

## Electronic Supplementary Information For

### The Growth and Enhanced Catalytic Performance of Au@Pd Core-Shell Nanodendrites

*Haihua Wang, Zhenhua Sun,\* Yi Yang, and Dangsheng Su\**

#### Experimental Details:

**Chemicals and materials:** All chemical reagents, gold trichloride ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ), sodium borohydride ( $\text{NaBH}_4$ ), hexadecyl trimethyl ammonium bromide (CTAB), silver nitrate ( $\text{AgNO}_3$ ), L-ascorbic acid (AA), hydrochloric acid (HCl), hexadecyl trimethyl ammonium chloride (CTAC), palladium (II) chloride ( $\text{PdCl}_2$ ) were purchased from Alfa Aesar and used without further purification. Deionized water (18.2 M $\Omega$ ) was used through the all experimental processes.

#### The synthesis of gold nanopolyhedra:

Gold nanopolyhedra were grown using the seeded growth method. Specifically, the seeds were prepared by the addition of a freshly prepared, ice-cold aqueous  $\text{NaBH}_4$  solution (0.01 M, 0.6 mL) into an aqueous mixture solution composed of  $\text{HAuCl}_4$  (0.01 M, 0.25 mL) and CTAB (0.1 M, 7.5 mL), followed by rapid inversion mixing for 2 min. The resultant seed solution was kept at room temperature for 1.5 h before use. The growth solution was prepared by the sequential addition of CTAB (0.1 M, 6.4 mL),  $\text{HAuCl}_4$  (0.01 M, 0.8 mL), and ascorbic acid (0.1 M, 3.8 mL) into water (32 mL). The CTAB-stabilized seed solution was diluted 10 times with water. The diluted seed

solution (0.06 mL) was then added into the growth solution for the growth of Au polyhedra. The resultant mixture solution was mixed by gentle inversion for 10 s and then left undisturbed overnight. The average diameter of the as-prepared Au polyhedra is  $(43 \pm 1)$  nm, and their ensemble SPRW is 535 nm.

**The synthesis of Au@Pd core-shell nanodendrites:**

Firstly, Au nanopolyhedra solution (2 mL) was by centrifugation at 8000 rpm for 15 min and then re-dispersed in 1 mL of 0.1 M CTAB solution. The solution was centrifuged again for removing residual CTAB and then re-dispersed in 1 mL of 0.1 M CTAC solution for further use. Secondly, the synthesis of Au@Pd nanodendrites was by adding in turn CTAC solution (5 mL, 0.1 M), a certain amount of  $\text{H}_2\text{PdCl}_4$  solution (0.01 M), ascorbic acid solution (0.06 mL, 0.1M) and above Au nanopolyhedra re-dispersed in CTAC solution into a 15-mL plastic tube. The resultant mixture solution was mixed by gentle inversion for 10 s and then left undisturbed overnight. If there was no special emphasis, the molar quantity of  $\text{H}_2\text{PdCl}_4$  was 1.2  $\mu\text{mol}$ .

**The synthesis of Au@Pd core-shell nanocubes:**

The synthesis of Au@Pd core-shell nanocubes was similar to that of Au@Pd core-shell nanodendrites, however, the CTAC solution was replaced with the CTAB solution.

## **Characterization:**

The TEM and HRTEM images were performed on an FEI Tecnai F20 microscope with an acceleration voltage of 200 kV. HAADF-STEM characterizations were carried out using an FEI Tecnai F30 microscope equipped with an Oxford energy dispersive X-ray (EDX) analysis system with an acceleration voltage of 300 kV. Extinction spectra were measured on a Cary 5000 UV/Vis/NIR spectrophotometer. The XRD patterns were collected on a D/max 2400/PC diffractometer (JEOL Ltd., Japan) with Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The  $0.02^\circ$  steps per second  $2\theta$  range from  $30$  to  $90^\circ$  were selected to analyze the crystal structure and orientation. For the TEM, HRTEM, HAADF-STEM, 1 mL of each of the as-grown nanocrystal solutions was centrifuged at 8000 rpm for 10 min. The precipitate was redispersed in 1 mL of deionized water, centrifuged again at 8000 rpm for 10 min, and finally redispersed in 0.2 mL of deionized water. Samples were deposited on Si substrates for XRD characterizations and on carbon film-coated copper grids for TEM, HRTEM, and HAADF-STEM characterization. The elemental analysis was performed on inductively-coupled plasma-atomic emission spectrometer (ICP-AES, IRIS Intrepid).

