Electronic Supplementary Information for:

# Shape dependence of nanoceria on completely catalytic oxidation of o-xylene

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## Experimental Details for EPR measurement

Electron spin resonance (EPR) spectra in the X-band were recorded at -196 $^{o}$C with a CW spectrometer JES-FA200 (JEOL) at a microwave power of 1 Mw, a modulation frequency of 100 kHz, and central field of 325 mT. Before the measurement, the samples (100 mg) were pretreated in a flow of $N_2$ (30 ml/min) at 300 $^{o}$C for 120 min and cooled down to room temperature. After degassed in vacuo at 100 $^{o}$C for 15 min, the samples were exposed to pure $O_2$ for 10 min at room temperature (10 ml/min) and then cooled down to -196 $^{o}$C. After this adsorption, the samples were purged with $N_2$ for 10 min at room temperature (10 ml/min) in order to eliminate excess $O_2$ molecules not chemisorbed and remaining in the cell, which would cause dipolar broadening on the EPR signals of the generated surface species.

**Table S1** Catalytic oxidation of *o*-xylene over different catalysts

| Catalyst | $C_{o\text{-xylene}}$ (ppm) | WHSV ($ml \cdot h^{-1} \cdot g^{-1}$) | $T_{50}$ ($^{o}$C) | $T_{90}$ ($^{o}$C) | Reference |
|---|---|---|---|---|---|
| 1% Pd/AC | 1,500 | 30,000 | 175 | 188 | 1 |
| 1% Pd/γ-$Al_2O_3$ | 1,000 | 30,000 | 170 | 190 | 2 |
| 1%Pd/$Co_3O_4$(3D) | 150 | 60,000 | 193 | 204 | 3 |
| 0.2% Pd/HFAU | 1,700 | 39,000 | 225 | 235 | 4 |
| 1% Pt/C | 1,000 | 36,000 | 200 [a]<br>155 [b] | 210 [a]<br>177 [b] | 5 |
| 5% Cu/γ-$Al_2O_3$ | 800 | 7,200 | 290 | 330 | 6 |
| NaX zeolite | 210 | 3,2000 | 250 | — [c] | 7 |
| $CeO_2$ nanorods | 250 | 60,000 | 195 | 239 | This study |

[a] first run;

[b] second run;

[c] o-xylene conversion lower than 90% in whole temperature range.

**Table S2** Physicochemical properties of $CeO_2$ nanomaterials.

| sample | BET ($m^2/g$) | Average size (nm)[a] | Size (nm) [b] | Exposed planes |
|---|---|---|---|---|
| particles | 75.0 | 12.8 | 8-13 | (111) + (100) |
| cubes | 76.9 | 13.4 | 8-20 | (100) |
| rods | 88.2 | 11.6 | 40-300 (length)<br>8-13 (diameter) | (111) + (100) |

[a] Calculated using the Scherrer equation over the peak due to (111) plane;

[b] Estimated by TEM images.

**Table S3** XPS binding energies of individual peaks of the Ce 3d spectra for $CeO_2$ nanomaterials with different shapes.

| sample | $Ce^{4+}$ | | | | | | $Ce^{3+}$ | | | | $[Ce^{3+}]$ (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\nu$ | $\nu''$ | $\nu'''$ | $u$ | $u''$ | $u'''$ | $\nu_0$ | $\nu'$ | $u_0$ | $u'$ | |
| particles | 882.1 | 888.3 | 897.7 | 900.8 | 907.1 | 916.2 | 879.8 | 884.8 | 898.9 | 902.7 | 24.4 |
| cubes | 881.6 | 887.8 | 897.4 | 900.3 | 906.6 | 915.7 | 879.7 | 884.6 | 898.3 | 902.9 | 21.1 |
| rods | 881.4 | 887.8 | 897.1 | 900.2 | 906.4 | 915.6 | 879.5 | 884.4 | 898.0 | 902.6 | 23.5 |

The $Ce^{3+}$ concentration in $CeO_2$ nanomaterials was calculated by analysis of the integrated peak area, with the equation shown as following:

$$[Ce^{3+}] = \frac{A_{\upsilon 0} + A_{\upsilon'} + A_{u0} + A_{u'}}{A_{\upsilon 0} + A_{\upsilon'} + A_{u0} + A_{u'} + A_{\upsilon} + A_{\upsilon''} + A_{\upsilon'''} + A_{u} + A_{u''} + A_{u'''}}$$

where $A_i$ is the integrated area of peak “i”.

