# Electronic Supplementary Information (ESI)

# Surface Selective Growth of Ceria Nanocrystals by CO Absorption

Yeheng He, Xin Liang, Biaohua Chen

*Faculty of Chemical Technology, Beijing University of Chemical Technology.*

## Experimental Section

Chemicals: All reagents were of analytical grade and used as received without further purification. Deionized water was used throughout. $(NH_4)_2Ce(NO_3)_6$, NaOH, ethanol, oleic acid were supplied by TianJin GuangFu Fine Chemical Research Institute. Pure helium and carbon monoxide (equilibrium gas is helium, the percentage of carbon monoxide is 4.98%) were of chemical grade and purchased from Beijing Haipu Gas Company. LTD.

Synthesis of ceria nanoparticles: In a typical synthesis, [1] 0.5 g NaOH was dissolved in distilled water (10 ml), and then a mixture of 15 ml ethanol and 4 ml oleic acid was added into the solution under magnetic stirring. 4.4 g $(NH_4)_2Ce(NO_3)_6$ was dissolved in 5 ml of water and added dropwise to the mixed solvent to form a yellow precipitate. The obtained solution was transferred into a 100 ml stainless autoclave. The vessel was purged with helium ten times to exhaust air, pressurized up to 0.8 MPa and heated at 120 $^oC$ for 12h under vigorous stirring. Then the reactor was cooled down to room temperature and the products were collected by centrifugation and washed several times with ethanol.

Synthesis of ceria nanocubes: The procedure for the synthesis of ceria NCs was similar to that for ceria NPs, except that helium gas was replaced by carbon monoxide.

TEM analysis: The sizes and morphologies of the ceria nanocrystals were examined by a JEOL JEM-2010 transmission electron microscope (TEM) at 120 kV, and a high-resolution transmission electron microscope (HRTEM) at 200 kV.

XRD analysis: The products were characterized by a Bruker D8-advance X-ray diffractometer (XRD) with Cu Kα radiation (λ=1.54056Å).

Uv-vis analysis: The Uv-vis spectra were obtained on a Shimadzu UV-3600 UV-vis spectrophotometer. Ceria NPs and NCs samples were dispersed in cyclohexane and prepared in the same concentration for UV-vis detection, cyclohexane was used as reference.

FT-IR analysis: The FT-IR spectra for ceria NPs and NCs were obtained on a Bruker Tensor27 infrared spectrometer at room temperature.

XPS analysis: The XPS spectra for ceria NPs and NCs were detected on a Thermo-Fisher ESCALAB 250 X-ray photoelectron spectrometer.

## The X-ray diffraction (XRD) analysis

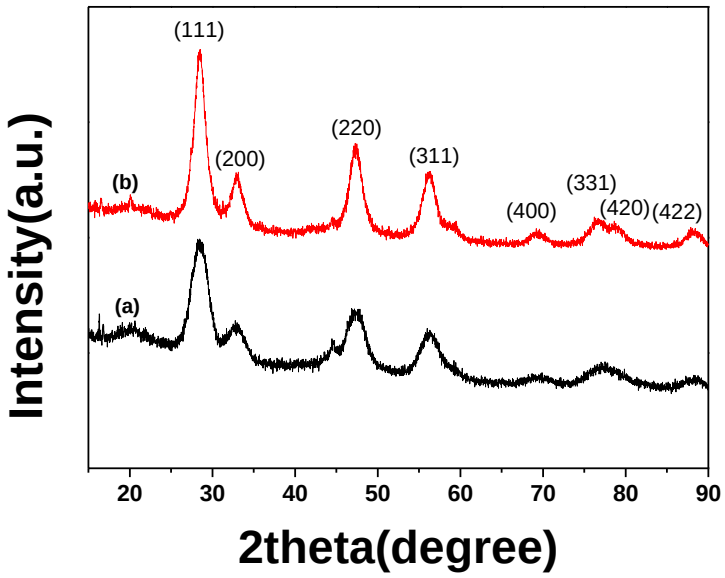


**Fig. S1 XRD patterns of the as-prepared (a) ceria nanoparticles and (b) ceria nanocubes.**

The reflection peaks were assigned to the cubic phase of ceria (*Fm*3*m*, *a*=5.41134Å, JCPDS Card No. 34-0394).

## The Uv-vis analysis

Fig. S2 shows the adsorption spectra of as-prepared ceria NPs and NCs with a strong absorption band below 400nm in both of them. The band gap width ($E_g$) of the as-prepared ceria NPs and NCs could be obtained by using the following Equation (1), in which hυ epresents the photo energy, α the absporption coefficient, C the constant and n=1/2. [2]

$$\alpha h\nu = C(h\nu - E_g)^n \quad (1)$$

Fig. S3 displays the plot of $(\alpha h\upsilon)^2$ versus hυ for as prepared ceria NPs and NCs. The band gap of ceria NPs and NCs was calculated to be 3.69 eV and 3.63 eV, respectively. Compared to the bulk ceria ($E_g$=3.15 eV), both the ceria NPs and NCs exhibited a strong quantum confinement effect, which is attributed to their smaller sizes than Bohr radius of ceria (7-8nm). Detailed observation on the adsorption spectra reveals a slightly red shift of ceria NCs in comparision with ceria NPs.

