# Electronic supplementary information

# Synthesis and Electrocatalytic Properties of Tetrahexahedral, Polyhedral, and Branched Pd@Au Core-Shell Nanocrystals

**Ling Zhang,[a,b] Wenxin Niu,[a,b] Wenyue Gao,[a,b] Saadat Majeed,[a,b,c] Zhongyuan Liu,[a,b] Jianming Zhao,[a,b] Saima Anjum,[a,b,d] Guobao Xu*[a]**

[a] *State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun 130022, China. Fax: +86-431-85262747; Tel: +86-431-85262747; E-mail: guobaoxu@ciac.jl.cn*

[b] *University of the Chinese Academy of Sciences, Chinese Academy of Sciences, No. 19A Yuquanlu, Beijing 100049, China.*

[c] *Department of Chemistry, Bahauddin Zakaryia University Multan, 60800, Pakistan.*

[d] *Department of Chemistry, Faculty of Sciences, The Islamia University of Bahawalpur, 63100, Pakistan.*

## Experimental Section

**Materials.** $PdCl_2$ and $HAuCl_4 \cdot 4H_2O$ were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Cetyltrimethylammonium bromide (CTAB) was obtained from Fluka (Switzerland). L-Ascorbic acid, hydrogen peroxide (30%), $AgNO_3$ and HCl was obtained from Beijing Chemical Reagent Company. 3-Aminophthalhydrazide (Luminol, ≥ 98%) was purchased from Aldrich. All the chemicals were of analytical grade and used without further purification. Doubly distilled water was used throughout the experiments. A 10 mM $H_2PdCl_4$ solution was prepared by dissolving 0.1773 g $PdCl_2$ in 10 mL of 0.2 M HCl solution and further diluting to 100 mL with doubly distilled water.

**Synthesis of Pd nanocubes with the average size of 76 nm.** 76 nm Pd cubes were obtained with the seed-mediated method as previously reported.[1] First, 22 nm cubic Pd seeds were synthesized. Briefly, 500 μL aliquot of 10 mM $H_2PdCl_4$ solution was added to 9420 μL of 12.5 mM CTAB aqueous solution heated at 95 °C under stirring. After 5 minutes, 80 μL of freshly prepared 100 mM ascorbic acid aqueous solution was added, and the reaction was allowed to proceed for 20 min. Second, 76 nm Pd nanocubes were synthesized by the overgrowth of the smaller Pd seeds. 125 μL aliquot of 10 mM $H_2PdCl_4$, 40μL aliquot of 22 nm Pd cubes, and 25 μL aliquot ascorbic acid solutions were added into 5 mL of 50 mM CTAB solution which was kept at 40 °C, sequentially. The reaction proceeded for 14 hours at 40 °C. Then, the 76 nm Pd nanocubes were washed for one time with CTAB aqueous solution and dispersed in 1 mL of 100 mM CATB aqueous solution, then stored at 30 °C for future use.

**Synthesis of Pd@Au core-shell nanocrystals.** In a typical synthesis of tetrahexahedral Pd@Au core-shell nanocrystals, 5 mL of 100 mM CTAB aqueous solutions were kept at 30 °C for 10 min.

Then 300 μL aliquot of 10 mM $HAuCl_4$, 70 μL aliquot of 10 mM $AgNO_3$, 140 μL aliquot of 1 M HCl, 56 μL aliquot of 100 mM ascorbic acid, and 50 μL aliquot of 76 nm cubic Pd seed aqueous solutions were added successively into CTAB solutions. The reaction solutions were left overnight without disturbing. For polyhedral Pd@Au core-shell nanocrystals with the mixed low-index facets, $AgNO_3$ solutions were not added; for branched nanocrystals, HCl aliquot solutions were not added, and the other conditions are the same as those of tetrahexahedral Pd@Au core-shell nanocrystals. The resultant nanocrystal solutions were centrifuged at 6000 rpm for 3 min and the precipitate was washed with water for three times for the further characterization.

For the synthesis of smaller tetrahexahedral nanocrystals, 5 mL of 100 mM CTAB aqueous solutions were kept at 30 °C for 10 min. Then 250 μL aliquot of 10 mM $HAuCl_4$, 50 μL aliquot of 10 mM $AgNO_3$, 100 μL aliquot of 1 M HCl, 40 μL aliquot of 100 mM ascorbic acid, and 50 μL aliquot of 22 nm cubic Pd seed aqueous solutions were added successively into CTAB solutions. The other conditions are the same as the typical synthesis. The size of the tetrahexahedral nanocrystals were about 56 nm.

**Electrocatalysis properties of Pd@Au core-shell nanocrystals** The electrocatalysis properties of the Pd@Au core-shell nanocrystals with tetrahexahedral, polyhedral, branch-like shapes (from typical synthesis) were estimated with electrochemically catalyze oxidation of $H_2O_2$ in the neutral phosphate buffer solutions (pH 7.0) and electrochemiluminescence (ECL) of luminol-$H_2O_2$ system. Electrochemical measurements were carried out in a conventional three-electrode cell at the room temperature with a 660c electrochemical working station (Chenhua Inc. Xi'an). ECL intensity was monitored through the bottom of the three-electrode cell with a BPCL Ultra-Weak luminescence analyzer with a photomultiplier tube (PMT, -700 V). The working electrodes were Pd@Au core shell NCs modified glassy carbon electrode. The auxiliary electrode and the reference electrode are a thin gold grid and an Ag/AgCl electrode (saturated KCl), respectively.

