Controlled Synthesis of Non-Epitaxial Grown Pd@Ag Core-Shell Nanocrystals of Interesting Optical Performance

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Electronic Supporting Information

Methods

Materials. Sodium tetrachloropalladate(II) (Na_2PdCl_4) and silver nitrate ($AgNO_3$), and potassium bromide (KBr)were obtained from Beijing Chemical Reagent Company. Cetyltrimethylammonium chloride (CTAC) and L-Ascorbic acid (AA) were purchased from Alfa Aesar. Cetyltrimethylammonium bromide (CTAB) were bought from Sigma Aldrich. Ultrapure water was used throughout the experiments.

Synthesis of Pd Seeds. Pd seeds were synthesized according to the literature. In brief, 0.5 mL of 10 mM Na_2PdCl_4 solution was added to 10 mL of 12.5 mM CTAB solution that was heated at 95 °C under stirring. After 5 min, 80 μL of 100 mM AA solution was added. The reaction was stopped after 20 min by centrifugation (14000 rpm*15 min) and washed with 20 mM CTAC solution for three times. Finally, Pd seeds were dispersed in 2 mL of 10 mM CTAC solution.

Synthesis of Pd@Ag Core-shell Nanocrystals (NCs). Typically, 100 μL seed solution was added to 5 mL of 20 mM CTAC solution and heated at 60 °C for 10 min. Then, 50 μL of 10 mM $AgNO_3$ and 150 μL of 100 mM AA were quickly added all in once with pipette. The solution was left undisturbed at 60 °C for 6 h and centrifuged (10000 rpm × 10 min) two times for further characterization. To evaluate the effects of Br^- ions, different amount of KBr solution (10 μL of 0.1 M, 10 μL of 10 mM; 10 μL of 1 mM) was added. Only in the case of 10 μL of 1 mM KBr solution, Pd@Ag core-shell NCs with well defined shapes were obtained.

For size tuning, 800, 400, 200, 100, and 50 μL seed solutions were respectively added while other conditions were kept constant. Synthesis of Au@Ag core-shell NCs was based on the method described in Reference S1.

Characterization. Hitachi S-4800 was used to obtain the scanning electron microscopy (SEM) images under the accelerating voltage of 10 kV. Transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), and corresponding element analysis mapping were done on Tecnai G2 F20 U-TWIN under the accelerating voltage of 200 KV. UV−vis spectra were taken on a Hitachi U-3010 UV−vis spectrophotometer.

Calculation. The black, red and blue curves in Fig. 3B represented the calculated normalized extinctions for Pd@Ag core-shell nanocrystals with the sizes of 30 nm, 46 nm and 60 nm, respectively. The cut corners in all the three cases were 5 nm. The size of the Pd seeds was set to be 18 nm, which was located in the center of the nanocrystals. The calculations were carried out using DDA method. The distances between adjacent dipoles in the simulation were 1 nm, and the numerical accuracy of optical spectrum calculations was better than 1%.

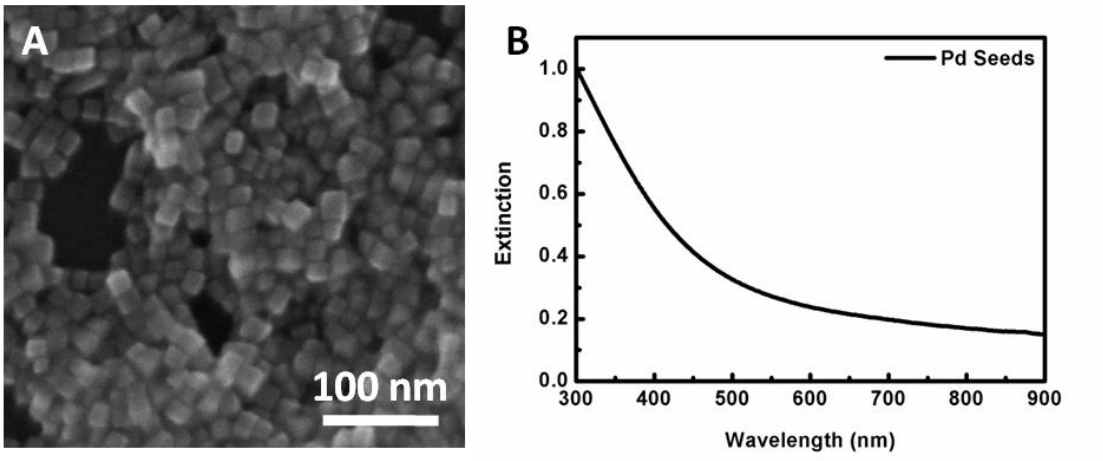

Figure S1. (A) SEM and (B) UV-vis spectrum of Pd seeds.

