Supporting information

Double Shelled Hollow Nanospheres with Dual Noble Metal Nanoparticle Encapsulation for Enhanced Catalytic Application

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1. EXPERIMENTAL SECTION

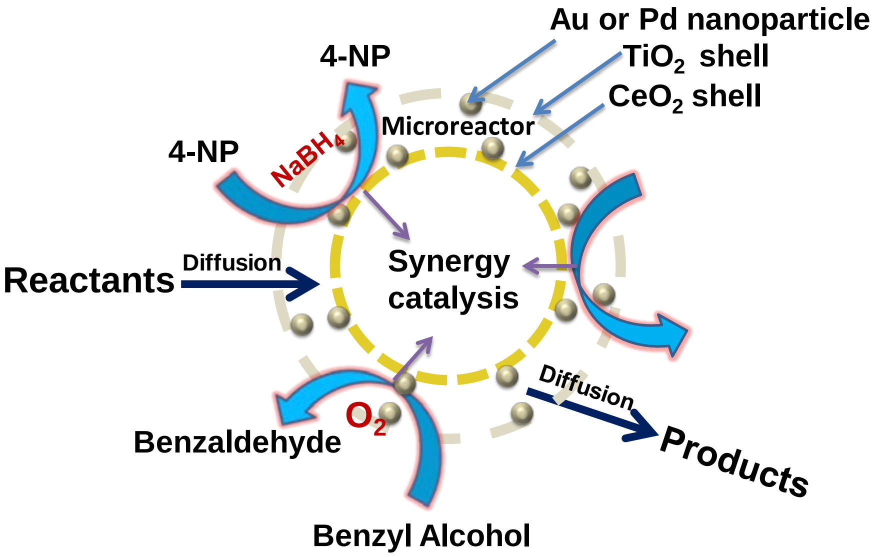
1.1. Synthesis of SiO_2 spheres. The monodisperse SiO_2 spheres were synthesized via a Stöber sol-gel method according to the previous report.[1] Typically, 280 mL of absolute ethanol was mixed with 8 mL of TEOS. A mixture of water (56 mL) and ammonia solution (8.4 mL) was injected into the above solution at room temperature while under magnetic stirring in a 500 mL beaker. After reacting for 24 h, the colloidal SiO_2 spheres were collected by centrifugation. The SiO_2 spheres were washed three times with deionized water and absolute ethanol and then dried in an oven at 65°C for 6 h.

2. CATALYTIC TESTS

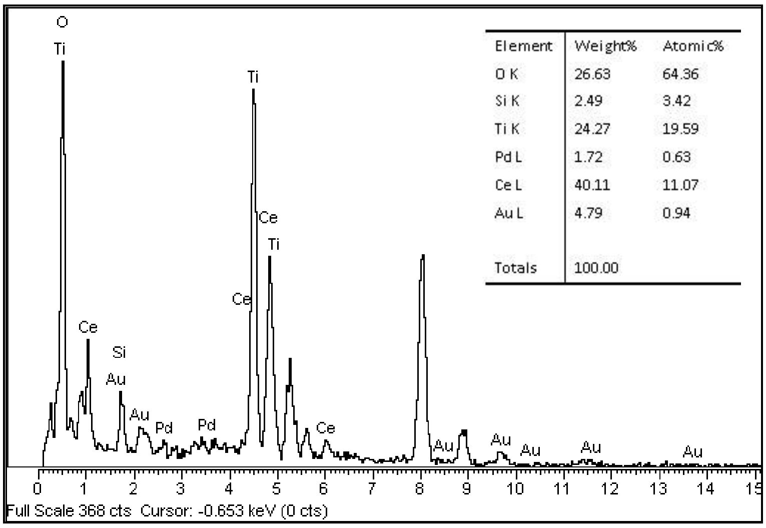
2.1. Catalytic test of benzyl alcohol aerobic oxidation over various double shelled “ball bearing” structured and single shelled hollow nanocatalysts. In order to activate the performance of catalysts, all the catalysts were treated at 300 °C for 2 h with H_2 before the catalytic test. The selective oxidation of benzyl alcohol was carried out in 3-neck flask (25 mL) at a constant oxygen flow (20 mL/min). In a typical experiment, the catalyst (100 mg), K_2CO_3 (1 mmol), biphenyl (0.15 mmol) (as an internal standard), and benzyl alcohol (1 mmol) were suspended in toluene (10 mL) and heated to 80 °C for 3 h. For qualitative and quantitative analysis of the products and reactants, high performance liquid chromatography (HPLC) (HITACHI, D 2000 with a 25 cm Lachrom C18 column, and UV-visible detector with measurement wavelength at 254 nm) was employed. The products were identified by comparison with authentic samples.

