Electronic Supplementary Material (ESI) for Chemical Communications **Template-free synthesis of core-shell CeO₂ nanospheres**

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Experimental section

Synthesis of core-shell CeO₂

Cerous nitrate (Ce(NO₃)₂·6H₂O, 99.0%), urea (CO(NH₂)₂, 99.0%), and citric acid (C₆H₈O₇·H₂O, 99.0%), hydrogen peroxide (H₂O₂, 30%) and n-butanol (C₄H₁₀O, 99.0%) were purchased from Sinopharm Chemical Reagent Co. Ltd. Deionized water was used throughout.

Preparation of CeO₂ core-shell nanostructures is synthesized through a typical hydrothermal process. Ce(NO₃)₂·6H₂O (0.07 g), urea (0.01 g), C₆H₈O₇·H₂O (0.017 g) were dissolved in 16 mL of 7:1 water/n-butanol mixture. After continuous stirring for 20 min, 100 μ L H₂O₂ was added into the mixture. The transparent mixture was then put into a Teflon-lined stainless steel autoclave of 25 mL capacity. After being sealed, the autoclave was heated at 120 °C for 24 h in a drying oven. After cooling the reaction mixture to room temperature, the products were washed with deionized water and absolute ethanol at 3 times. Subsequently, the products were dried in a drying oven for 7 h at 60 °C without any further treatment.

Characterization

The phase identity, composition were recorded by using a Rigaku D/Max 2200PC diffractometer with a graphite monochromator and Cu-K α radiation(λ =0.15418nm). The structure, size, and shape of the products were characterized by a transmission electron microscope (TEM, JEM100-CXII) with an accelerating voltage of 80 kV, a field-emission scanning electron microscope (FE-SEM, Hitachi, S4800), and a high-resolution transmission electron microscope (HRTEM, JEM-2100) with an accelerating voltage of 200 kV.

The surface areas were calculated by the Brunauer-Emmett-Teller (BET) method and the pore size distribution was calculated from the desorption branch using the Barrett-Joyner-Halenda (BJH) theory.

The catalytic properties of the products was evaluated through the CO oxidation experiment. In a typical experiment, 25 mg catalyst particles mixed with 300 mg silica sand were placed in the reactor. The reactant gases (1% CO, 10% O₂, and 89% N₂) passed through the reactor at a rate of 30 mL/min. The composition of the gas exiting the reactor was analyzed with an online infrared gas analyzer, which simultaneously detects CO and CO₂ with a resolution of 10ppm. The results were further confirmed with a Shimadzu gas chromatograph (GC-14).

Reaction equation

The following reactions are involved in the formation of CeO₂ NPs.

$$CO(NH_2)_2 + 3H_2O \rightarrow CO_2 + 2NH_4^+ + 2OH^-$$
(1)
$$C_2^{4+} + 4OH^- + C_2(OH)$$
(2)

$$Ce^{+} + 4OH^{-} \rightarrow Ce(OH)_4 \tag{2}$$

$$Ce(OH)_4 \rightarrow CeO_2 + 2H_2O \tag{3}$$



Figure S1. XRD pattern of the nanoparticles prepared by the CA-assisted hydrothermal process at 120 $^\circ\,$ C



Figure S2. HRTEM images of the edge of nanosphere synthesized at 120 °C for 24 h.



Figure S3. TEM investigation of formation process of CeO_2 core-shell structures: after a) 4 h , b) 8 h, c) 12 h, d) 16 h, e) 20 h and f) 24 h at 120 °C.



Figure S4. N_2 adsorption-desorption isotherm of the as-prepared core-shell CeO₂ inset is the corresponding BJH pore size distribution curve.