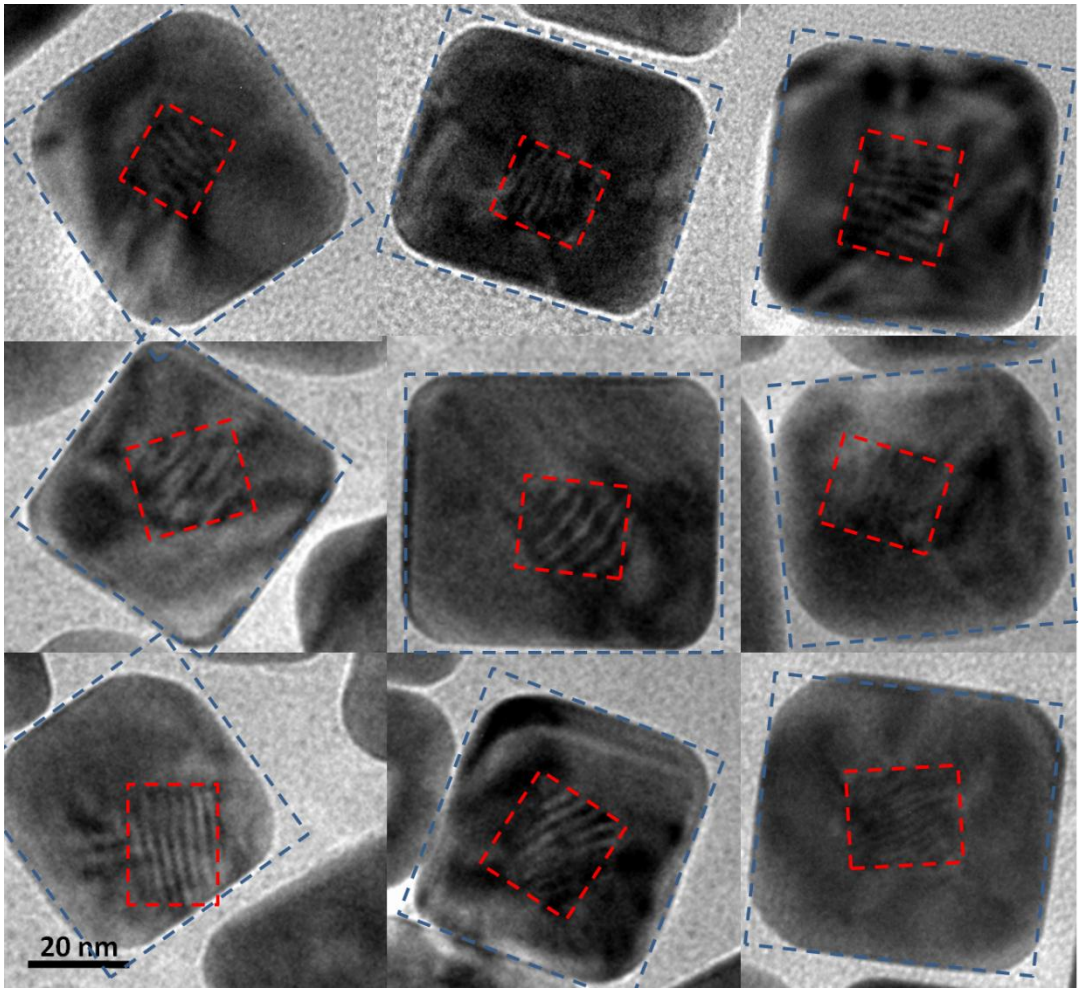

Figure S2. TEM images of individual 50 nm Pd@Ag core-shell NCs. Areas enclosed by blue dotted squares are the position of shells, while areas enclosed by red dotted squares are the position of cores.

