

Electronic supplementary information

Facile synthesis and electrochemiluminescence application of concave trisoctahedral Pd@Au core-shell nanocrystals bound by {331} high-index facets

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Experimental Sections

Materials. PdCl₂, HAuCl₄·4H₂O and KBr were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Cetyltrimethylammonium chloride (CTAC, 98.0%) was obtained from Tianjin Guangfu Fine Chemical Research Institute (China). Cetyltrimethylammonium bromide (CTAB) was obtained from Fluka (Switzerland). Luminol was purchased from Aldrich. L-Ascorbic acid and hydrogen peroxide were obtained from Beijing Chemical Reagent Company. All the chemicals were of analytical grade and used without further purification. Doubly distilled water was used throughout the experiments. A 10 mM H₂PdCl₄ solution was prepared by dissolving 0.1773 g PdCl₂ 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 22 nm. Briefly, 500 μL aliquot of 10 mM H₂PdCl₄ 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. Pd seeds were collected and washed with 5 mM CTAC aqueous solution twice by centrifugation (16000 rpm, 5 min). Then the cubic Pd seeds were dispersed in 1 mL of 5 mM CTAC aqueous solution and stored at 30 °C for future use.

Synthesis of TOH Pd@Au core-shell nanocrystals. In a typical synthesis, 5 mL of 5 mM CTAC aqueous solutions were kept at 30 °C for 10 min. Then Pd seeds solution, 100 μL of 100 mM ascorbic acid and 125 μL of 10 mM HAuCl₄ aqueous solutions were added successively. The volumes of the Pd seeds added for the nanocrystals of 147, 128, 113, 94 and 70 nm were 2.5, 5, 7.5, 10 and 35 μL, respectively. When HAuCl₄ solutions was added, the colorless growth solutions became pale yellow and then colorless soon. Afterwards, the colorless solutions turned into pink within 1 min, and gradually become bright orange except for the nanocrystals with the size of 70 nm which was dark pink. The growth process of nanocrystals was monitored by the UV-vis absorption spectrometer, and the reaction was fulfilled within 30 min. The resultant nanocrystals solutions were centrifuged at 10000 rpm for 2 min and the precipitate was washed with water for three times for the further characterization.

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, energy-dispersive X-ray spectroscopy (EDS) spectrum, and elemental mapping images were all obtained using a FEI Tecnai G2 F20 microscope operated at 200 kV. UV-vis extinction spectra were obtained using WFZ UV-2802PC spectrometer. Electrochemical measurements were carried out in a conventional three-electrode cell with a 832B electrochemical workstation (CHI Inc.). The auxiliary electrode and the reference electrode were a glassy carbon grid and a Ag/AgCl electrode (saturated KCl), respectively. TOH Pd@Au core-shell nanocrystal modified glassy carbon electrode was prepared by dropping 94 nm TOH Pd@Au core-shell nanocrystal solution onto fresh glassy carbon electrode and drying at room temperature. electrochemiluminescence intensities were monitored through the bottom of the three-electrode cell with a BPCL Ultra-Weak luminescence analyzer.

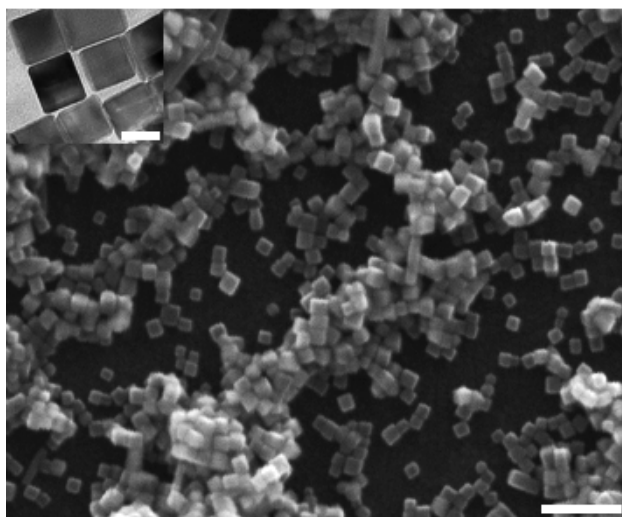


Fig. S1. SEM image of cubic Pd seeds (scale bar: 200 nm), inset: TEM image of cubic Pd seeds (scale bar: 20 nm).

