Supplementary Material

Ligand-Engineered Hydrothermal Synthesis of {100}-Terminated Ceria Nanocrystals and Their Role as Supports in OER

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1. Synthesis of CeO_2 nanocrystals with various termination facets

CeO_2 NCs with {100} surface termination was synthesized following a previously reported protocol [1,2]. In a typical preparation, 7.5 mL of an aqueous cerium nitrate solution (16.7 mM, $Ce(NO_3)_3 \cdot 6H_2O$, Alfa Aesar, 99.5%) was mixed with 7.5 mL of toluene, 75 μL of tert-butyl amine (denoted as "TBA", from TCI, > 98%), and 0.19 mL of 2-octenoic acid (Millipore Sigma, 85%, predominantly *trans*) in a Teflon-lined autoclave. The autoclave was then placed in an oven preheated to 180 °C and maintained at that temperature for 24 hours, followed by natural cooling to room temperature. The organic upper layer was separated using a separatory funnel, and ethanol was added to the filtrate to precipitate the products, which were collected by centrifugation. Further purification was carried out by repeated washing and centrifugation using a hexane/ethanol (1:2 v/v). The final products, denoted as "CeO_2-OA", were dried, weighed, and stored in hexane for further use.

Mixed-facet CeO_2 NCs, designated as "CeO_2-OL-TA", exposing both {100} and {111} facets, were synthesized using the same protocol described above, with the exception that 75 μL of TBA + 0.19 mL of 2-octenoic acid was replaced by 750 μL of oleic acid and 150 μL of thioglycolic acid as the capping ligands. Further optimization of this synthesis was conducted by substituting oleic acid + thioglycolic with various organic acids, as listed in Table 1. In addition to the use of a single organic acid, combinations of capping ligands, specifically (1) stearic acid and thioglycolic acid, (2) stearic acid and oxalic acid, (3) oleic acid and oxalic acid, were used in a 1:1 molar ratio during the synthesis.

CeO_2 NCs without preferred facet termination were synthesized by precipitation in a strongly alkaline medium. In a typical procedure, 35 mL of an aqueous cerium nitrate solution (16.7 mM) was titrated with 10 mL of 350 mM ammonium hydroxide (NH_4OH, J. T. Baker, 91%). The resulting mixture was transferred to a Teflon-lined autoclave and subjected to the same heating, washing, and collection steps described above. The products are referred to as "CeO_2-NC".

Each synthesis was repeated several times (> two times) by using multiple autoclaves to ensure sufficient product quantity for further analysis and characterization.

2. Catalyst manipulation

To evaluate the effectiveness of various CeO_2 NCs as supports capable of strongly interacting with catalyst NiO_x for the OER, NiO_x NCs were synthesized and deposited onto CeO_2 NCs to form the catalyst–support composite. The composite was then processed into a catalyst ink and subsequently applied onto a pre-cleaned glassy carbon (GC) electrode. The composite formation, ink preparation, and electrode fabrication procedures are described separately below.

Composite formation:

A total of 212.0 mg of $Ni(NO_3)_2 \cdot 6H_2O$ (Millipore Sigma, 99.99%) was added to 126.5 mg of CeO_2-OA and dispersed in 20.0 mL of deionized water to form a uniform suspension. The mixture was then titrated with 10.0 mL of a 220.4 mM NH_4OH solution in a conical flask under constant stirring. The resulting light-green suspension was allowed to stand for several minutes before centrifugation at 9,000 rpm to separate the precipitate from the supernatant. The collected precipitate, consisting of $Ni(OH)_2$ and CeO_2-OA, was dried overnight and subsequently annealed at 500 °C for 4 h in a tube furnace. During calcination, $Ni(OH)_2$ deposited on CeO_2-OA was converted to NiO_x *via* dehydrogenation. The final product is referred to as "NiO_x/CeO_2-OA".

In parallel, 345.0 mg of $Ce(NO_3)_3 \cdot 6H_2O$ and 232.0 mg of $Ni(NO_3)_2 \cdot 6H_2O$ were dissolved in 60.0 mL of deionized water, after which 11.0 mL of a 654.5 mM NH_4OH solution was added dropwise to titrate the mixture. The resulting homogeneous suspension was left to stand overnight and then centrifuged to separate the precipitate from the supernatant. The precipitate was dried at room temperature for several hours and subsequently calcined at 500 °C for 4 h. The resulting mixed oxide product was designated as "NiO_x–CeO_2-NC".