A semi-empirical equation (2) has been proposed to describe the relationship between the ceria band gap and the size of the nanocrystals.[3]

$$E_{g(nano)} = E_{g(bulk)} + \frac{h^2\pi^2}{2R^2}\left[\frac{1}{m_e} + \frac{1}{m_h}\right] - \frac{1.8e^2}{\varepsilon R} \quad (2)$$

Where R is the radius of the nanocrystals, $E_{g(nano)}$ and $E_{g(bulk)}$ represent the band gap width of ceria nanocrystals and coarsely crystalline, respectively. h is the Planck constant, $m_e$ and $m_h$ are the effective mass of electron and hole ($m_e/m_h$=0.42 for ceria), e is the electron charge and ε is the relative dielectric constant of ceria and it is ~24. The band width of the as-prepared ceria NPs and NCs obtained after analysis is 3.69 eV and 3.63 eV, thus the size calculated is 3.7 and 4.7 nm, respectively.

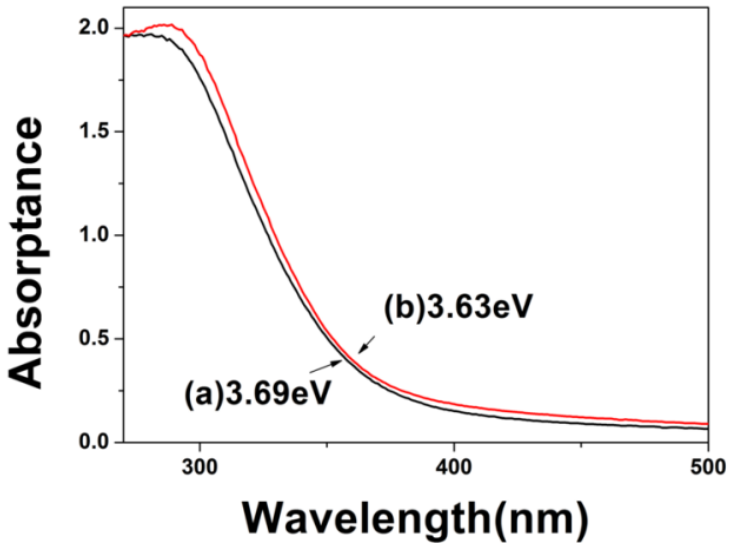


**Fig. S2 The adsorption spectra for as-prepared (a) ceria NPs and (b) ceria NCs.**

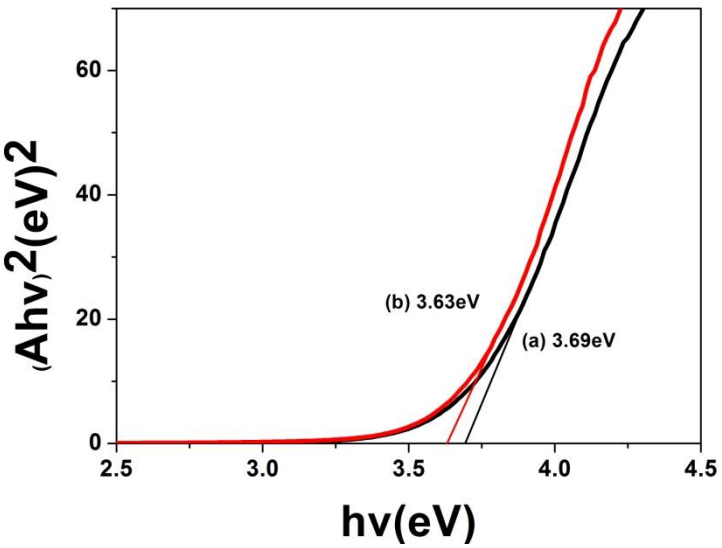


**Fig. S3 Plot of $(\alpha h\upsilon)^2$ versus hυ for as prepared (a) ceria nanoparticles and (b) ceria nanocubes.**

[S1] Z. Huo, C. Chen, X. Liu, D. Chu, H. Li, Q. Peng and Y. Li, *Chem. Commun.*, 2008,

3741-3743.

[S2] N. S. Arul, D. Mangalaraj, P. C. Chen, N. Ponpandian and C. Viswanathan, *Mater. Lett.*, 2011, **65**, 2635-2638.

[S3] T. Trindade, P. O'Brien and N. L. Pickett, *Chem. Mater.*, 2001, **13**, 3843-3858.