2.2. Catalytic test Suzuki-Miyaura coupling of aryl iodides over various double shelled "ball bearing" structured and single shelled hollow nanocatalysts. The Suzuki –Miyaura coupling of aryl iodides was carried out in one-port flask (25 mL) with a reflux condensing tube. All reactions and manipulations were run under air atmosphere. Typically, a reaction tube was charged with aryl iodide (0.5 mmol), aryl boronic acid (1 mmol), catalyst (25 mg), K_2CO_3 (1 mmol) and absolute ethanol (10 mL). The mixture was stirred at 80 °C, and monitored by HPLC at specific time. The crude product was characterized by HPLC analysis (HITACHI, D 2000 with a 25 cm Lachrom C18 column, and UV-visible detector with measurement wavelength at 254 nm)

2.3. Catalytic test of 4-nitrophenol reduction over various double shelled "ball bearing" structured and single shelled hollow nanocatalysts. In order to activate the performance of the catalysts, all the catalysts were treated at 500 °C for 2 h, and reduced by NaBH4 (0.5 M) before the catalytic test. The catalytic performance of the catalysts was checked by employing the reduction of 4-nitrophenol to 4-aminophenol with $NaBH_4$ aqueous solution at room temperature as a model reaction. The @CeO_2/Au, @CeO_2/Au@Pd/TiO_2, @CeO_2/Au@Au/TiO_2, @CeO_2/Pd, @CeO_2/Pd@Au/TiO_2, and @CeO_2/Pd@Pd/TiO_2 catalysts were used for the catalytic tests. Typically, the catalyst (2 mg) was added into minipore water (40 mL) to form a homogeneous suspension by ultrasonication. Then, $NaBH_4$ aqueous solution (0.5 M, 0.5 mL) was added into the above suspension, and the suspension was stirred at room temperature for 10 min. Then, 4-nitrophenol (0.012 M, 0.25 mL) was infused into the above suspension. After stirring several seconds, the mixture was rapidly transferred to the quartz cell to monitor the reaction progress by measuring the UV-vis absorption spectra of the mixture to evaluate the catalytic activity and stability of the catalysts, as the reactant of 4-nitrophenol has a strong absorption peak at 400 nm, while the product of 4-aminephenol has a median absorption peak at 295 nm.



Scheme S1. Schematic illustration for the catalytic mechanism using double shelled @CeO_2/M@M/TiO_2 (M=Au and/or Pd) nanospheres as microreactors for various catalytic reactions.



Element	Weight%	Atomic%
O K	26.63	64.36
Si K	2.49	3.42
Ti K	24.27	19.59
Pd L	1.72	0.63
Ce L	40.11	11.07
Au L	4.79	0.94
Totals	100.00	

Figure S1. EDX characterization of double shelled @CeO_2/Au@Pd/TiO_2 spheres.

