

Supporting Information for

**Confining Alloy or Core-shell Au/Pd Bimetallic Nanocrystals in
Silica Nanorattles for Enhanced Catalytic Performance**

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Experimental Section

Chemicals and Reagents.

Tetraethoxysilane (TEOS, A.R), hydrochloric acid (HCl), ammonia solution ($\text{NH}_3 \cdot \text{H}_2\text{O}$), and ethanol ($\text{C}_2\text{H}_5\text{OH}$) were obtained from Sinopharm Chemical Reagent Beijing Co., Ltd. 3-(2-Aminoethyl)aminopropyltrimethoxysilane (ATS) was purchased from Fluka. Tetra-n-butyl titanate (TBT) and acetonitrile were purchased from Sigma. All reagents were used as received without any further purification.

Synthesis of Core-shell $\text{SiO}_2/\text{ATS}@\text{TiO}_2$ Solid Spheres.

In a typical reaction, solution A (20 mL 1 mM TEOS in ethanol), solution B (20 mL 0.05 mM ATS in ethanol) and solution C (20 mL 28 % aqueous NH_3 and 60 mL ethanol) and were prepared. For fabricating the SiO_2/ATS core, solution A and B were added drop wise into the solution C synchronously. The reaction was kept for 3 h at 30 °C. The SiO_2/ATS spheres were collected by centrifugation and washed with ethanol and water repeatedly. For coating TiO_2 shell, 0.2 mg/mL SiO_2/ATS spheres was dispersed in mixed solvent of ethanol/acetonitrile (3/1 v/v) and then mixed with 0.3 mL of ammonia. Finally, the mixed solvent of ethanol/acetonitrile (3/1 v/v) containing 0.65 mL of TBT was added to above suspension under stirring. After reacting for 1 h, the obtained $\text{SiO}_2/\text{ATS}@\text{TiO}_2$ solid spheres were cleaned by three cycles of centrifugation.

Synthesis of Alloy Au/Pd @TiO₂ spheres by One Pot Hydrothermal Reaction.

Fresh prepared SiO₂/ATS@TiO₂ solid spheres of 30 mg were dispersed into deionized water (10 mL) by sonication, and then a certain amount of HAuCl₄ (50 mM) and H₂PdCl₄ (50 mM) were added. The pH of the mixed solution was adjusted to around 3.0 using HCl (0.1 M) solution. After stirred for 1 h at room temperature the mixture was transferred into a sealed Teflon-lined autoclave and heated at 180°C for 4 h. After that, the autoclave was cooled naturally to room temperature. The product was collected and washed with deionized water for three times by centrifugation, then dried in vacuum oven at ambient temperature.

Figure S1 The TEM image of silica spheres with three layer sandwich structure

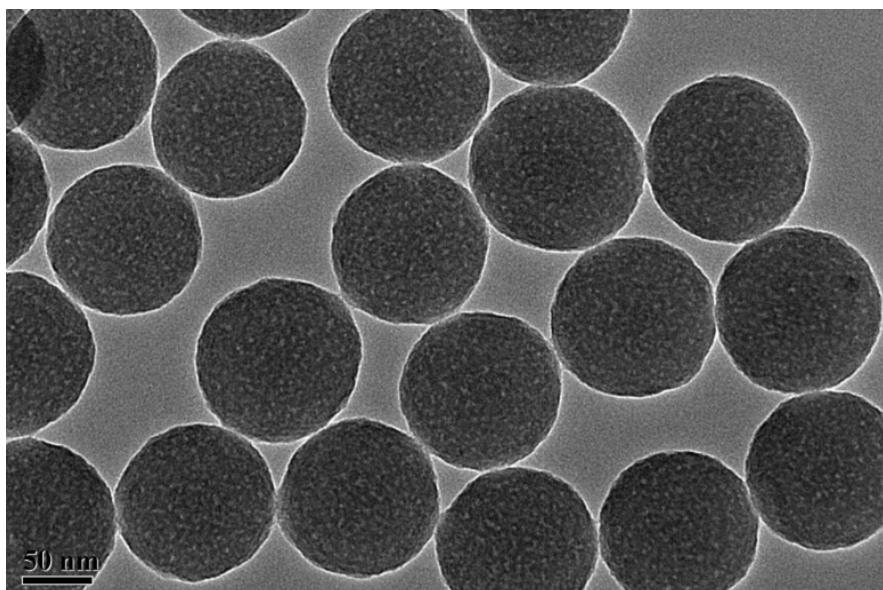


Figure S2 The SEM image of alloy Au/Pd@SiO₂ (Au₃Pd₁).