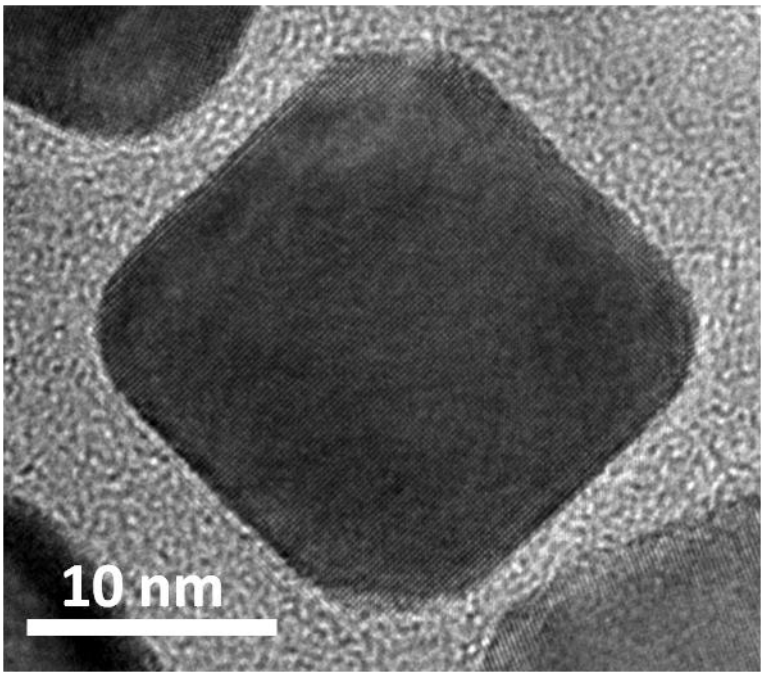

Figure S3. HRTEM image of Pd cubes.

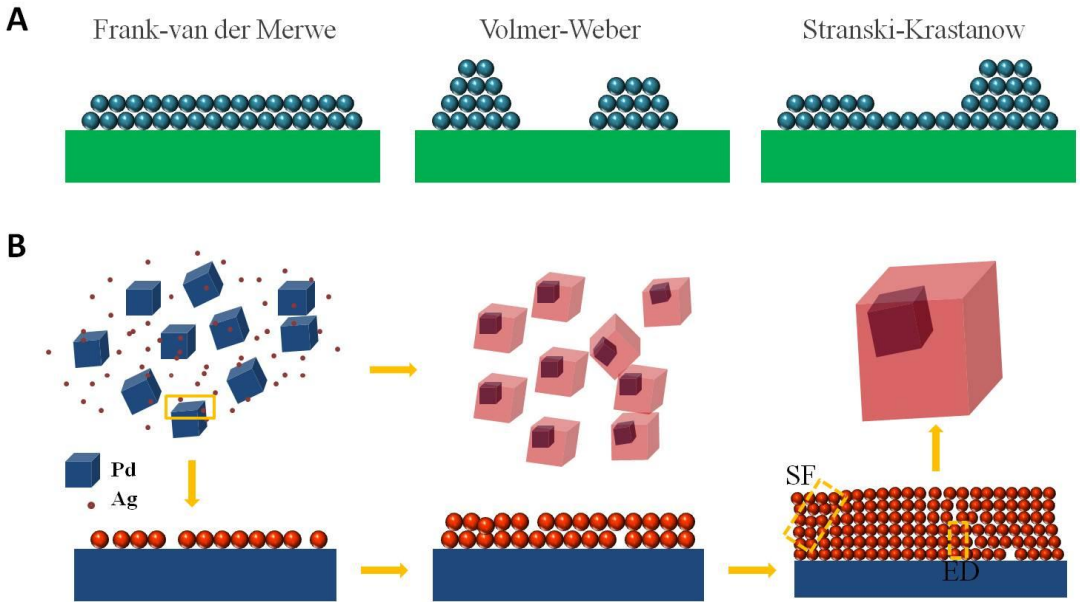

Figure S4. Illustration of the growth mechanism. (A) Three classic growth modes of the films. (B) Growth mechanism of Pd@Ag core-shell NCs.

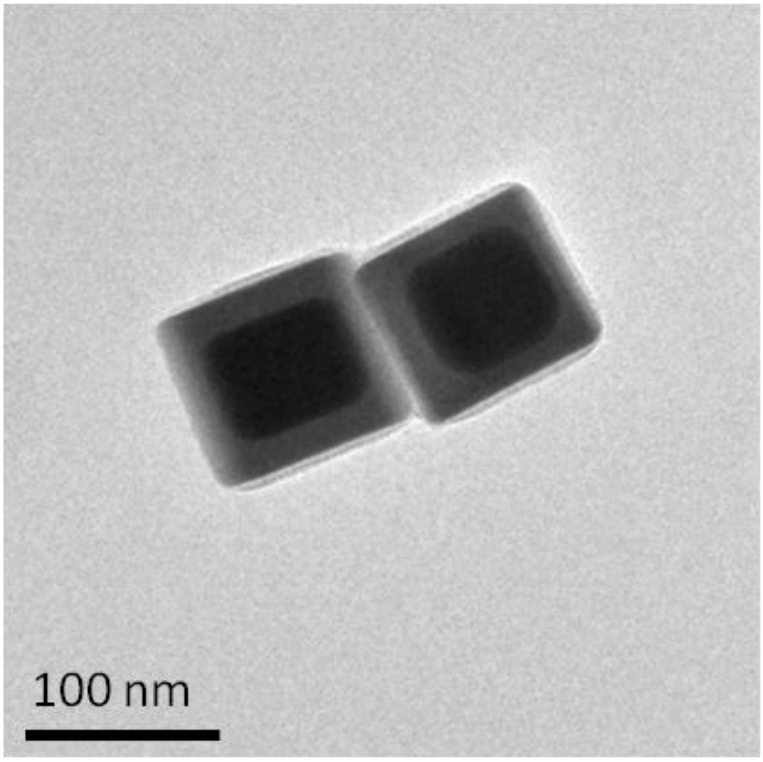

Figure S5. TEM image of Au@Ag core-shell NCs.

