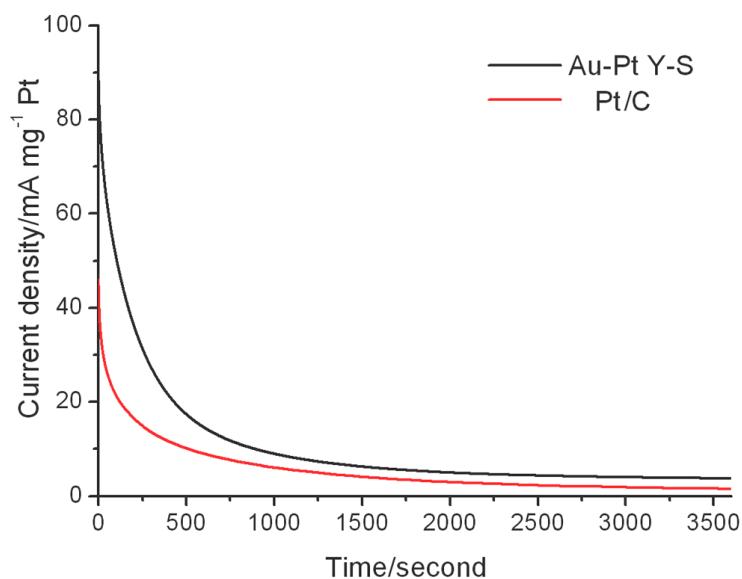


Figure S6. Current versus time curves for CH₃OH oxidation reaction catalyzed by Au-Pt yolk-shell (black line) and commercial Pt/C (red line) catalysts respectively, in 0.5 M KOH aqueous solution with 0.5 M CH₃OH, recorded at -0.3 V at room temperature and air atmosphere.

Explanation of Figure S6

Long-term chronoamperometric curves for electrooxidation of CH₃OH are investigated to further evaluate the activity and stability of Au-Pt Y-S catalyst, which are measured in 0.5 M KOH aqueous solution with 0.5 M CH₃OH for 3600 s, recorded at -0.3 V. As shown in Figure S6, the current densities reach a stable state after a brief period. The current density for Au-Pt Y-S catalyst keeps a high level (about 2.5 times higher than that for commercial Pt/C) though it is decayed at the outset of the tests. Moreover, the current density for commercial Pt/C catalyst is still decaying slightly even after 3600 s, while that for Au-Pt Y-S catalyst has reached rather stable about 3200 s later.