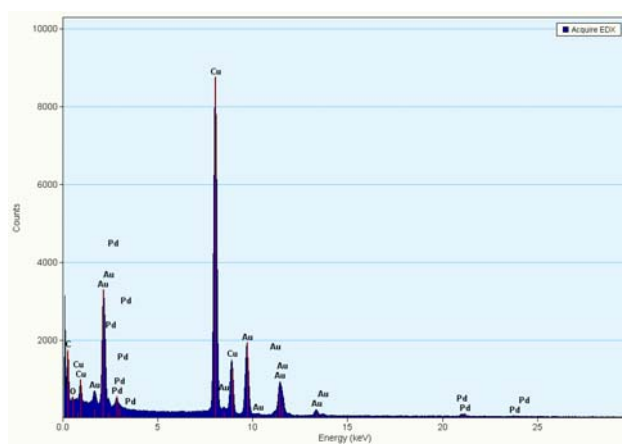


Fig. S2. EDX spectrum of TOH Pd@Au core-shell nanocrystals.

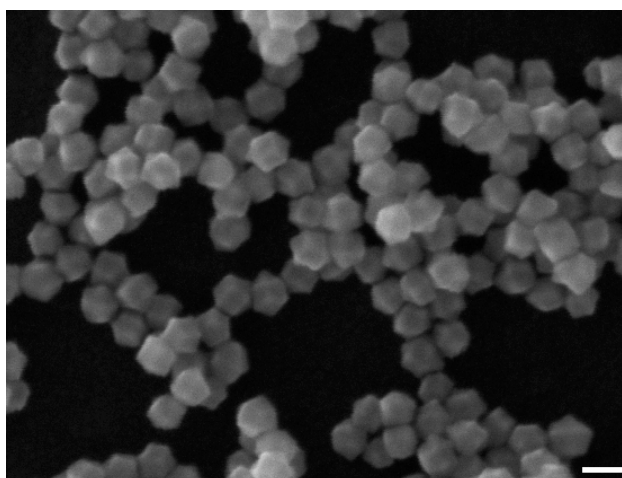


Fig. S3. Enlarged SEM image of TOH Pd@Au core-shell nanocrystals with the size of 70 nm (scale bar: 100 nm).

