

Electronic Supplementary Information

Unveiling the Size Effect of Pt-on-Au Nanostructures Towards CO and Methanol Electrooxidation by *In-Situ* Electrochemical SERS

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Experimental details

Materials:

Oleylamine, platinum 2,4-pentanedionate ($\text{Pt}(\text{acac})_2$), sodium citrate, methanol, HAuCl_4 , HCl , H_2SO_4 , HClO_4 , and HNO_3 were purchased from Shanghai Reagent Corporation, China. All chemicals were used without further purification. Ar (99.999%) and CO were purchased from Linde Gas (Xiamen) Co., Ltd. Milli-Q water ($18.2 \text{ M}\Omega \cdot \text{cm}$) was used throughout the study, and all glass wares were cleaned with aqua regia before use.

Method:

1. Synthesis of platinum nanoparticles

50 mg Platinum 2,4-pentanedionate ($\text{Pt}(\text{acac})_2$) and 15 mL oleylamine were put in a round-bottomed flask and kept stirring for 20 min at room temperature to ensure the complete dissolution of $\text{Pt}(\text{acac})_2$. Next, the sample was heated to 100°C under Ar atmosphere and hold for 20 min. Then, 0.2 g borane tert-butylamine complex (BTB) was dissolved in 3 mL oleylamine. Finally, the above-mentioned BTB solution was added to the $\text{Pt}(\text{acac})_2$ solution. The mixtures were further heated to 140°C in 10 minutes. After reacting for 60 min, the mixtures were naturally cooled. The products were precipitated with ethanol, centrifuged, and washed with ethanol for two-three times. The obtained solid is Pt nanoparticles with size around 2.1 nm. It was then dispersed in toluene for further use. The Pt nanoparticles with larger size were prepared with a seed-mediated growth method using the obtained 2.1 nm Pt as the seeds. The size of the Pt nanoparticles was manipulated by controlling the amount of Pt seeds added.

2. Synthesis of Gold Nanoparticles

200 mL of H_2O and 2.42 mL of 0.825% HAuCl_4 were add in a round-bottom

flask. The mixtures were heated to boiling under vigorously stirring. 1.5 mL 1% sodium citrate (CA) was then injected quickly into the solution. After reaction for another 20 min, remove the heating mantle and naturally cool down to obtain 55 nm Au sols.

3. Preparation of core-satellite nanocomposites

The core-satellite nanocomposites were prepared using a self-assembly method.¹ Pt nanoparticles were dispersed in 1 mL toluene, into which 1 mL 0.1 M NOBF₄ was added. The mixtures were shaken for about 10 minutes to ensure the complete replacement of the ligand on the surface of the Pt nanoparticles. After adding 3 mL toluene and 3 mL cyclohexane, the mixtures were then centrifuged at a speed of 10,000 rpm for 10 min. The supernatant was removed, and the resulting nanoparticles were dissolved in 1 mL acetonitrile. Pt nanoparticles with positively charged surfaces were then obtained. Took an appropriate amount of the obtained Pt nanocatalyst into 500 uL acetonitrile solution and mix ultrasonically. 1 mL 55 nm Au dispersions were concentrated to 100 uL. 50 uL of the concentrated Au dispersion was added to the above Pt dispersion and oscillated ultrasonically for 1 h to allow the positively charged Pt nanoparticles assemble on the negatively charged Au, leading the formation of Pt-on-Au core-satellite nanocomposites. Finally, the mixtures were separated by centrifugation. The solids, i.e., the Pt-on-Au core-satellite nanocomposites, were dispersed in acetonitrile for further use.

4. Characterization and electrochemical test

Transmission electron microscope (TEM) images were taken on JEM-1400 at 100 kV. Raman spectra were recorded on an Xplora Plus Raman instrument with a 50xobjective. The excitation laser lines were 638 nm with a laser power of 2.6 mW. The electrochemical experiments were completed on the CHI 630E. An appropriate amount of the above-mentioned nanocomposite was deposited on the surface of the glassy carbon electrode (Jinhuice.com, Nanjing, China) and used as the working electrode.

