Supporting information

Experimental Section

Materials. Cerium (III) sulfate octahydrate, sodium hydroxide, 3-(N-Morpholino)propanesulfonic acid (MOPS), tetraethylorthosilicate (TEOS), and styrene were of analytical pure and purchased from Sinopharm Chemical Reagent Co.,Ltd. All chemicals were used as received without further purification. Milli-Q water (typically 18.2 MΩ.cm at 25 °C) was used for all experiments. Multi-walled carbon nanotube (MWCNT, d = 35 nm) was purchased from Shenzhen Nanotech Port Co. Ltd. and treated with mixed acids to improve the hydrophilicity.

Preparation of SiO_2@CeO_2 core-shell nanoparticles.

In a typical synthesis, Silica nanoparticles were prepared according to the classical Stöber method.[1] Typically, TEOS(1 mL), deionized water (2 mL) and ammonia solution (28 wt%, 3 mL) were mixed into ethanol (150 mL), which was allowed to react for one day at room temperature. For preparing SiO_2@CeO_2 nanoparticles, 0.5232 g MOPS was dissolved in 50 mL water (0.05 M) and then sodium hydroxide was added till the desired pH of 7.35 was obtained. Then 0.05 g SiO_2 was dispersed in this above buffer solution via ultrasound. Under the protection of inert atmosphere, 0.03 g $Ce_2(SO_4)_3$ was added and the mixed solution was incubated under vigorously stirring at 70 °C for 2 h. The resulting product was collected via washing-and-centrifugation cycles, dried at 80 °C and then calcined at 400 °C for 2 h. To

tune the thickness of CeO_2 shells, 0.025 g SiO_2, 0.06 g or 0.09 g $Ce_2(SO_4)_3$ were used and other reaction conditions remain unchanged.

Preparation of other seeds@CeO₂ core-shell nanoparticles.

Polystyrene spheres (d = 460 nm) were synthesized following the literature procedures.[2] 0.05 g MWCNT or 1 mL PS (100 mg/mL) was dispersed in 50 mL 0.05 M pH = 7.35 MOPS buffer solution under ultrasound and then 0.09 g $Ce_2(SO_4)_3$ was added under inert atmosphere protection. The mixed solution was further incubated under vigorously at 70 °C for 2 h. The resulting product was collected via washing-and-centrifugation cycles and dried at 80 °C. To obtain CeO_2 hollow structure, the cores were selectively removed by heat treatment at 400 °C for 2 h.

Preparation of y-Au@CeO₂ nanocatalyst.

Gold nanoparticles were loaded on silica spheres according to the literature[3] and then they were dispersed in 50 mL 0.05 M pH = 7.35 MOPS buffer solution under ultrasound. Finally, $Ce_2(SO_4)_3$ was added under inert atmosphere protection and the mixed solution was further incubated under vigorously at 70 °C for 2 h. The resulting product was collected via washing-and-centrifugation cycles, dried at 80 °C and then calcined at 400 °C for 2 h. The silica cores were etched by 5 M sodium hydroxide at room temperature for 5 h to achieve the target catalyst.

Characterization.

Scanning electron microscopy (SEM) experiments were recorded on Field

Emission Scanning Electron Microscopy (JSM-6701F, JEOL). Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) images were collected on JEOL-2100F operated at 200 kV. X-ray diffraction (XRD) partterns were carried out on a Rigaku D/MAX-2500 with Cu Kα radiation at 50 kV and 250 mA. The loading of Au was characterized by Inductive Coupled Plasma Emission Spectrometer (Shimadzu ICPE-9000). N_2 sorption isotherms were carried out on Quantachrome Autosorb AS-1 with samples pretreatment degassed at 150 °C for 12 h.

Catalytic tests

The catalytic activities of samples for CO oxidation were collected in a continuous–flow microreactor with internal diameter of 6 mm. To avoid catalytic "hot spots", the catalysts (~50 mg) and quartz particles (60/80 mesh) were mixed with the weight ratio 1:9. The feed gas contains 1 vol% CO, 21 vol% O_2 and balance He at a flow rate of 50 cm^3 min^{-1}, corresponding to a space velocity of 60000 $cm^3 h^{-1} g_{cat}^{-1}$.