## **Catalytic performance test:**

**Electrocatalytic performance:** All electrochemistry measurements were carried out at ambient temperature in a three-electrode cell using the Epsilon-BAS electrochemical workstation. The work electrodes were assembled by fixing the nanoparticles (Au@Pd nanostructures or Au polyhedra) onto the glass carbon

electrodes (diameter: 3 mm, geometric area: 0.071 cm<sup>2</sup>). Specifically, 25 mL of Au@Pd nanostructures or Au polyhedra solution were centrifuged at 8000 rpm for 10 min. And then the precipitate was redispersed in 1 mL of water, centrifuged again at 8000 rpm for 10 min, finally redispersed in 0.1 mL of water to form a suspension. 0.006 mL of Nafion® NR50 solution (sigma aldrich) were added into the suspension and then mixed uniformly by ultrasound wave to form a slurry. 0.005 mL of the slurry was dropped onto a glass carbon electrode (GCE) and the above process was repeated twice after the water evaporated at ambient temperature. Saturated calomel electrode (SCE) and platinum sheet electrode (2×1×0.05 cm) was served as reference and counter electrodes, respectively. The electrolyte solutions were purged with high-purity N<sub>2</sub> gas before use for about 1 h.

According to the literature,<sup>[1]</sup> the electrochemically active surface area (ECSA) of Au@Pd core-shell nanostructures can be calculated. Firstly, the electric quantity can be calculated on the basis of the area of reductive peak labeled by broken frame in Fig. 4a. The electric quantity of Au@Pd core-shell nanodendrites and nanocubes are 278.95 and 14.42 μC, respectively. Secondly, the ECSA of Au@Pd nanodendrites and nanocubes are therefore determined to be 0.6879 and 0.03401 cm<sup>2</sup> by dividing the amount of reduction charge (1377 μC) by its conversion factor of 424 μC cm<sup>-2</sup>. Finally, ECSA of Au@Pd nanodendrites and nanocubes per unit of Pd mass can be obtained by dividing the mass of Pd onto the electrode surface and they are 1.4 and 0.06 m<sup>2</sup>/g<sub>Pd</sub>. It should be pointed out that the Pd mass of Au@Pd nanodendrites and

nanocubes onto the glass carbon electrode were 0.04688 and 0.05625 mg, respectively.

**Catalytic activity for Suzuki coupling:** In the Suzuki coupling reaction, benzenboronic acid (2 mmol),  $K_3PO_4 \cdot 3H_2O$  (4 mmol), and 1 mL of the concentrated Au@Pd nanostructures or Au polyhedra solution were added to 5 mL of ethanol/water mixture with a volume ratio of 4:1. The mixture was stirred and heated to 85 °C under reflux, and then iodobenzene (1 mmol) was added. After the reaction for 15 min, the product was extracted with  $CH_2Cl_2$  and analyzed by gas chromatography (Agilent 7890 A) to obtain the yield of biphenyl. Specifically, 1 mL of the concentrated Au@Pd nanodendrites and nanocubes solution contained 0.100 mg (0.943  $\mu\text{mol}$ ) Pd, 0.065 mg (0.332  $\mu\text{mol}$ ) Au and 0.105 mg (0.991  $\mu\text{mol}$ ) Pd, 0.057 mg (0.0289  $\mu\text{mol}$ ) Au, respectively. While, 1 mL of the concentrated Au polyhedra contained the same Au amounts (0.065 mg, 0.332  $\mu\text{mol}$ ) with 1 mL of the concentrated Au@Pd nanodendrites for the control experiment.