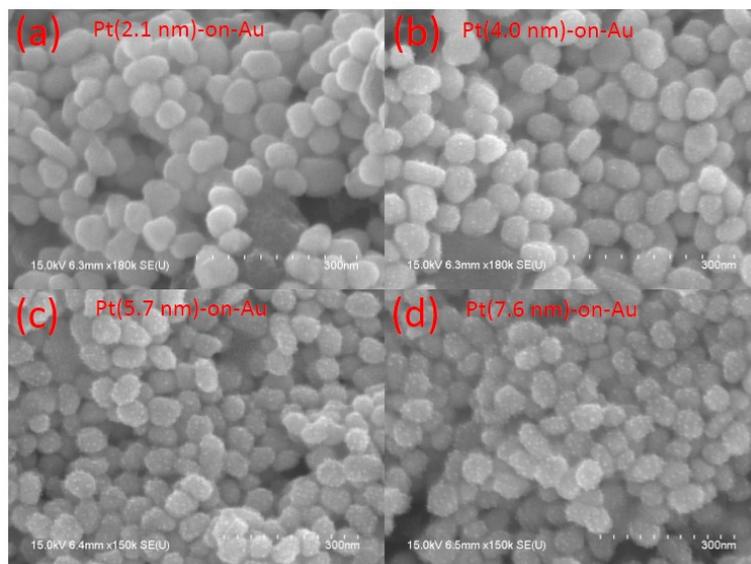


Fig. S1. SEM images of the Pt-on-Au core-satellite nanostructure catalysts. (a), (b), (c), and (d) are Pt-on-Au core-satellite nanocomposites consisting of Pt nanoparticles with size of 2.1 nm, 4.0 nm, 5.7 nm, and 7.6 nm, respectively.

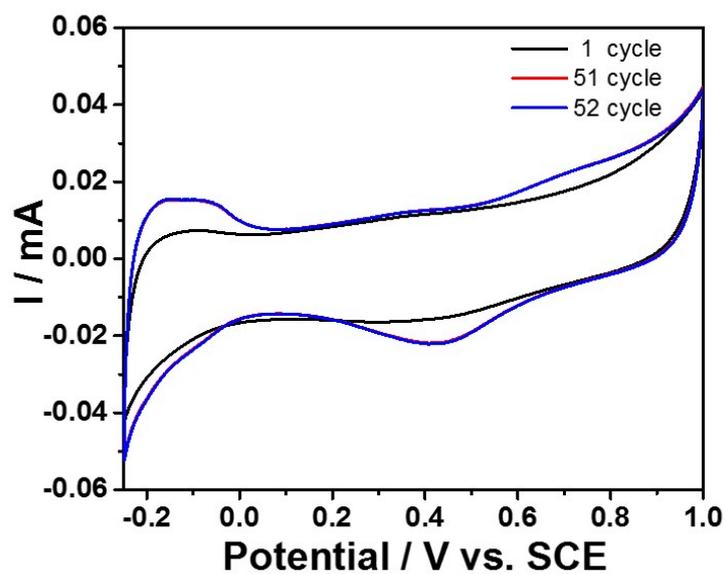


Fig. S2. CVs of Pt (2.1 nm)-on-Au cores-satellite nanocomposites activated in 0.1 M HClO₄ at 100 mV/s with different cycles.

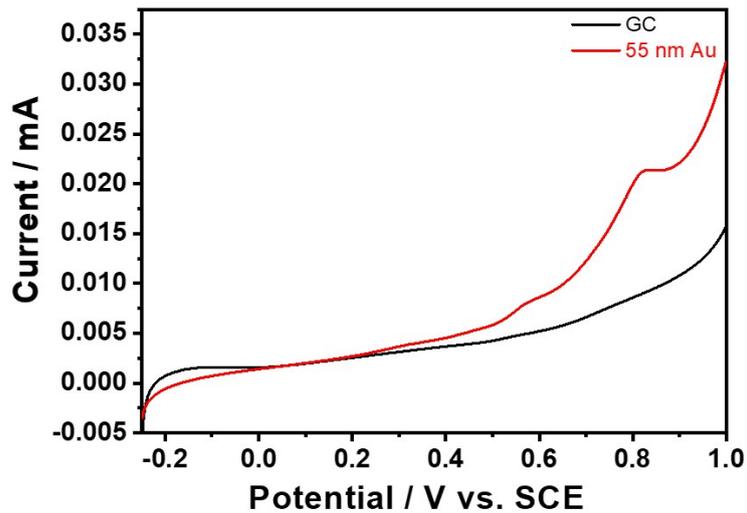


Fig. S3. CO stripping voltammograms for glassy carbon electrode and Au nanoparticles in 0.1 M HClO₄ at a scan rate of 20 mV/s. The pure Au nanoparticles only display a small oxidation peak after 0.8 V vs. SCE during the electrooxidation of CO, which is much less active than Pt. This should result from the fact that Au nanoparticles with a very large diameter (~55 nm), which are quite inert in catalysis, are used here in order to generate strong Raman enhancement.