Reference

1   W. Stöber, A. Fink and E. Bohn, *J. Colloid Interface Sci.*, 1968, **26**, 62.

2   Z. Yang, Z. Niu, Y. Lu, Z. Hu and C. C. Han, *Angew. Chem. Int. Ed.*, 2003, **115**, 1987.

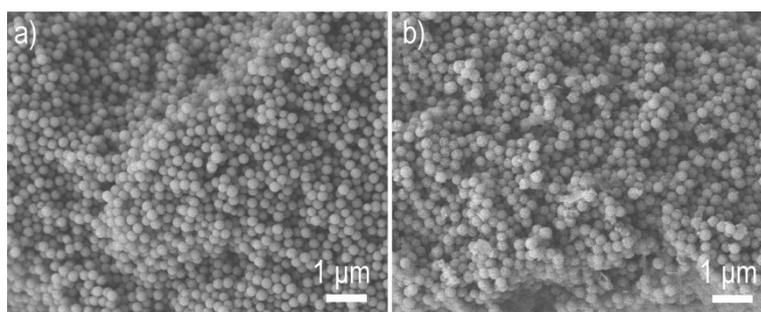3   Z. Chen, Z. M. Cui, F. Niu, L. Jiang and W. G. Song, *Chem. Commun.*, 2010, **46**, 6524.

Figure S1. SEM images of Silica before (a) and after (b) cerium oxide surface coating.
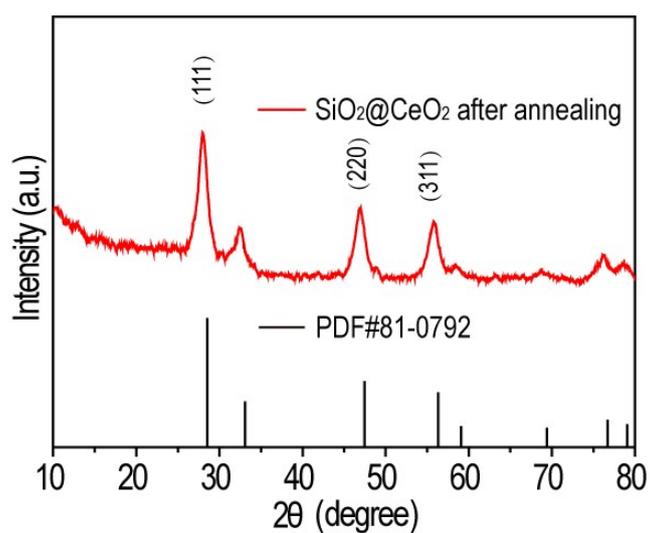

Figure S2. XRD patterns of $SiO_2@CeO_2$ after annealed at 400 ^{o}C in air.
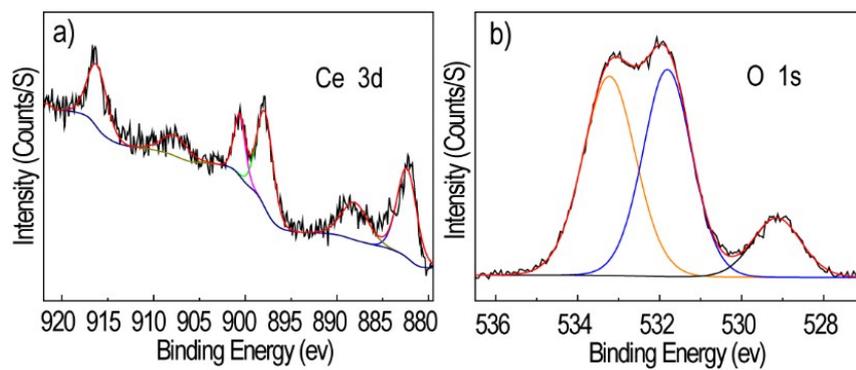
Figure S3. XPS spectra of $SiO_2@CeO_2$ after annealed at 400 °C in air: (a) Ce 3d, (b) O 1s.
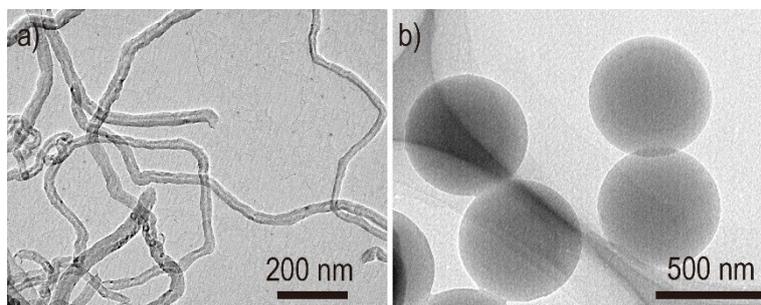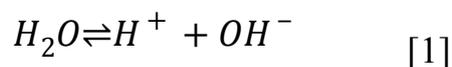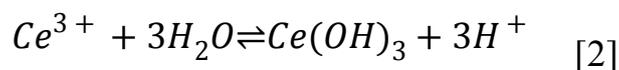