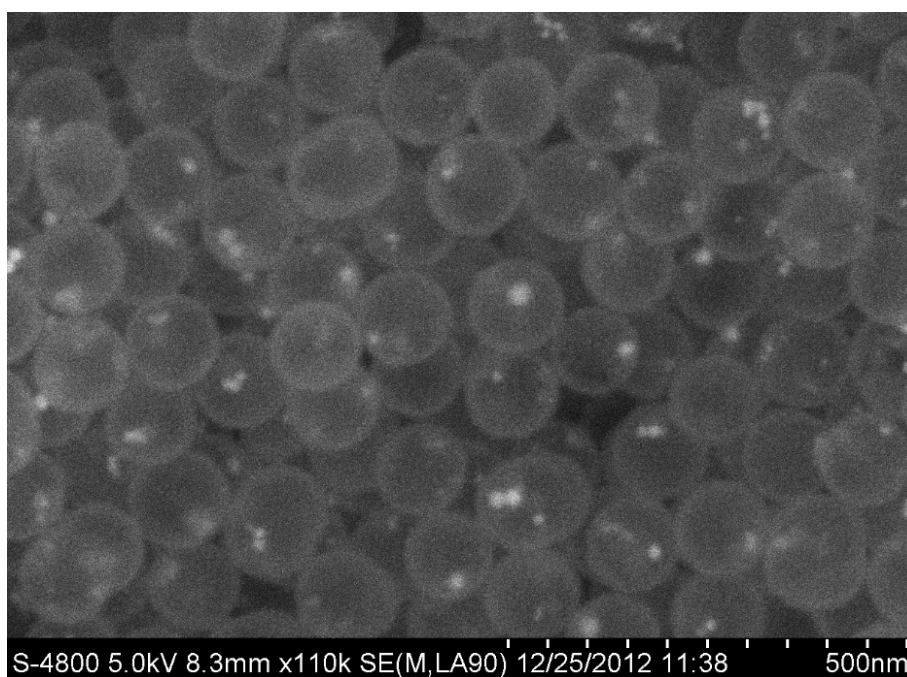


Figure S3 (a) The wide scan survey X-ray photoelectron spectrum (XPS) of Au₃Pd₁,
(b) and (c) high resolution spectrum of Au and Pd element, respectively.