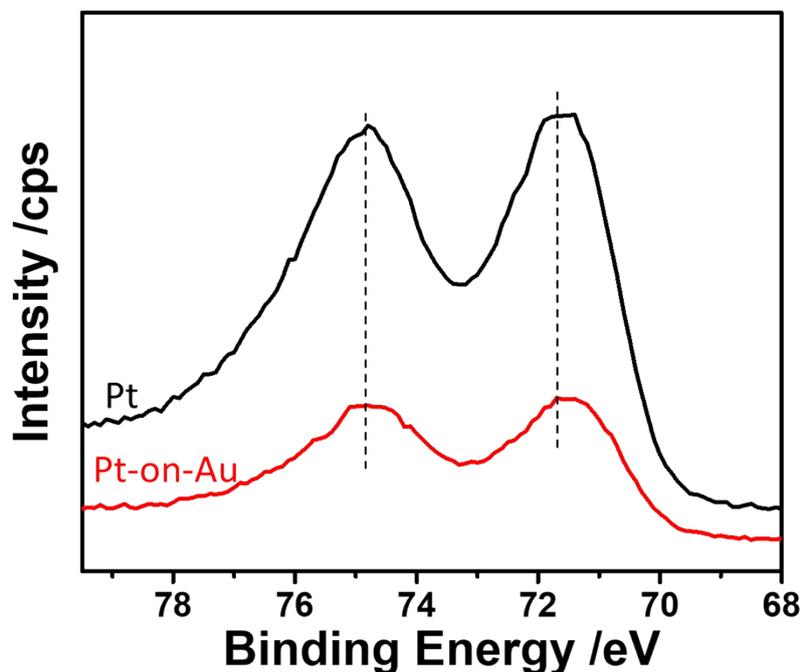


Fig. S4. XPS spectra of the pure Pt (2.1 nm) and Pt (2.1 nm)-on-Au nanocatalysts. The binding energies for the Pt 4f of Pt-on-Au shift to lower values compared to that of pure Pt, which indicates that electrons would transfer from Au to Pt.

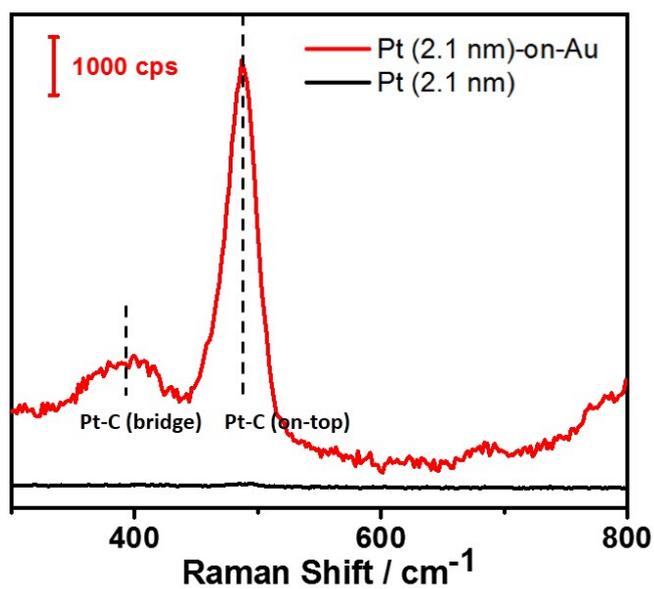


Fig. S5. The electrochemical SERS spectra for CO electrooxidation on Pt-on-Au and pure Pt in 0.1 M HClO₄ at -0.2 V (vs. SCE).