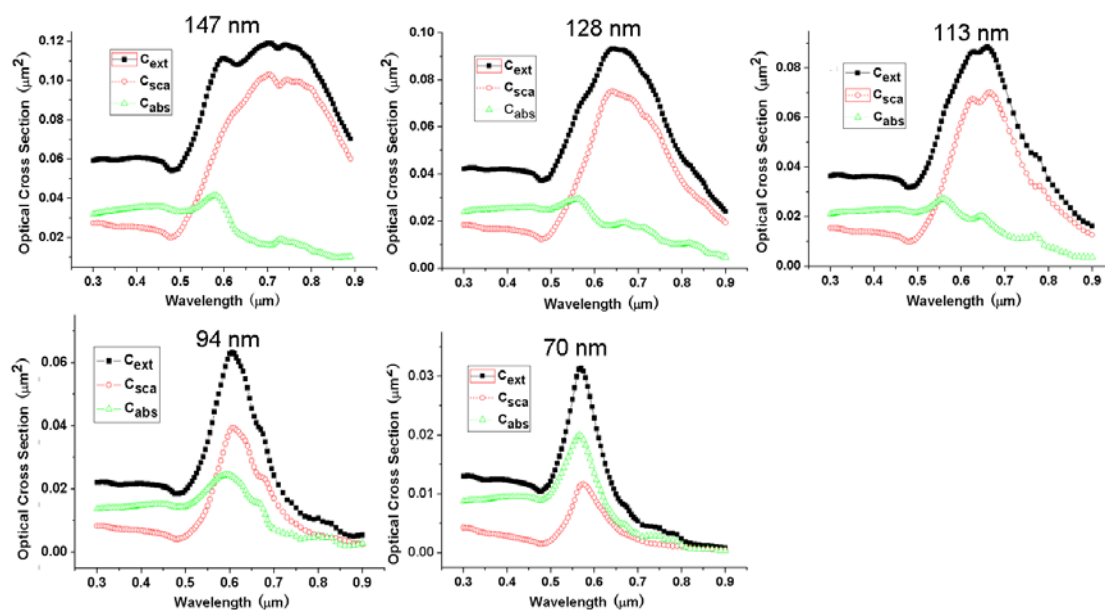


Fig. S4 Extinction (C_{ext}), scattering (C_{sca}) and absorption (C_{abs}) cross sections of TOH Pd@Au nanocrystals with different sizes using discrete dipole approximation method ($C_{\text{ext}} = C_{\text{sca}} + C_{\text{abs}}$).

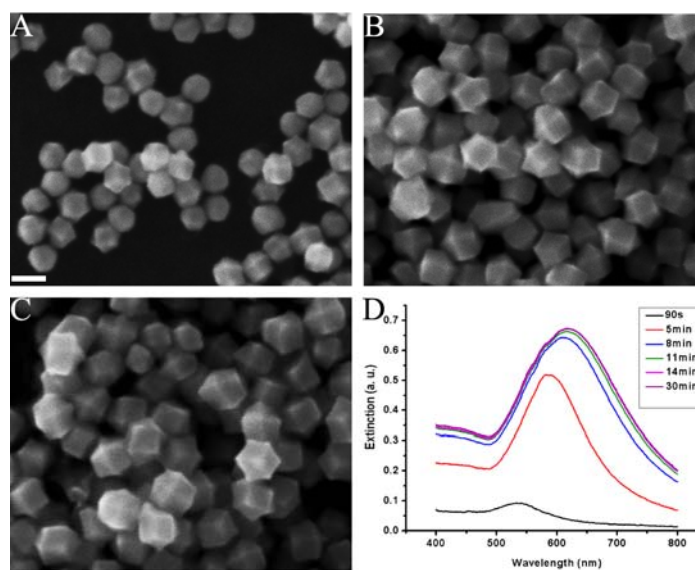


Fig. S5 (A-C) SEM images of TOH Pd@Au core-shell nanocrystals taken at different times after the addition of HAuCl_4 , 2 min (A), 7 min (B) and 20 min (C). Scale bar: 100 nm. (D) UV-vis extinction spectra of TOH Pd@Au core-shell nanocrystals at the different reaction times. The other conditions are the same as (c) in Fig. 3A.

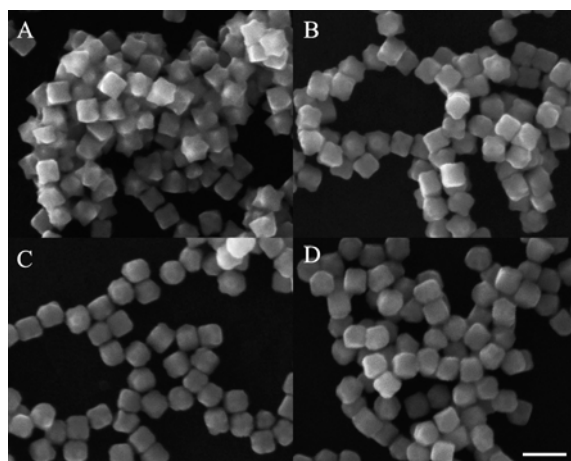


Fig. S6 Pd@Au core-shell nanocrystals synthesized by adding different concentrations of KBr. (A) 5 mM, (B) 10 mM, (C) 15 mM and (D) 20 mM. The other conditions are the same as (c) in Fig. 3A. Scale bar: 200 nm.