Figure S4. TEM images of MWCNT (a) and PS (b) without CeO_2 coating.

Scheme S1. The relationship between the ionic product of cerium precursor (*Kap*) and pH derived by the hydrolysis balance of Ce³⁺ ions. *Kw* is the dissociation constant for water.

$$H_2O \rightleftharpoons H^+ + OH^- \qquad [1]$$

$$K_w = [H^+][OH^-]$$

$$pH = -\lg[H^+]$$

$$Ce^{3+} + 3H_2O \rightleftharpoons Ce(OH)_3 + 3H^+ \qquad [2]$$

$$K_{ap} = [Ce^{3+}(aq)][OH^-(aq)]^3$$

$$K_{ap} = [Ce^{3+}(aq)][K_w \cdot 10^{pH}]^3$$
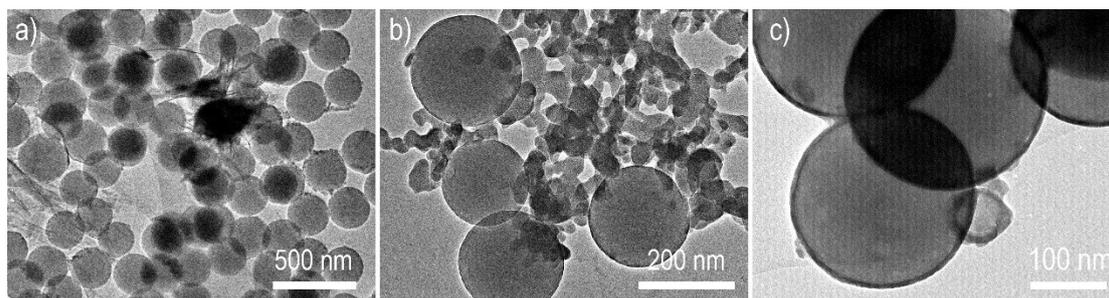
Figure S5. TEM images of SiO₂@CeO₂ prepared by using ammonia (a), the MOPS buffer solution at pH=7.6 (b) and the piperazine-1,4-bisethanesulfonic acid (PIPES) buffer solution at pH=7.36 (c) as the precipitant. Ammonia and high-pH MOPS buffer solution lead to fast self-nucleation and obvious phase separation, demonstrating the importance of controlling the kinetics of the deposition. That the PIPES buffer solution works well confirms that the key role of the buffer solution is to provide suitable amount of hydroxide ions.
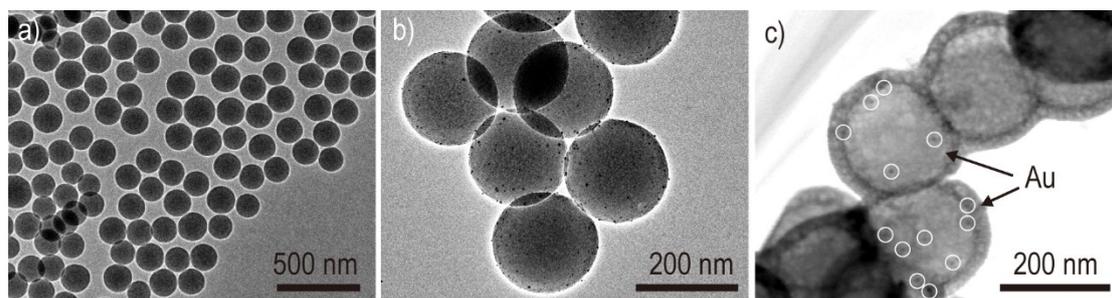
Figure S6. TEM images (a-c) of products obtained at each stage during the whole process for preparing y-Au@CeO$_2$ nanocatalyst, (a) SiO$_2$, (b) Au/SiO$_2$, (c) Au/SiO$_2$@CeO$_2$.
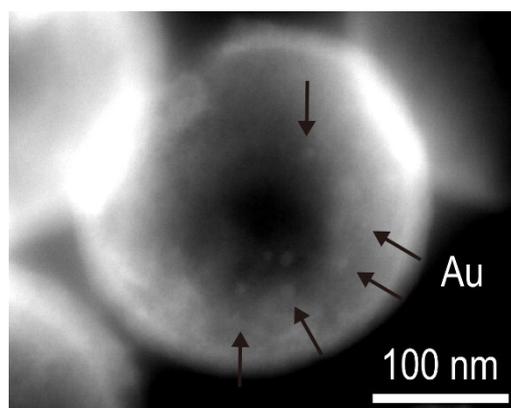