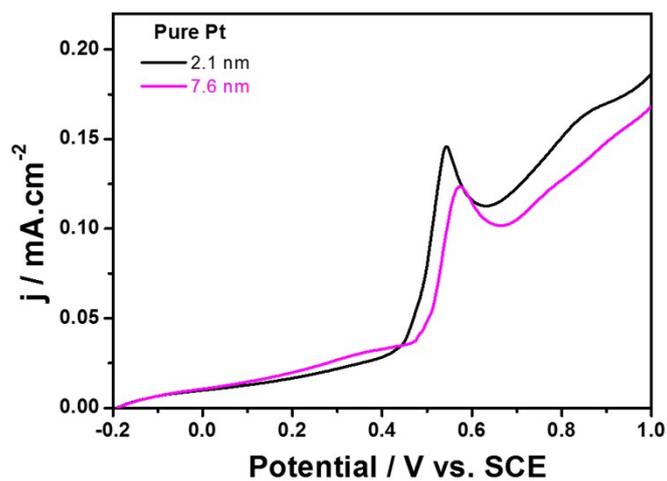


Fig. S6. CO stripping voltammograms for pure Pt nanocatalysts with different sizes in 0.1 M HClO₄ at a scan rate of 20 mV/s.

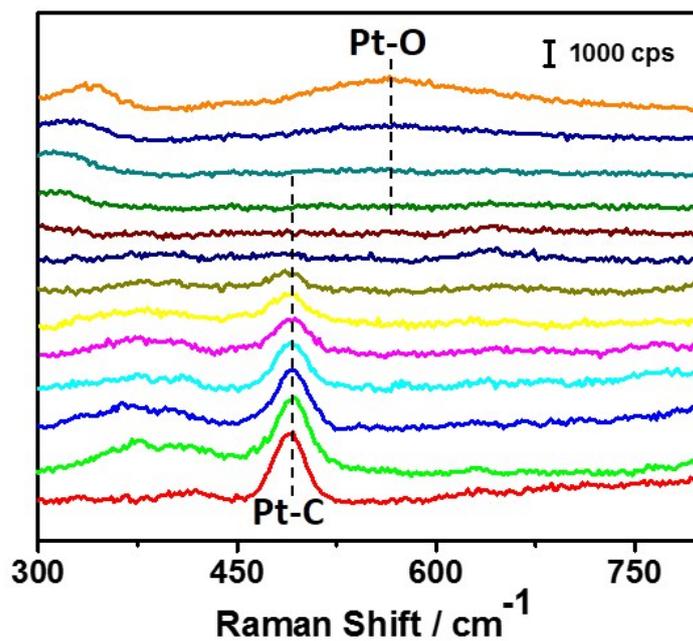


Fig. S7. The electrochemical SERS spectra for methanol electrooxidation on Pt (2.1 nm)-on-Au core-satellite nanocatalysts.

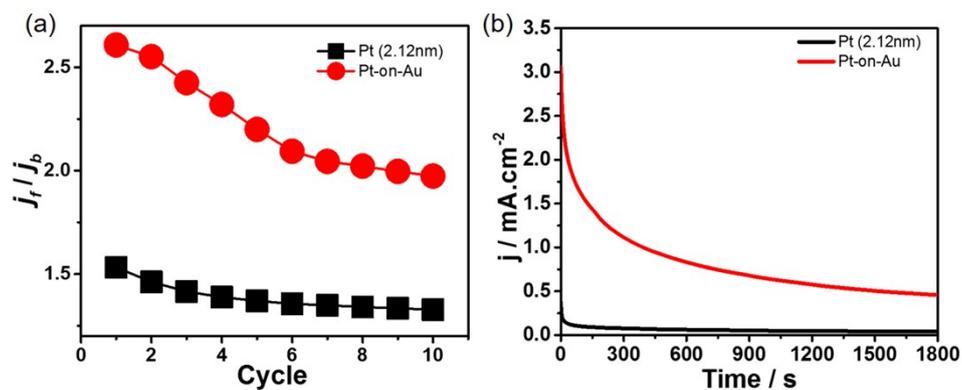


Fig. S8. (a) Comparison of the j_f/j_b ratio of methanol oxidation on Pt and Pt-on-Au nanocomposite as a function of scanning cycles. (b) Amperometric $i-t$ curve recorded at a potential of 0.6 V vs. SCE for methanol oxidation on Pt and Pt-on-Au.