## **Electronic Supplementary Information**

## Facile Synthesis of Core-Shell Au@CeO<sub>2</sub> Nanocomposites with Remarkably Enhanced Catalytic Activity for CO Oxidation

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## **Experimental Section**

**Reagents.** The reagents (including glucose, HAuCl<sub>4</sub>·3H<sub>2</sub>O, CeCl<sub>3</sub>·7H<sub>2</sub>O and urea) used were all analytical grade (A.R.) in purity, and bought from Beijing chemical reagent factory and Sinopharm Chemical Reagent Co., Ltd.

**Synthesis of Au@CeO<sub>2</sub> submicrospheres**: In a typical procedure, 3.75 g of glucose was dissolved in 60 mL of deionized water to form a clear solution. 1.8 mL of HAuCl<sub>4</sub> aqueous solution (10 mM) was added drop by drop into the above-mentioned solution under vigorous stirring for 15 min, and the mixture was named as solution A. 0.88 g of urea was dissolved in 34.8 mL of deionized water to form a clear solution, and 0.7 g of CeCl<sub>3</sub>·7H<sub>2</sub>O was added to above solution. The resulting mixture was kept for 15 min under stirring, and the mixture was named as solution B. Subsequently, the solution B was added drop by drop into the solution A under vigorous stirring for 15 min to form a clear yellow solution. Then, the yellow solution was transferred and sealed in the Teflon-sealed stainless steel autoclave. The autoclave was kept at 160 °C for 20 h. When the reaction was completed, the formed suspensions were usually deeply brown in color. A rinsing process including three cycles of washing procedure with deionized water was required before oven drying at 100 °C for 12 h. Finally, the solid powder was calcined in a muffle furnace under air atmosphere at 600 °C for 6 h.

**Synthesis of CeO<sub>2</sub> submicrospheres**: In a typical procedure, 3.75 g of glucose was dissolved in 60 mL of deionized water to form a clear solution A. 0.88 g of urea was dissolved in 34.8 mL of

deionized water to form a clear solution, and 0.7 g of CeCl<sub>3</sub>·7H<sub>2</sub>O was added to above solution. The resulting mixture was kept for 15 min under stirring, and the mixture was named as solution B. Subsequently, the solution B was added drop by drop into the solution A under vigorous stirring for 15 min to form a clear solution. Then, the solution was transferred and sealed in the Teflon-sealed stainless steel autoclave. The autoclave was kept at 160 °C for 20 h. When the reaction was completed, the formed suspensions were usually deeply brown in color. A rinsing process including three cycles of washing procedure with deionized water was required before oven drying at 100 °C for 12 h. Finally, the solid powder was calcined in a muffle furnace under air atmosphere at 600 °C for 6 h.

Synthesis of the supported Au/CeO<sub>2</sub> submicrospheres: An aqueous solution of HAuCl<sub>4</sub>·3H<sub>2</sub>O (10 mM, 10 mL) was added to deionized water (190 mL) and heated to the boiling point. A sodium citrate solution (38.8 mM, 20 mL) was then added, and the resulting mixture was kept for 30 min under stirring to form wine red solution. Subsequently, 1.85 g of CeO<sub>2</sub> submicrosphere powder was added to above wine red solution and stirred for 12 h. The final products were separated from the reaction solution by centrifuging at 8000 rpm for 15 min, and the solid powder was dried at 100 °C for 12 h.

Synthesis of intermediate states of Au@CeO<sub>2</sub> submicrospheres at different reaction time: In a typical procedure, 11.25 g of glucose was dissolved in 180 mL of deionized water to form a clear solution. 5.4 mL of HAuCl<sub>4</sub> aqueous solution (10 mM) was added drop by drop into the above-mentioned solution under vigorous stirring for 15 min, and the mixture was named as solution A. 2.64 g of urea was dissolved in 104.4 mL of deionized water to form a clear solution, and 2.1 g of CeCl<sub>3</sub>·7H<sub>2</sub>O was added to above solution. The resulting mixture was kept for 15 min under stirring, and the mixture was named as solution B. Subsequently, the solution B was added drop by drop into the solution A under vigorous stirring for 15 min to form a clear yellow solution. Then, the resulting mixture was divided into four equal parts and transferred to Teflon-lined stainless steel autoclaves, in which the samples were heated at 160 °C for 10 min, 1 h, 6 h, and 20 h, respectively. When the reactions were completed, the formed suspensions were collected with glass vials.

Synthesis of Au@C submicrospheres: In a typical procedure, 24 g of glucose was dissolved in 383 mL of deionized water to form a clear solution. 11.5 mL of HAuCl<sub>4</sub> aqueous solution (10 mM) was added drop by drop into the above-mentioned solution under vigorous stirring for 10 min. Then, the solution was transferred and sealed in the Teflon-sealed stainless steel autoclave. The autoclave was kept at 160 °C for 20 h. When the reaction was completed, the formed suspensions were usually deeply brown in color. The final products were separated from the reaction medium by filtering, and

the solid powder was dried at 100 °C for 12 h.