**Instruments.** Scanning electron microscopy (SEM) images were taken using an FEI XL30 ESEM FEG scanning electron microscope operated at 25 kV. Transmission electron microscopy (TEM) images, high-resolution TEM image, high-angle annular dark-field scanning transmission electron microscopy images, and elemental mapping images were all obtained using a FEI Tecnai G2 F20 microscope operated at 200 kV. Energy dispersive spectrometer (EDS) spectrum was obtained with Hitachi S-4800 scanning electron microscope operated at 20.9 kV. Au, Pd, and Ag elemental analysis of Pd@Au core-shell NCs were performed with the inductively coupled plasma optical emission spectrometer (ICP-OES, iCAP6300, Thermo Scientific, USA).

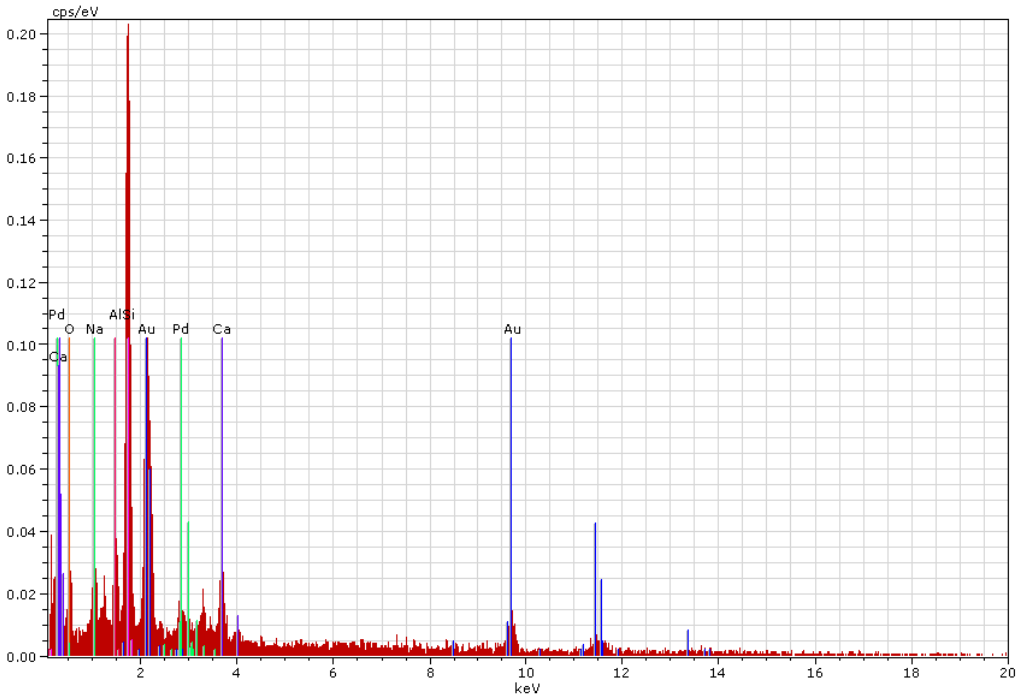


Fig. S1 EDS spectrum of THH Pd@Au core-shell nanocrystals with 150 nm in the typical synthesis.

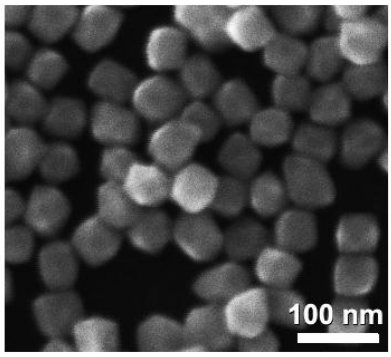


Fig. S2 SEM image of 56 nm Pd@Au core-shell nanocrystals synthesized from smaller Pd nanocube seed of 22 nm.

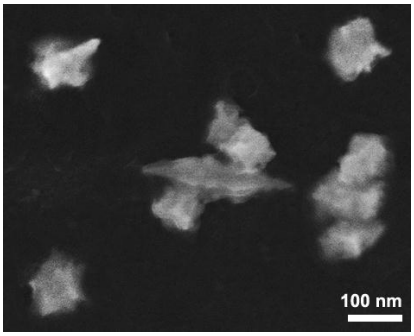


Fig. S3 SEM image of Pd@Au core-shell nanocrystals produced when HCl was substituted with KCl, other conditions were similar to those of THH in the typical synthesis.

Table S1. ICP analysis of Pd@Au nanocrystals with different shapes.

| Mass percentage (%) | THH[1] | Polyhedral[1] | Branch[1] | Branch[2] |
|---|---|---|---|---|
| Au | 95.77 | 96.12 | 95.56 | 95.37 |
| Pd | 4.08 | 3.87 | 4.23 | 4.24 |
| Ag | 0.15 | 0.02 | 0.21 | 0.39 |

[1]Nanocrystals synthesized in the typical synthesis;

[2]Nanocrystals produced when HCl was substituted with KCl, other conditions were similar to those of THH in the typical synthesis.

## References

(S1) W. Niu, Z.-Y. Li, L. Shi, X. Liu, H. Li, S. Han, J. Chen and G. Xu, Cryst. Growth & Des., 2008, 8, 4440.