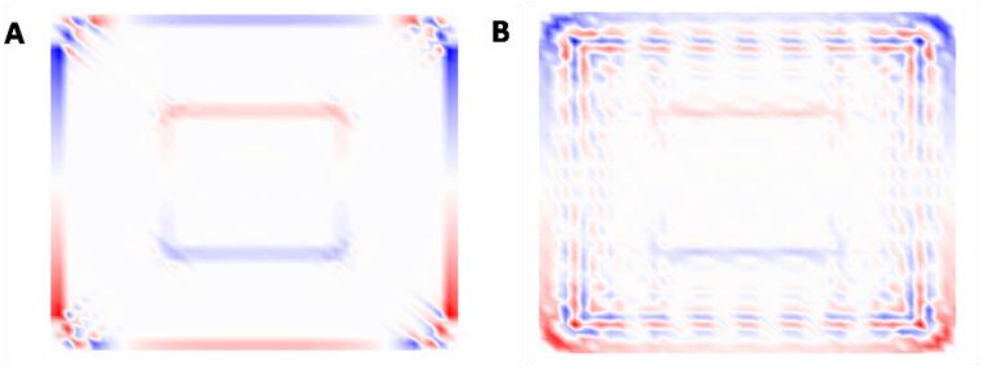

Figure S6. Calculated charge density distribution for different resonant peaks of Pd@Ag core-shell NCs with the side length of 50 nm: (A) for the calculated 345 nm peak; (B) for the calculated 480 nm peak. Blue and red colors stand for positive and negative charges, respectively, while the shades of colors represent the charge density.

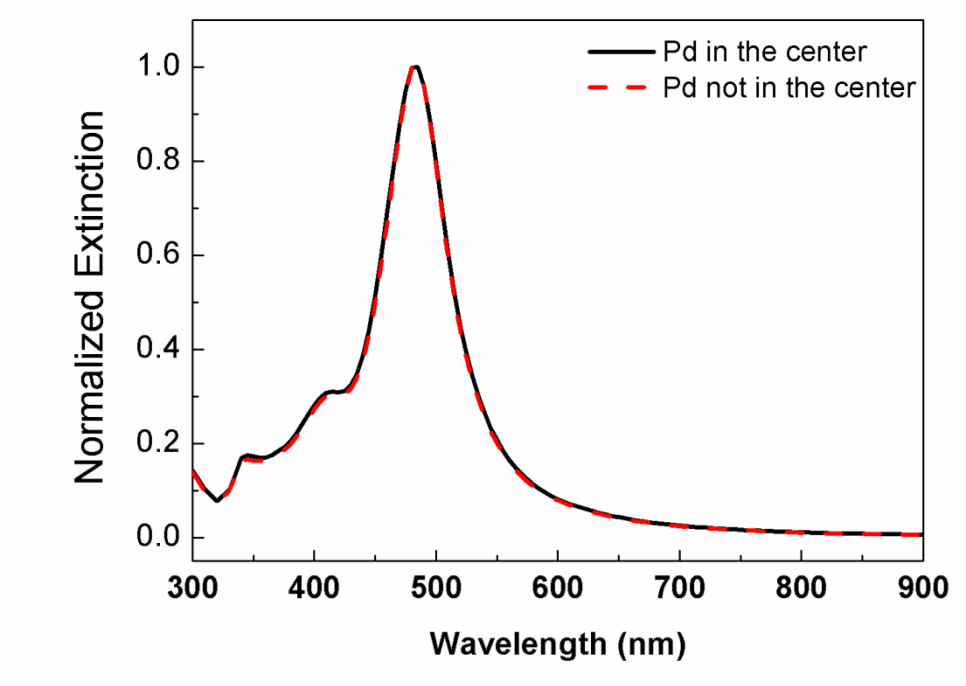

Figure S7. Calculated extinction spectra of 46 nm Pd@Ag nanocrystals with Pd in the center (black solid curve) and in the corner (red dashed curve), respectively. The two curves almost overlap with each other, indicateing that the asymmetric arrangment of the core-shell does not singificantly change the optical characteristics of the core-shell NCs.

Reference

[1] J. Gong, F. Zhou, Z. Li and Z. Tang, *Langmuir*, 2012, **28**, 8959.