Electronic Supplementary Information

Selective hydrogenation of nitroaromatics by ceria nanorods

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Experimental Section

All chemicals are of analytical grade and were used as received without further purification.

Synthesis of Materials. Ceria nanorods, nanocubes, nano-octahedrons and nanoparticles were synthesized by literatures reported before. For the nanorods and nanocubes, 0.868 g of cerium (III) nitrate hexahydrate and 9.6 g of sodium hydroxide were dissolved in 5 and 35 mL of deionized water, respectively. Then, these two solutions were mixed in a Teflon bottle, and this mixture was kept stirring for 30 min with the formation of a milky slurry. Subsequently, the Teflon bottle with this mixture was held in a stainless steel vessel autoclave, and then heated at 373 K for nanorods and 453 K for nanocubes. After the hydrothermal treatment, fresh white precipitates were separated by centrifugation, washed with deionized water and ethanol several times, followed by drying at 60 °C in air overnight. The products after drying were yellow powders.

To obtain nano-octahedrons, 0.434 g of cerium (III) nitrate hexahydrate and 0.0038 g of trisodium phosphate hexahydrate were dissolved in 40 mL distilled water. After being stirred at room temperature for 1 h, the mixed solution was transferred into a 50 mL Teflon-lined stainless autoclave and heated at 170 °C for 12 h under autogenous pressure and static conditions in an electric oven. Upon leaving the solution cool to room temperature, the precipitates were separated by centrifuging, washed with distilled water and ethanol three times in turn, and then dried at 60 °C for 1 day. The amount of nitrogen and phosphor on the ceria surface was determined by XPS to be negligible.

For nanocubes with 8-15 nm, 15 mL 0.5 M cerium(III) nitrate aqueous solution was transferred to a 50 mL Teflon-lined stainless-steel autoclave, then a mixture of 12 mL deionized water, 0.015 mol sodium oleate and 3 mL ethanol was added to the autoclave in the ambient environment with stirring. The sealed autoclave was transferred to an oven at 180 °C and held at the temperature for 24 h before cooling to room temperature naturally. The resulting deposit was centrifuged with ethanol, and then was dried in air at 373 K overnight. Then the power was calcined at 400 °C for 4 h in air to diminish the oleic acid on the ceria surface.

To obtain CeO_2, 60 g of ceric ammonium nitrate and 200 g of urea were dissolved into 2000 ml of distilled water and the mixture was heated gradually to 90 °C under stirring and kept at this temperature for 27 h. After filtration and being washed with water, the precipitate was dried at 373 K for 12 h, and finally calcined at 400 °C for 4 h in air.

Characterization. X-ray powder diffraction patterns (XRD) of the product were obtained on a Japan RigakuDMax-γA rotation anode X-ray diffractometer equipped with graphite monochromatized Cu KR radiation ($\lambda = 1.54178$ Å). X-ray photoelectron spectroscopy (XPS) was conducted on Thermo-VG Scientific ESCALAB 250. Scanning electron microscope (SEM) measurements were carried out using a Zeiss Supra 40 microscope. Transmission electron microscope (TEM) photographs were taken on a Hitachi model H-800 transmission electron microscope at an accelerating voltage of 200 kV. The BET specific surface area (SBET) was measured by nitrogen adsorption at 77 K, using an ASAP 2020 analyser (Micromeritics Co. Ltd.), which was performed after degassing the sample at 473 K for 6 h under vacuum. The samples were calcined at 400 °C for 4 h before the BET determination.

Catalytic experiments. The catalytic hydrogenation of various aromatic nitro compounds were carried out in a tube by oil bath under the following reaction conditions: 80 ^{o}C, 2 or 4 mmol $N_2H_4.H_2O$, 15 mg of catalyst (8 mol %), 1mmol of substrates, and 2mL of ethanol and water (v/v, 1:1). The catalytic process performance was directed by GC (Agilent 7890A series) equipped with a FID detector and a HP-5 column (30 mm×0.32 mm×0.25 μm). The structure of the product was confirmed by comparison with a standard sample and by GC-MS (Agilent GC-MS 6890/5973).