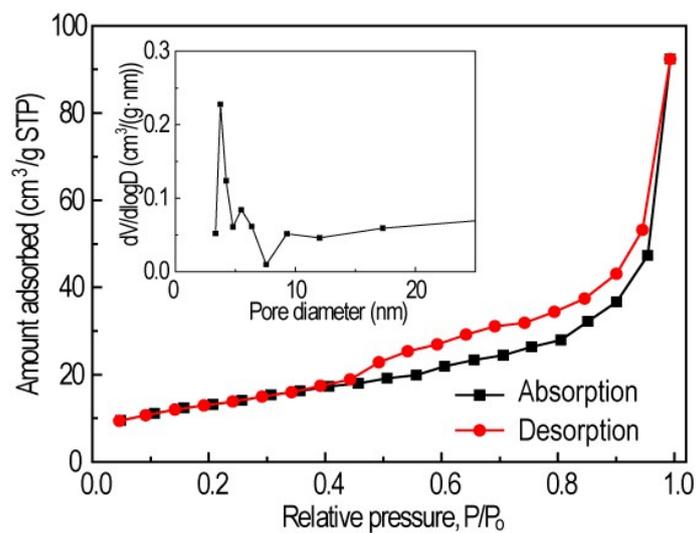Figure S7. Annular dark-field STEM image of y-Au@CeO$_2$.

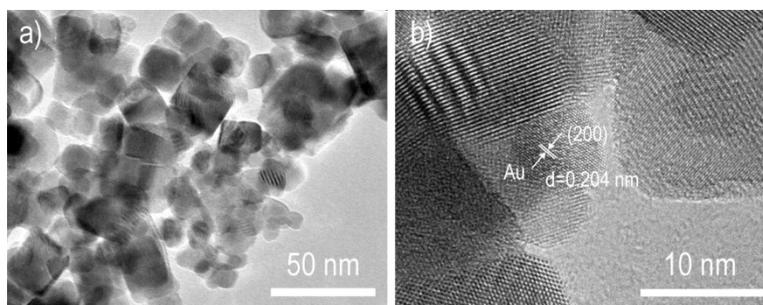Figure S8. Nitrogen adsorption-desorption isotherms and pore size distribution of y-Au@CeO$_2$.

Figure S9. Low (a) and high (b) magnification TEM images of Au/CeO$_2$ prepared by the traditional impregnation method.