Synthesis of Au@CeO<sub>2</sub> submicrospheres without adding glucose: In a typical procedure, 1.8 mL of HAuCl<sub>4</sub> aqueous solution (10 mM) was added into 60 mL of deionized water to form a clear solution under vigorous stirring for 15 min, and the mixture was named as solution A. 0.88 g of urea was dissolved in 34.8 mL of deionized water to form a clear solution, and 0.7 g of CeCl<sub>3</sub>·7H<sub>2</sub>O was added to above solution. The resulting mixture was kept for 15 min under stirring, and the mixture was named as solution B. Subsequently, the solution B was added drop by drop into the solution A under vigorous stirring for 15 min to form a clear yellow solution. Then, the yellow solution was transferred and sealed in the Teflon-sealed stainless steel autoclave. The autoclave was kept at 160 °C for 20 h. When the reaction was completed, a rinsing process including three cycles of washing procedure with deionized water was required before oven drying at 100 °C for 12 h.

Synthesis of CeO<sub>2</sub> submicrospheres without adding urea: In a typical procedure, 3.75 g of glucose was dissolved in 60 mL of deionized water to form a clear solution A. 0.7 g of CeCl<sub>3</sub>·7H<sub>2</sub>O was dissolved in 34.8 mL of deionized water and was stirred for 15 min, and the mixture was named solution as B. Subsequently, the solution B was added drop by drop into the solution A under vigorous stirring for 15 min to form a clear solution. Then, the solution was transferred and sealed in the Teflon-sealed stainless steel autoclave. The autoclave was kept at 160 °C for 20 h. When the reaction was completed, the formed suspensions were usually deeply brown in color. A rinsing process including three cycles of washing procedure with deionized water was required before oven drying at 100 °C for 12 h. Finally, the solid powder was calcined in a muffle furnace under air atmosphere at 600 °C for 6 h.

**Synthesis of 0.5% Au@CeO<sub>2</sub> catalyst:** In a typical procedure, 3.75 g of glucose was dissolved in 60 mL of deionized water to form a clear solution. 0.9 mL of HAuCl<sub>4</sub> aqueous solution (10 mM) was added drop by drop into the above-mentioned solution under vigorous stirring for 15 min, and the mixture was named as solution A. 0.88 g of urea was dissolved in 34.8 mL of deionized water to form a clear solution, and 0.7 g of CeCl<sub>3</sub>·7H<sub>2</sub>O was added to above solution. The resulting mixture was kept for 15 min under stirring, and the mixture was named as solution B. Subsequently, the solution B was added drop by drop into the solution A under vigorous stirring for 15 min to form a clear yellow solution. Then, the yellow solution was transferred and sealed in the Teflon-sealed stainless steel autoclave. The autoclave was kept at 160 °C for 20 h. When the reaction was completed, the formed suspensions were usually deeply brown in color. A rinsing process including three cycles of washing procedure with deionized water was required before oven drying at 100 °C for 12 h. Finally, the solid powder was calcined in a muffle furnace under air atmosphere at 600 °C for 6 h.

**Synthesis of 2% Au@CeO<sub>2</sub> catalyst:** In a typical procedure, 3.75 g of glucose was dissolved in 60 mL of deionized water to form a clear solution. 3.6 mL of HAuCl<sub>4</sub> aqueous solution (10 mM) was added drop by drop into the above-mentioned solution under vigorous stirring for 15 min, and the mixture was named as solution A. 0.88 g of urea was dissolved in 34.8 mL of deionized water to form a clear solution, and 0.7 g of CeCl<sub>3</sub>·7H<sub>2</sub>O was added to above solution. The resulting mixture was kept for 15 min under stirring, and the mixture was named as solution B. Subsequently, the solution B was added drop by drop into the solution A under vigorous stirring for 15 min to form a clear yellow solution. Then, the yellow solution was transferred and sealed in the Teflon-sealed stainless steel autoclave. The autoclave was kept at 160 °C for 20 h. When the reaction was completed, the formed suspensions were usually deeply brown in color. A rinsing process including three cycles of washing procedure with deionized water was required before oven drying at 100 °C for 12 h. Finally, the solid powder was calcined in a muffle furnace under air atmosphere at 600 °C for 6 h.