Figure S7

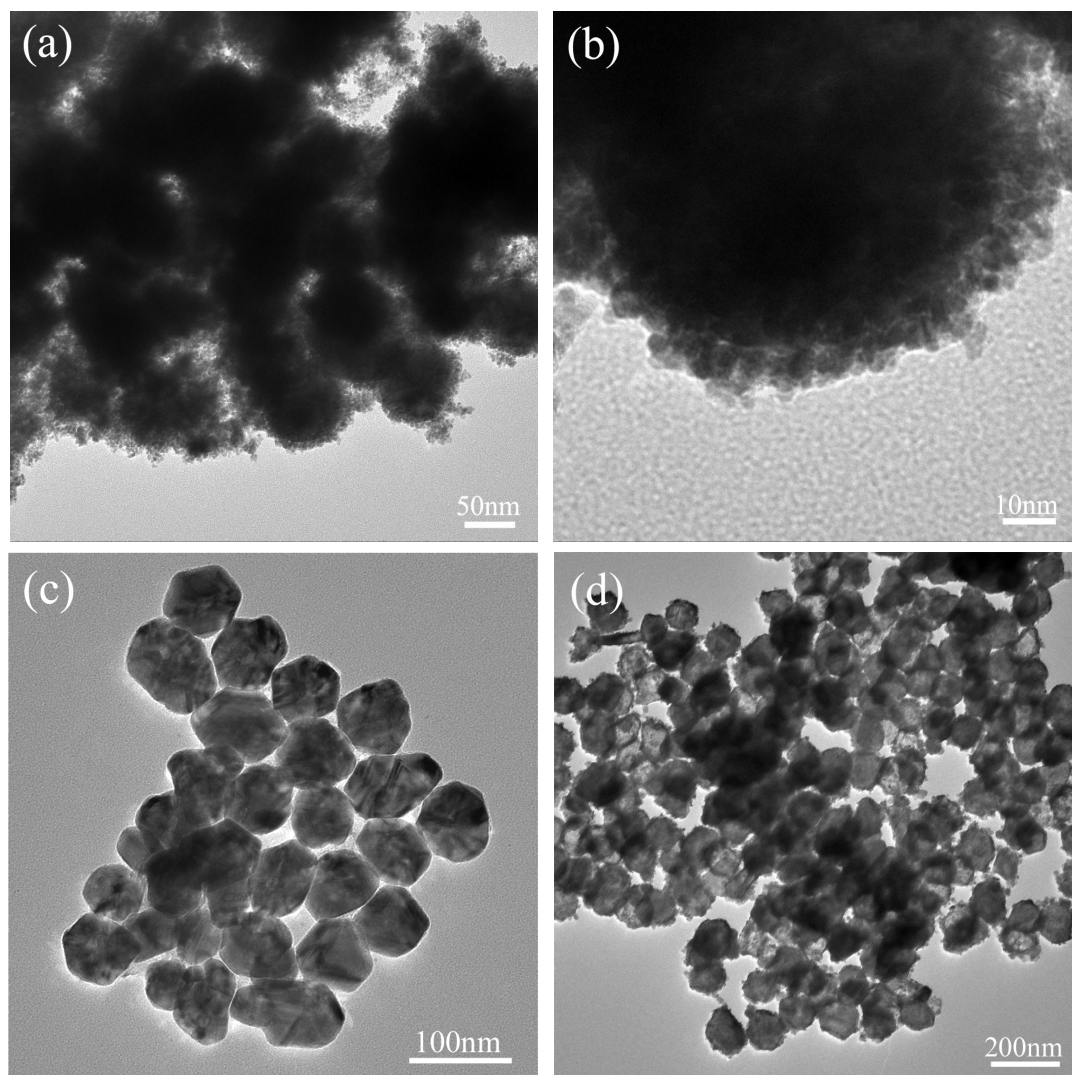


Figure S7. (a) Low- and (b) high-magnification TEM images of Au@Pt core-shell structure; (c) TEM image of Ag NPs; (d) TEM image of hollow Pt structure.

Figure S8

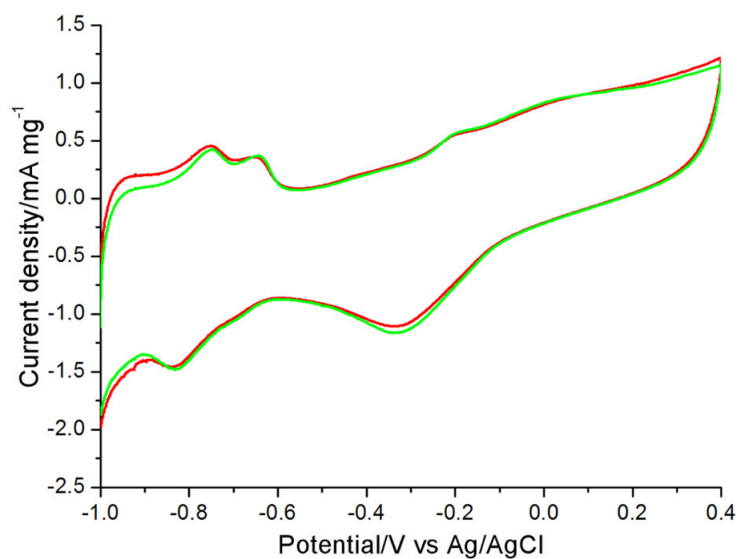


Figure S8: The initial CV (red line) and the CV after all the measurements (methanol oxidation and current-time curve) (green line) of Au-Pt yolk-shell catalyst in 0.5 M N₂-saturated KOH aqueous solution.

Explanation of Figure S8

The stability is also one of the indications to the performance of the catalyst. As shown in Figure S8, the CV doesn't change significantly compared to the initial one after all the measurements (methanol oxidation and current-time curve). Therefore, the ESA of the Au-Pt yolk-shell catalyst can almost keep a stable state after a long time use.

Figure S9

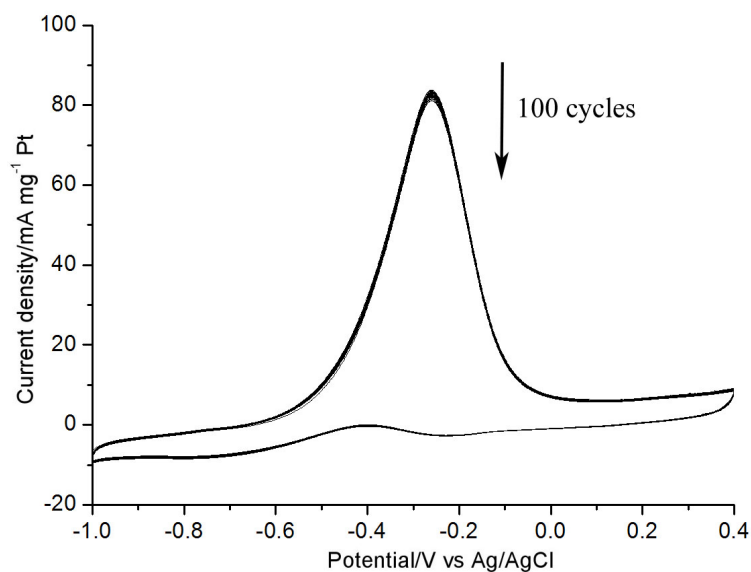


Figure S8: CVs during 100 cycles for CH₃OH oxidation reaction catalyzed by Au-Pt yolk-shell catalyst in 0.5 M KOH aqueous solution with 0.5 M CH₃OH at air atmosphere.