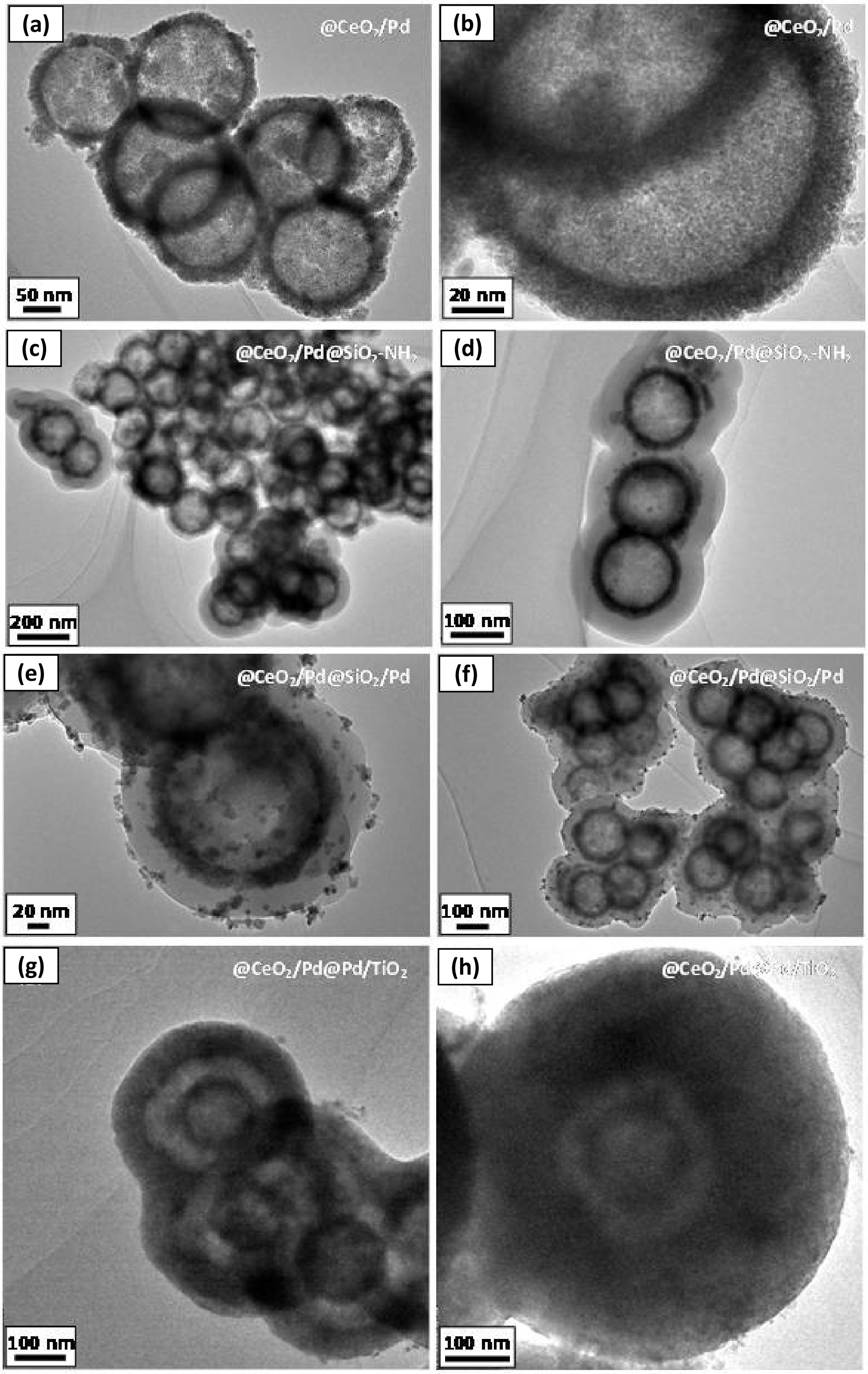


Figure S2. TEM images illustrating the formation process of double shelled @CeO_2/Pd@Pd/TiO_2 spheres: (a and b) @CeO_2/Pd, (c and d) @CeO_2/Pd@SiO_2-NH_2, (e and f) @CeO_2/Pd@SiO_2/Pd, and (g and h) @CeO_2/Pd@Pd/TiO_2.

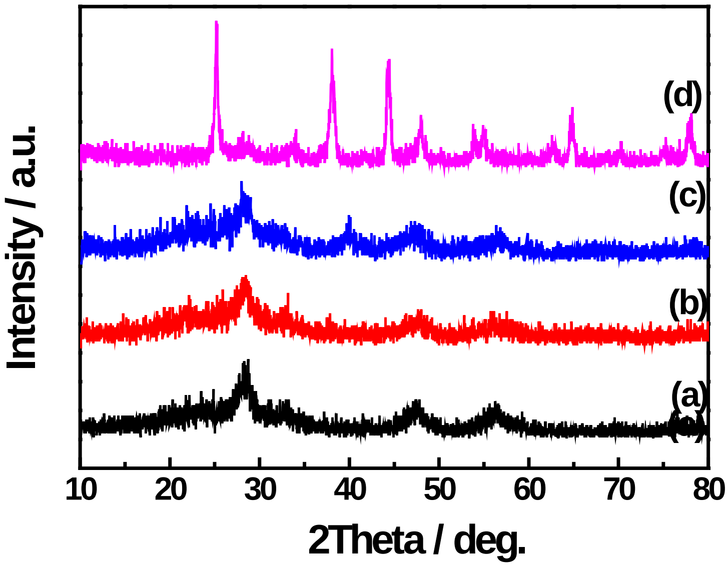


Figure S3. XRD patterns monitoring the formation of double shelled @CeO_2/Pd@Pd/TiO_2 spheres: (a) @CeO_2/Pd, (b) @CeO_2/Pd@SiO_2-NH_2, (c) @CeO_2/Pd@SiO_2-NH_2/Pd, and (d) @CeO_2/Pd@Pd@TiO_2.