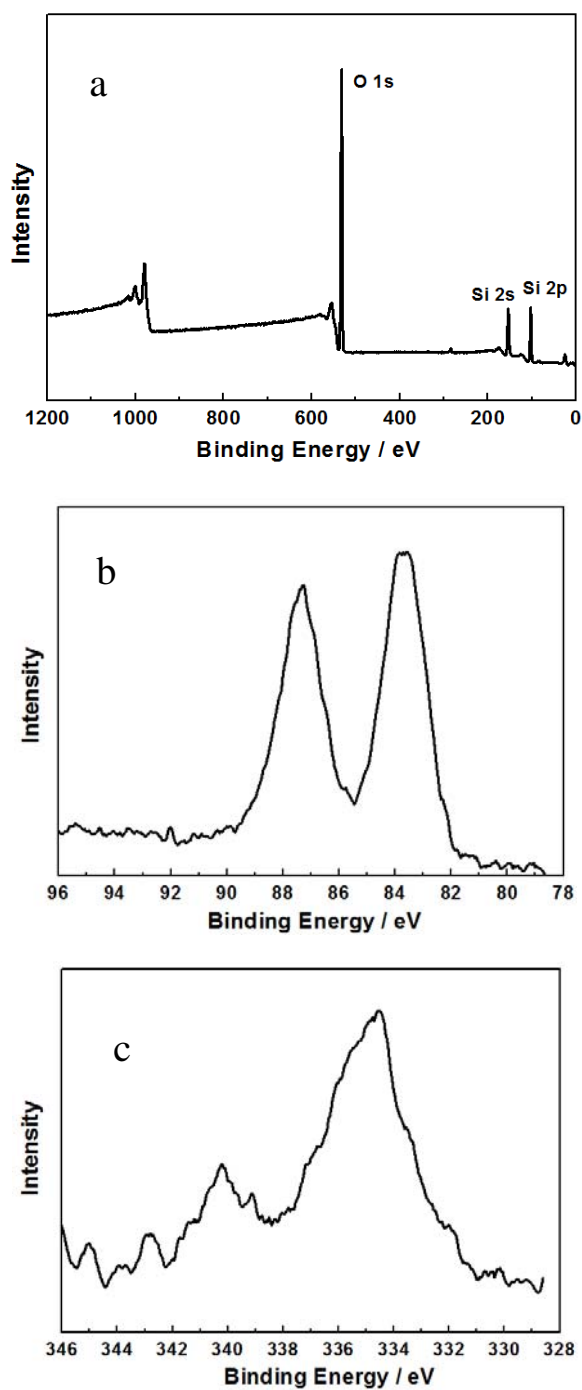


Figure S4 The UV-vis spectra of (a) Au@SiO₂, (b) the physical mixtures of Au@SiO₂ and Pd@SiO₂, (c) Au₁Pd₁@SiO₂ and (d) Pd@SiO₂.

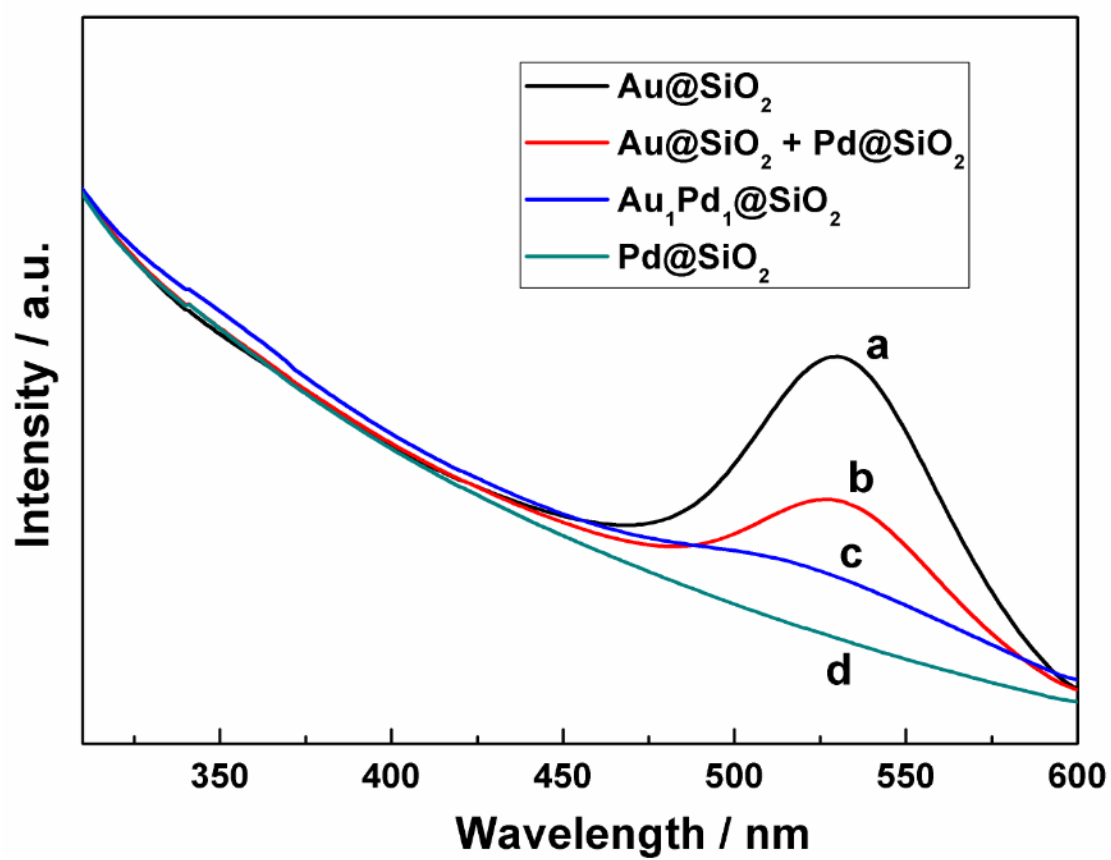


Figure S5 The schematic figure of the formation mechanism for the synthesis of the alloy or core-shell Au/Pd cores confined in the silica nanorattles by tuning reduction kinetics in hydrothermal solution.