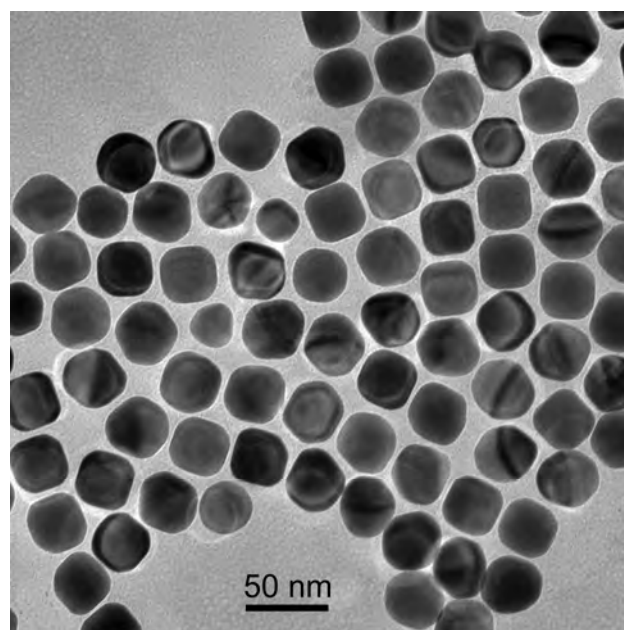


Fig.S1 TEM image of Au nanopolyhedra.

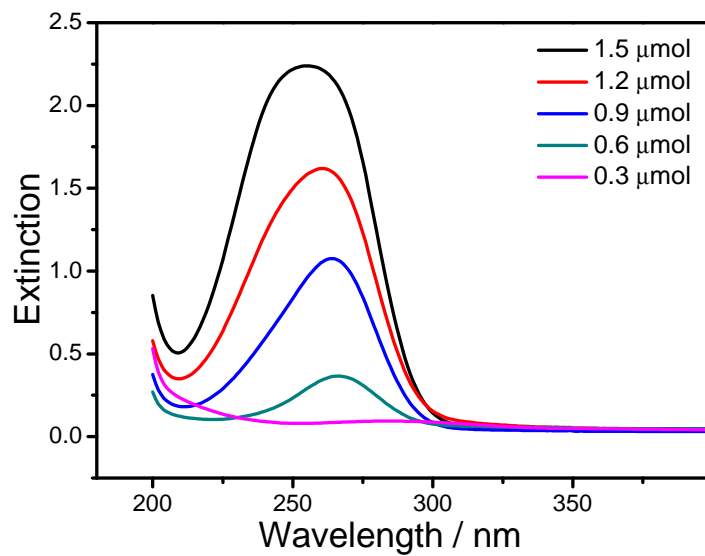


Fig. S2 The extinction spectra of the Au@Pd core-shell nanodendrites in the range of 200-400 nm at different amounts of H<sub>2</sub>PdCl<sub>4</sub> and their molar quantity are 0.3, 0.6, 0.9, 1.2 and 1.5 μmol, respectively.