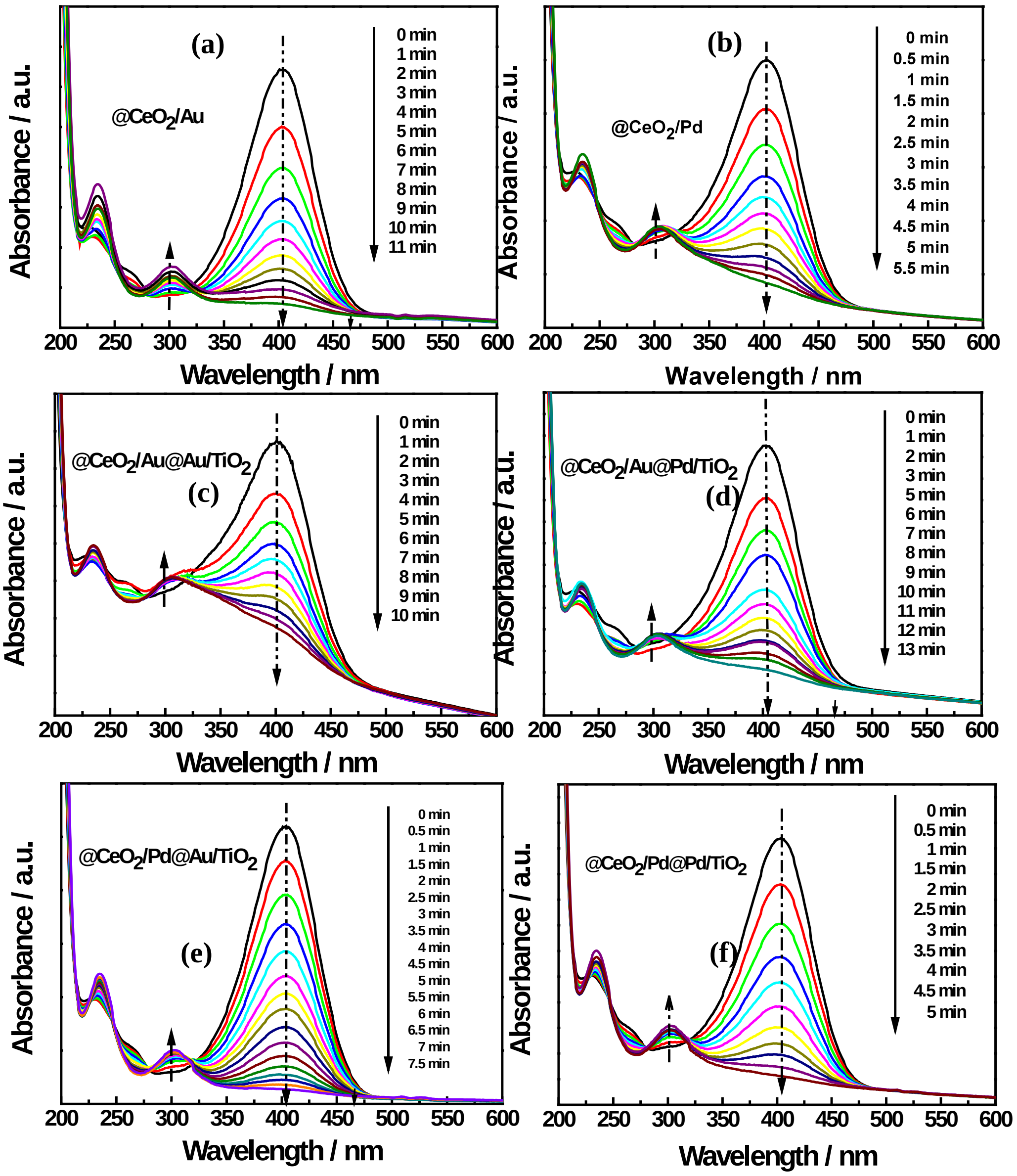


Figure S4. Catalytic tests for the reduction of 4-nitrophenol with different double shelled hollow structured catalysts of (a) @CeO_2/Au, (b) @CeO_2/Pd, (c) @CeO_2/Au@Au/TiO_2, (d) @CeO_2/Au@Pd/TiO_2, (e) @CeO_2/Pd@Au/TiO_2, and (f) @CeO_2/Pd@Pd/TiO_2.

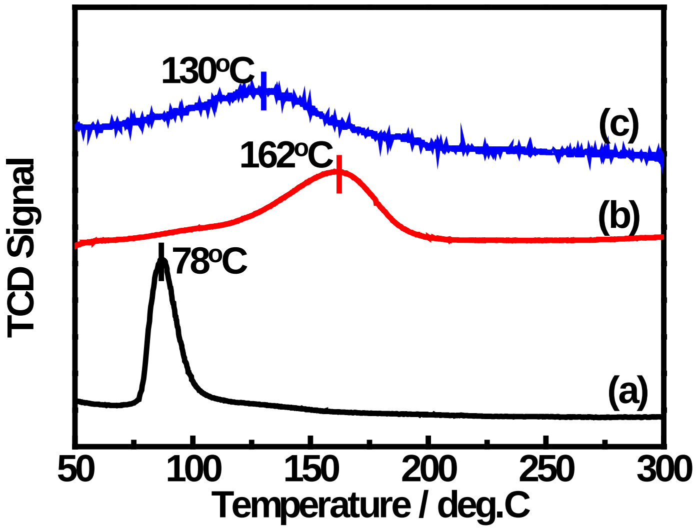


Figure S5. The H_2-TPR spectra for different catalysts of (a) @TiO_2/Pd@Pd/TiO_2, (b) @CeO_2/Pd, and (c) @TiO_2/Pd.