**Table S4** Integrated peak areas due to the desorption of different oxygen species during $O_2$-PTD experiment

| Sample | Chemisorbed $O_2$ | | Surface atomic oxygen | |
|---|---|---|---|---|
| | Peak max (°C) | Intensity (a.u.) | Peak max (°C) | Intensity (a.u.) |
| particles | 166 | 58.8 | 458 | 301.6 |
| cubes | 148 | 14.3 | | |
| rods | 134 | 88.9 | 488 | 37.1 |

**Table S5** Lattice strain of different crystal facets of nanoceria.

| Sample | Lattice strain (%) [a] | | |
|---|---|---|---|
| | (111) | (200) | (400) |
| particles | 1.0 | 0.8 | 0.5 |
| cubes | 0.3 | 0.8 | 0.3 |
| rods | 1.0 | 1.1 | 0.5 |

[a] Estimated by the single-line method from analysis of XRD line broadening using a pseudo-Voigt profile function.[8,9]

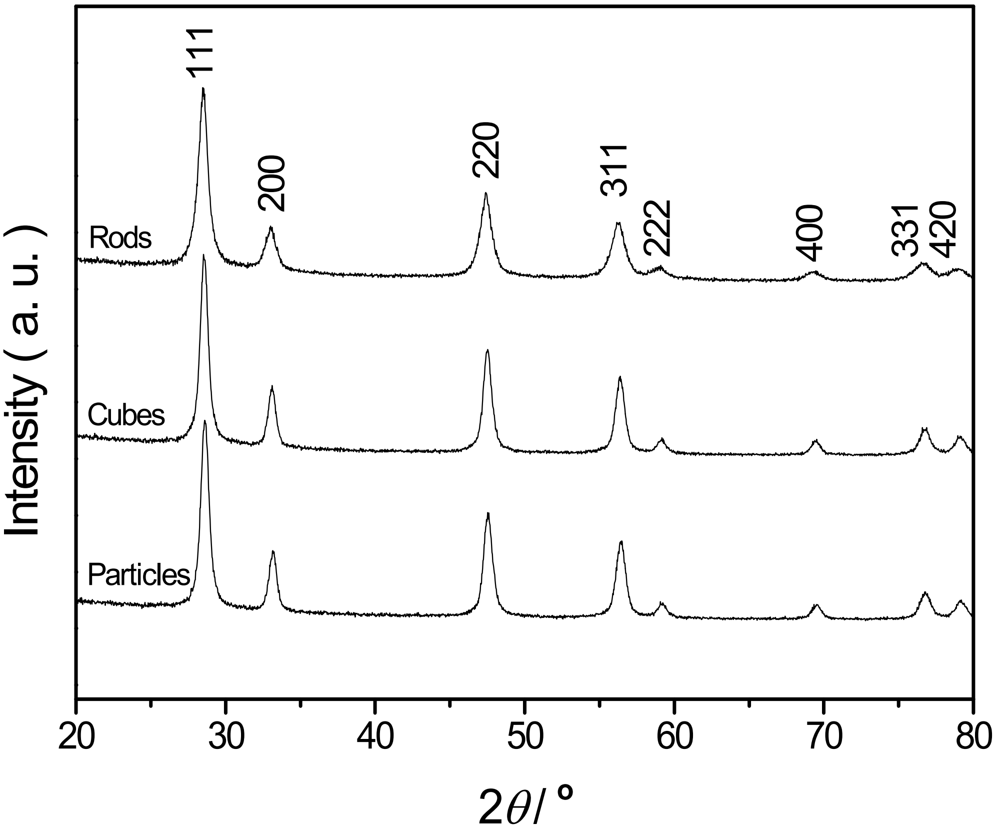

**Fig. S1** XRD patterns of the $CeO_2$ nanomaterials with different shapes.

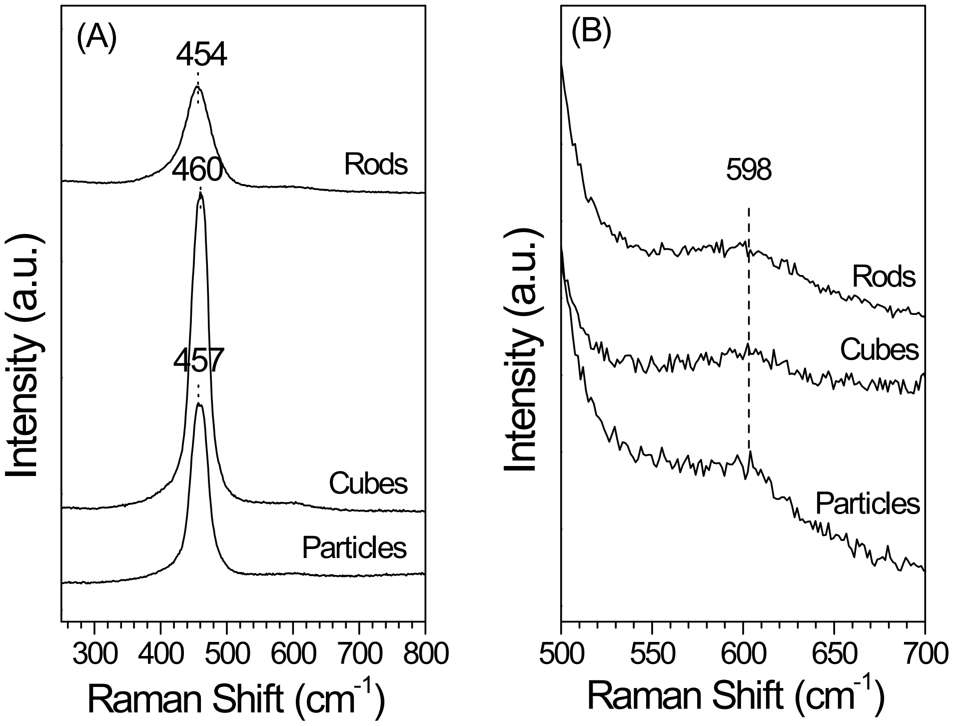

**Fig. S2** Raman shift of the $CeO_2$ nanomaterials with different shapes.

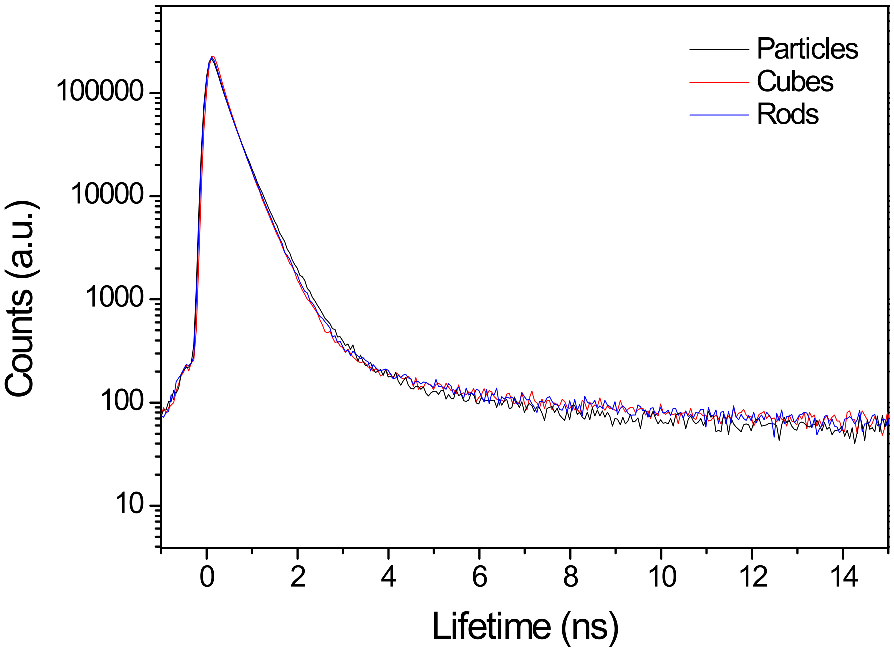

**Fig. S3** PAS spectra of $CeO_2$ with different shapes.

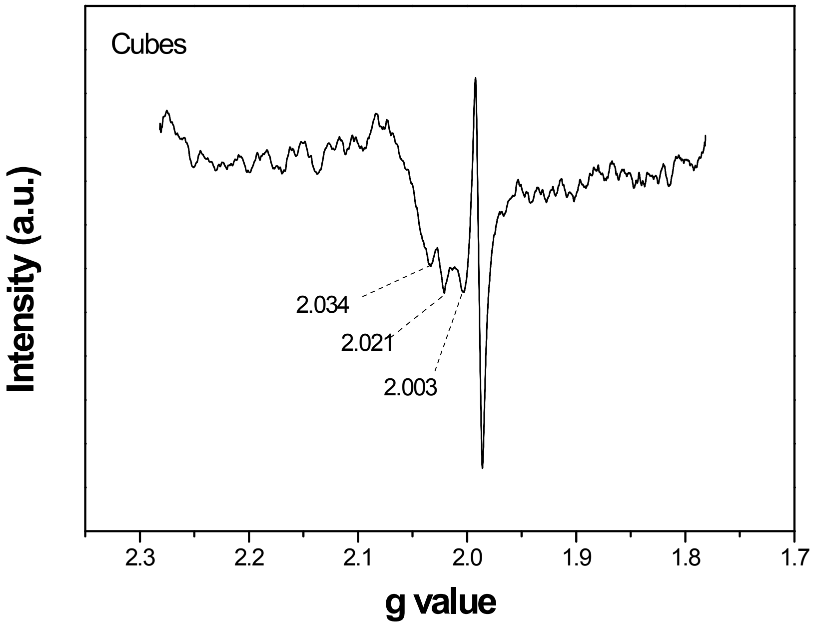

**Fig. S4** EPR profiles of $CeO_2$ nanocubes measured at -196 °C. Before the measurement, the samples was pretreated as follows: 1) pretreatment of 100 mg $CeO_2$ in 30 ml/min $N_2$ at 300°C for 120 min; 2) cooling down to room temperature and $O_2$ adsorption for 10min; 3) purging with $N_2$ for 10 min.

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