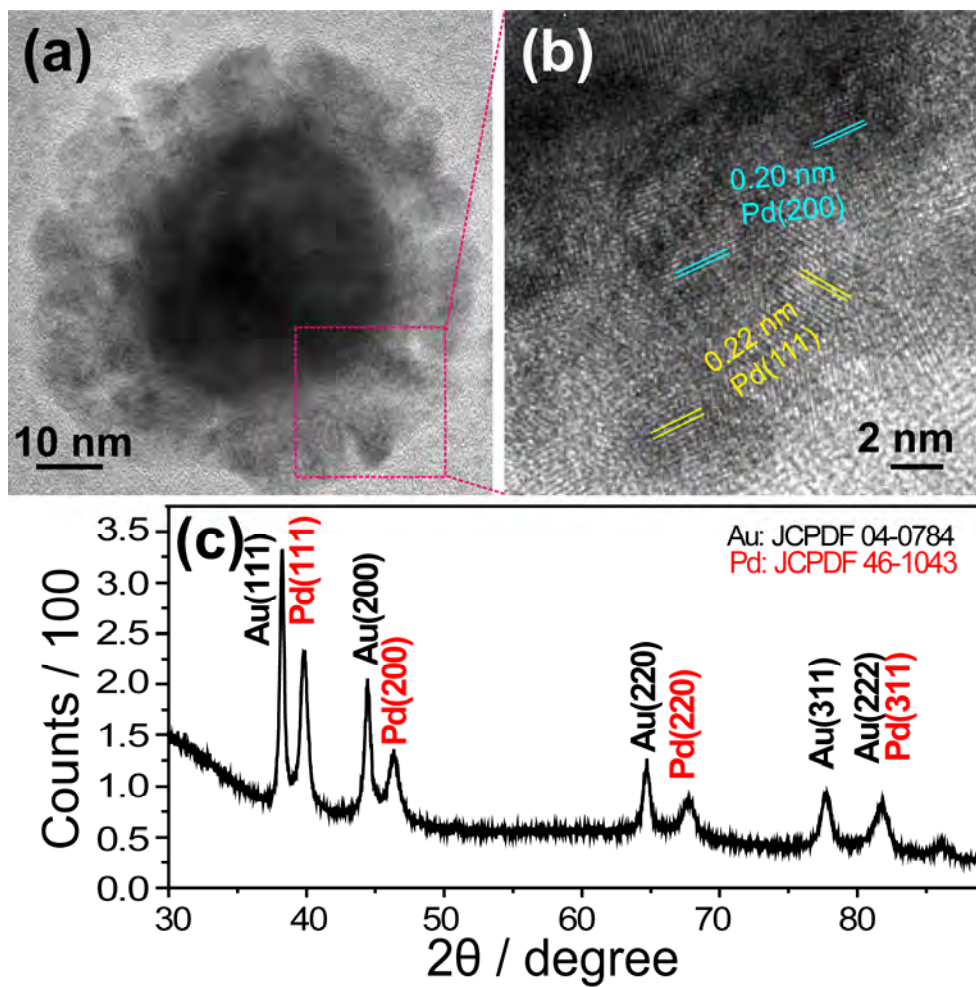


Fig. S3 Characterization of Au@Pd nanodendrites: a-b) The TEM and HRTEM images, respectively. c) XRD pattern. The diffraction peaks can be indexed as a combination of face-centered-cubic form of Au (JCPDS 04-0784) and Pd (JCPDS 46-1043).



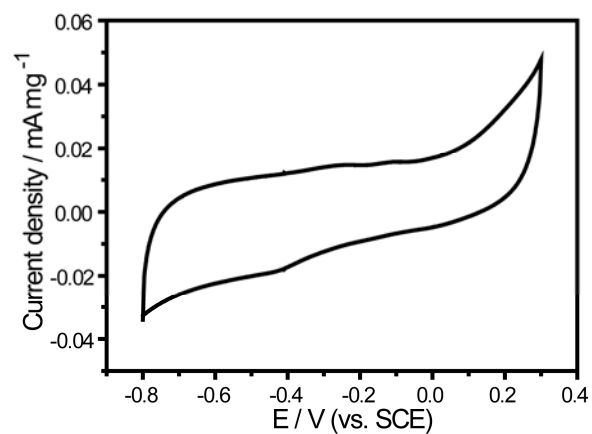


Fig. S4 Mass activity of Au polyhedra for methanol oxidation. CV curve was obtained in a N<sub>2</sub>-purged KOH (0.1 M) solution and methanol (0.25 M) with a scan rate of 50 mV s<sup>-1</sup>.

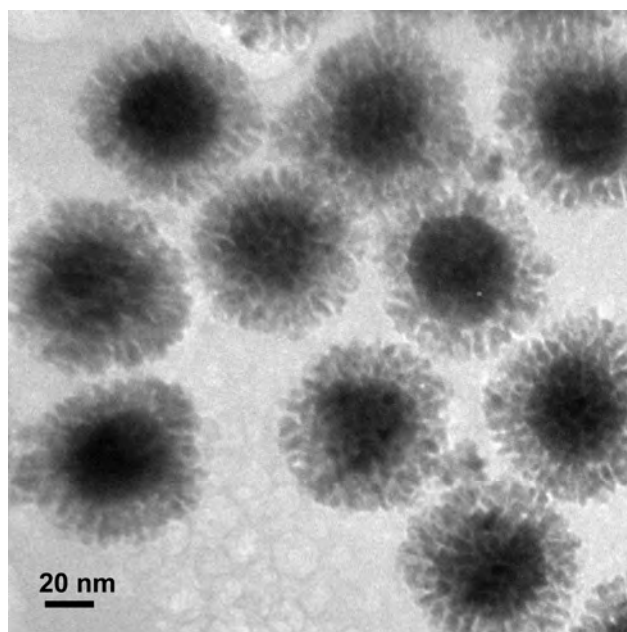


Fig. S5 TEM image of Au@Pd core-shell nanodendrites after four cycles of the Suzuki coupling reaction.

References:

- [1] W. Pan, X. K. Zhang, H. Y. Ma and J. T. Zhang, *J. Phys. Chem. C* **2008**, *112*, 2456.