**Catalytic activity measurement for CO oxidation**: All catalysts toward catalytic CO oxidation were evaluated using a fixed-bed stainless steel reactor coupled online with a gas chromatograph (GC-2014C, SHIMADZU), a molecular sieve column, and a thermal conductivity detector (TCD). The operation conditions were shown as follows: 200 mg of sieved catalyst (40-60 meshes), a gas mixture of 1% CO, 1.6% O<sub>2</sub> and 97.4% He (balance gas) with a total flow rate of 50 mL·min<sup>-1</sup> corresponding to a space velocity of 15,000 mL·h<sup>-1</sup>·g<sup>-1</sup><sub>cat</sub>, programmed-temperature rate at  $0.75 \,^{\circ}\text{C·min}^{-1}$ .

**Characterization**: Powder XRD patterns were recorded on a Panaltical X'Pert-pro MPD X-ray power diffractometer, using Cu K $\alpha$  radiation ( $\lambda = 1.54056$  Å). SEM was performed on a Hitachi S-4800 electron microscope. TEM were performed on FEI Tecnai G<sup>2</sup> F20 electron microscope operated at 200 kV with the software package for automated electron tomography. FTIR spectra (PE2000) were acquired to identify the structural vibration and surface functional groups of samples. The BET (Brunauer-Emmett-Teller) surface area, pore volume and pore size of catalysts were measured using a Quadrasorb SI-MP instrument. Prior to each measurement, the sample was heated to 300 °C and kept at this temperature for 3 h. Au content was determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Thermo Fisher Scientific). XPS spectra were performed by an ESCALAB 250 Xi XPS system of Thermo Scientific, where the analysis chamber was 1.5×10<sup>-9</sup> mbar, and the X-ray spot was 500 µm.



Fig. S1 (a) HAADF-STEM image of pre-Au@CeO<sub>2</sub> submicrospheres and (b) the corresponding line-scan profiles.



Fig. S2 (a) TEM image and (b) corresponding EDX pattern of the product without adding glucose.



**Fig. S3** (a) TEM image and (b) corresponding EDX pattern of the product without adding urea (before calcination).



**Fig. S4** (a) TEM image and (b) corresponding EDX pattern of the product without adding urea (after calcination).



Fig. S5 FTIR spectrum of Au@C submicrospheres.



Fig. S6 Schematic growth model for Au@CeO2 submicrospheres.



**Fig. S7** Ce 3d XPS spectra of Au@CeO<sub>2</sub> submicrospheres. Peak-S\* and Peak-S\*\* are the shake-up peaks of peak-I and peak-II, respectively.



Fig. S8  $N_2$  adsorption-desorption isotherms and their corresponding pore-size distribution curves (inset) of (a) Au@CeO<sub>2</sub> and (b) Au/CeO<sub>2</sub> catalysts.



**Fig. S9** Catalytic activity of 0.93% Au@CeO<sub>2</sub> (blue curve a), 0.55% Au@CeO<sub>2</sub> (red cure b), and 1.97% Au@CeO<sub>2</sub> (black cure c) for CO oxidation. Feed gas containing 1 vol.% CO, 1.6 vol.% O<sub>2</sub> and balance with He at a total flow rate of 50 mL·min<sup>-1</sup>, corresponding to a GHSV of 15,000 mL·h<sup>-1</sup>·g<sup>-1</sup><sub>cat</sub>.



**Fig. S10** (a) TEM image of 0.55% Au@CeO<sub>2</sub> submicrospheres and (b) corresponding HAADF-STEM mapping images. The size of Au NP cores is around 17 nm.



**Fig. S11** (a) TEM image of 1.97% Au@CeO<sub>2</sub> submicrospheres and (b) corresponding HAADF-STEM mapping images. The size of Au NP cores is around 23 nm.



Fig. S12 TEM images of core-shell Au@CeO<sub>2</sub> catalysts (a) before and (b) after 72 h reaction. The sizes of Au NP cores remain around 17 nm.



**Fig. S13** TEM images of Au/CeO<sub>2</sub> catalysts (a) before and (b) after 72 h reaction. The average sizes of Au NPs are increased from orginal 14 nm to 18 nm after the catalytic reaction.



Fig. S14 Schematic diagram of the reaction process over Au@CeO<sub>2</sub> and Au/CeO<sub>2</sub> catalysts.

Catalysts	Au <sup>a</sup> (wt%)	<sup>b</sup> BET surface area $(m^2 \cdot g^{-1})$	<sup>b</sup> Average pore diameter (nm)	<sup>b</sup> Total pore volume (cm <sup>3</sup> ·g <sup>-1</sup> )
Au@CeO <sub>2</sub>	0.93	82.5	2.2	0.091
Au/CeO <sub>2</sub>	1.0	80.6	2.1	0.082

Table S1 Physical properties of Au@CeO2 and Au/CeO2 catalysts.

<sup>a</sup>Au content was determined by ICP-MS; <sup>b</sup>Surface areas and pore size distributions of the samples were calculated by using the Brunauer-Emmett-Teller (BET) equation and the Barrett-Joyner-Halenda (BJH) method, respectively.