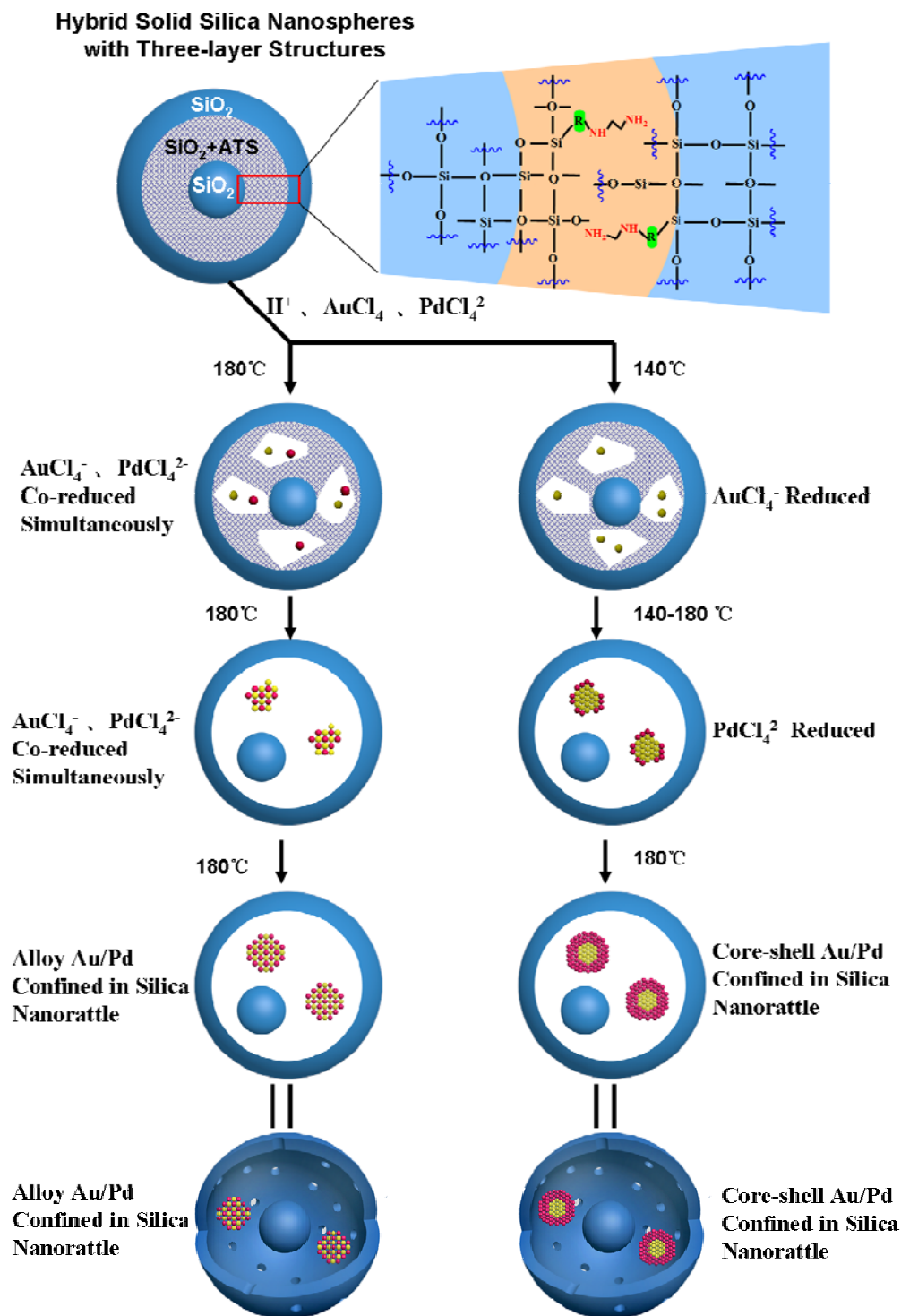


Figure S6 The TEM images of $\text{SiO}_2/\text{ATS}@/\text{TiO}_2$ solid spheres (a, b) and alloy $\text{Au}/\text{Pd}@/\text{TiO}_2$ spheres (c, d).