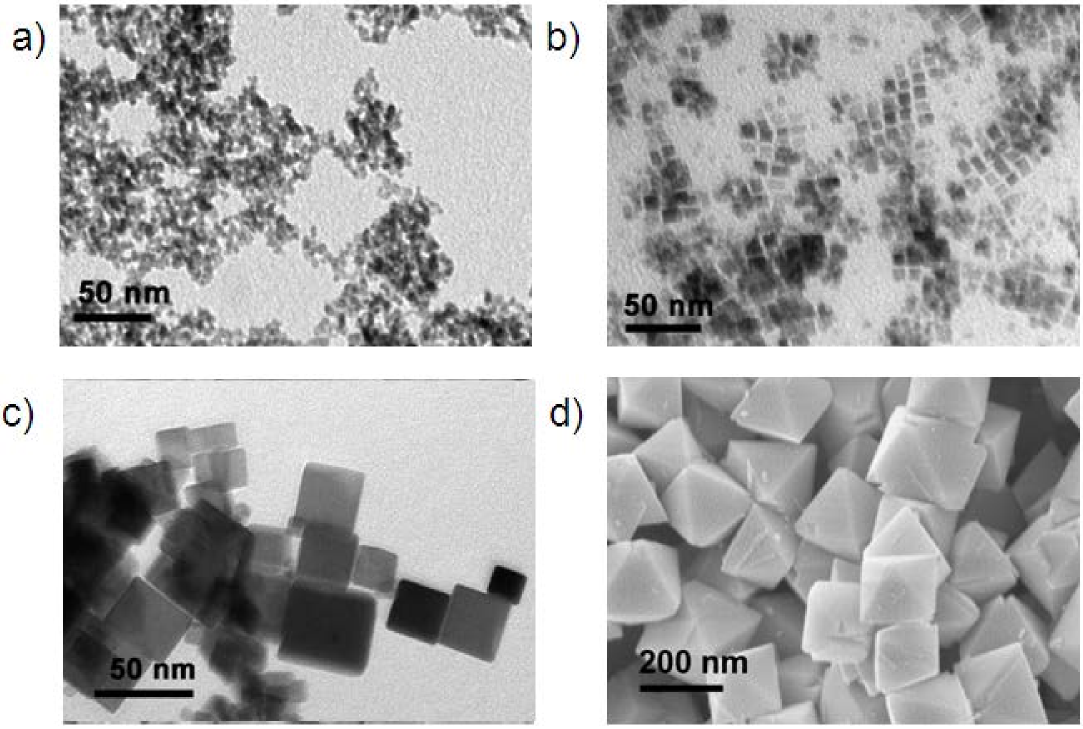

Fig. S1 TEM or SEM images of nano-CeO_2. a) TEM of CeO_2 nanoparticle ; b) TEM of CeO_2 nanocubes for 8-15 nm; c) TEM of CeO_2 nanocubes for 20-100 nm; d) SEM of CeO_2 nano-octahedra.

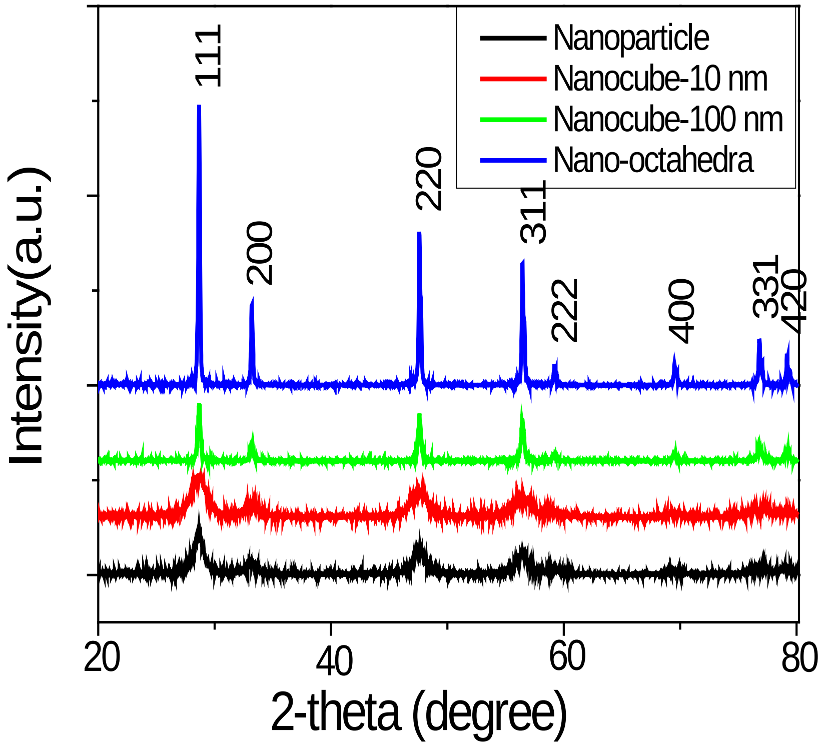

Fig. S2 X-ray diffraction (XRD) pattern of CeO_2 nanocubes and nano-octahedrons and nanoparticle

Table S1. Surface elemental composition of CeO_2 catalysts

Sample	Surface composition/at %			O/Ce	O Is/ at%		
	C	Ce	O		OA	OB	OC
Fresh	36.61	17.56	45.83	2.61	38.88	56.94	4.18
Reduced	32.72	19.84	47.44	2.39	51.18	18.53	30.29
Used	25.64	21.5	52.85	2.46	44.07	37.30	18.63