Supplementary Information

Design Strategies for Ceria Nanomorphologies:
Untangling Key Mechanistic Concepts

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Figure S1. Partial density of electronic states estimated for bulk \( \text{CeO}_2 \) and \( \text{CeO}_{1.5} \) using first-principles methods based on the hybrid DFT functional HSE06 (authors’ unpublished work)
Figure S2. TEM images of the nanorods prepared at high [Ce] and high [NaOH]: (a1) high-magnification top view of nanorod, showing elongated hexagonal cross section; (a2) low-magnification untilted top view of nanorods on nanocube; (a3) low-magnification 40° tilted view of Figure (a2), confirming that the particle with hexagonal cross section is a nanorod; (b1) high-magnification top view of nanorod, showing asymmetric hexagonal cross section; (b2) low-magnification untilted top view of nanorods; (b3) low-magnification 25° tilted view of Figure (b2), confirming that the particle with hexagonal cross section is a nanorod; (c1) high-magnification top view of nanorods, showing compressed hexagonal cross section; (c2) low-magnification untilted top view of nanorods; (c3) low-magnification 40° tilted view of Figure (b2), confirming that the particle with hexagonal cross section is a nanorod (authors’ unpublished work)
Figure S3. TEM images of: (a) (111) truncated nanocube; (b) enlargement of (111) truncation; (c) cuboid; (d) adjacent cuboids (authors’ unpublished work)
Figure S4. Oriented attachment of effectively (100) [but (200) as shown] truncated octahedra to form nanochains at 100°C, reprinted with permission from American Chemical Society.
Figure S5. TEM images of: (a) short nanorods (short time); (b) long nanorods (long time); (c) small nanocubes (short time); (d) large nanocubes (long time) (authors’ unpublished work)
Figure S6. XRD spectra of CeO$_{2-x}$ synthesised at different temperatures (precipitated and hydrothermal); peak broadening with decreasing temperature indicates decreasing crystallite size as well as increasing amorphisation; shifts to higher 2θ angles indicate lattice expansion from ionic radii increase from Ce$^{4+} \rightarrow$ Ce$^{3+}$ reduction, which occurs owing to charge compensation for the introduction of oxygen vacancies ($\text{V}^{\\circ}\\text{O}^{-}$) (authors’ unpublished work)
Figure S7. Laser Raman microspectra of CeO$_{2-x}$ obtained at different temperatures (precipitated and hydrothermal); blue shift of predominant peak at ~464 cm$^{-1}$ indicates increasing number of oxygen vacancies ($V^{\text{O}}_\text{••}$); peak at ~600 cm$^{-1}$ confirms presence of oxygen vacancies ($V^{\text{O}}_\text{••}$) (authors’ unpublished work)
Figure S8. Laser Raman microspectra of CeO$_{2-x}$ with different oxygen vacancy concentrations; two peaks at $\sim$580 cm$^{-1}$ and $\sim$1147 cm$^{-1}$ indicate presence of oxygen vacancies (authors’ unpublished work)
Figure S9. (a) XPS spectra of CeO$_{2-x}$ (shaded peaks for Ce$^{3+}$) for nanocubes, nanorods, and nanoctahedra; (b) XPS spectra of CeO$_{2-x}$, where role of defects in formation of trapping sites at binding energies $\sim$2 eV is highlighted; (c) PL spectra of CeO$_{2-x}$ and CeO$_{2}$-based heterojunction nanostructures, where defects are responsible for intensity variations; (d) EPR spectra of CeO$_{2-x}$ and CeO$_{2}$ nanotube (NT); (e) TEM image and EDS mapping of CeO$_{2-x}$ nanosheets decorated with NiO nanoparticles; (f,g) SAED patterns of CeO$_{2-x}$ with low (f) and high (g) oxygen vacancy concentrations, as indicated by comparison of diffuse rings.

(a) Adapted from authors’ work$^4$
(b) Adapted from authors’ work$^4$
(c) Adapted from authors’ work$^4$
(d) Authors’ unpublished work
(e) Adapted from authors’ work$^4$
(f) Adapted from authors’ work$^4$
(g) Adapted from authors’ work$^4$
Figure S10. STEM images and reconstructions of (111) facet of CeO$_2$ after vacuum annealing for: (a) 1 min; (b) 5 min;* reprinted with permission from American Association for the Advancement of Science.
Figure S11. (a) HAADF image of nanostructure; (b) EDS line scan across crystallite boundaries; (c) EDS line scan within crystallite; (d) EELS spectra at crystallite boundary (black dotted box d in (a)); (e) EELS spectra within crystallite (black dotted box e in (a)); (f,g) HAADF images showing Ce vacancies within CeO$_{2-x}$ crystallites (highlighted by yellow boxes); (h,i) KPFM analysis of CeO$_{2-x}$ nanosheet (voltage profile in inset of (i)) (adapted from authors’ work)

(a) Adapted from authors’ work
(b) Adapted from authors’ work
(c) Adapted from authors’ work
(d) Adapted from authors’ work
(e) Adapted from authors’ work
(f) Adapted from authors’ work
(g) Adapted from authors’ work
(h) Adapted from authors’ work
(i) Adapted from authors’ work

References