Explanation of Figure S9

The CO-tolerance stability is also an important factor to evaluate performance of the catalyst. Herein, the CO-tolerance stability is evaluated by cycle tests. As shown in Figure S9, the I_f/I_b value keeps in a fairly stable state during the test. That is the Au-Pt Y-S catalyst exhibits excellent CO-tolerance stability.

Figure S10

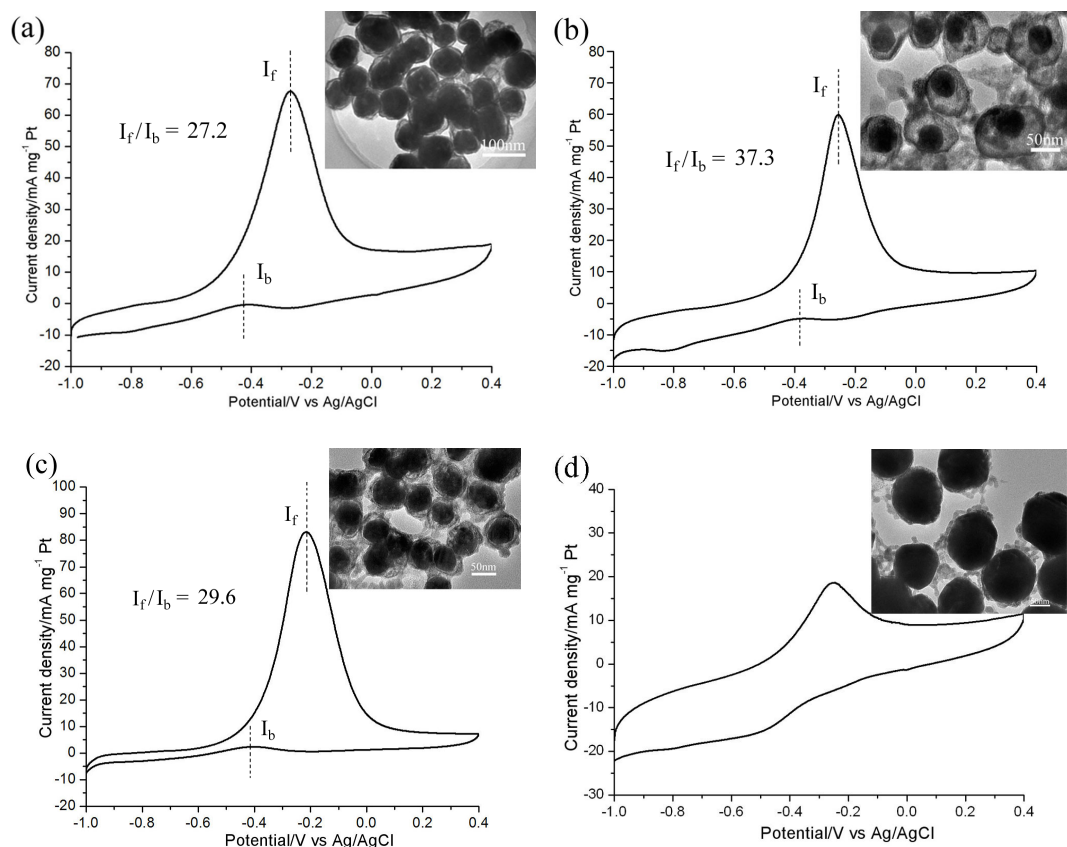


Figure S10: The initial CVs of Au-Pt yolk-shell catalyst with smaller space (a), bigger space (b), smaller Au core (c) and bigger Au core (d), the insets are the corresponding TEM images. .

The Explanation of Figure S10

We investigate the effect of the size of the space and the Au core to the electrocatalytic performance. As shown in Figure S10a and b, it can be found that the Au-Pt yolk-shell catalyst with bigger space owns better CO-tolerance ($I_f/I_b=37.3$) than that of the smaller one. The better CO-tolerance may be caused by that the methanol molecule can stay in the space longer and be oxidized more efficiently. In addition, we find that the size of Au core hardly affect the CO-tolerance (see Figure S10c and Figure 2b). However, the catalytic activity reduced significantly when the size of Au core increases so much (see Figure S10d). It is because that the content of Pt is too low to be able to catalyzing the methanol oxidation. Therefore, the smaller Au core and bigger space are beneficial to the electrocatalytic performance.

References:

- 1 M. Tsuji, N. Miyamae, S. Lim, K. Kimura, X. Zhang, S. Hikino, M. Nishio, *Cryst. Growth Des.* 2006, **6**, 1801.
- 2 (a) S. H. Sun, G. X. Zhang, D. S. Geng, Y. G. Chen, M. N. Banis, R. Y. Li, M. Cai, X. L. Sun, *Chem. Eur. J.* 2010, **16**, 829. (b) S. H. Sun, D. Q. Yang, D. Villers, G. X. Zhang, E. Sacher, J. P. Dodelet, *Adv. Mater.* 2008, **20**, 571.