Ink preparation:

Before preparing the catalyst ink, the oxide samples were first loaded onto carbon to achieve a carbon weight ratio of 40%. Specifically, a predetermined amount of carbon (Ketjenblack EC600JD, Lion Specialty Chemicals Co., Ltd.) was dispersed in ethanol, while each oxide sample, CeO_2-NC, NiO_x/CeO_2-OA, or NiO_x–CeO_2-NC, was dispersed in hexane and sonicated separately for 30 min. The two suspensions were then gradually combined and sonicated for an additional 2 h, followed by centrifugation to remove the supernatant. The resulting precipitates were dried overnight and designated as CeO_2-NC/C, NiO_x/CeO_2-OA/C, or NiO_x–CeO_2-NC/C.

Catalyst ink was subsequently prepared by mixing 5.0 mg of the carbon-supported catalyst with 1.0 mL of acetone and 20.0 μL of 5% Nafion® solution [3].

Electrode fabrication:

For electrochemical measurements, a 4 M KCl–saturated Ag/AgCl electrode and a graphite rod were used as the reference and counter electrodes, respectively. A total of 30.0 μL of the catalyst ink was drop-cast onto a clean GC rotating disk electrode (RDE, 5 mm diameter; Pine Research Instrumentation), and allowed to dry at room temperature, which then served as the working electrode.

3. Characterization methods

X-ray diffraction (XRD) patterns were collected using a PANalytical X'pert diffractometer equipped with a Cu $K_{\alpha 1}$ radiation source. Transmission electron microscopy (TEM) samples were prepared by drop-casting a small volume of the CeO_2 hexane suspension onto copper TEM grids, followed by cleaning with absolute ethanol. TEM images were acquired using a Hitachi H-8100, a Thermo Fisher Talos 200X, and a JEOL 2100F field-emission microscope. Electrochemical measurements were carried out at room temperature on a Gamry 1000E workstation in a three-electrode configuration. Potentials were converted to the reversible hydrogen electrode (RHE) scale using $E_{RHE} = E_{Ag/AgCl} + 1.0258$ (V). The OER overpotential was calculated as $E_{OER} = E_{RHE} - 1.23$ (V).

4. Supplemental figures

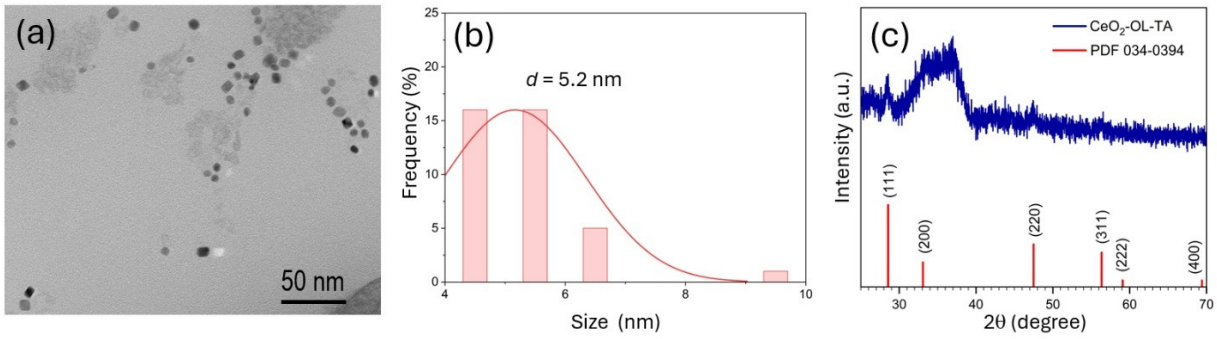

Figure S1. TEM image, particle size distribution, and XRD pattern of CeO_2 truncated nano-octahedra (CeO_2-OL-TA) with mixed {100}/{111} facets. (a) Low-magnification TEM image; (b) particle size distribution profile derived from (a); and (c) XRD pattern. The vertical bars at the bottom of (c) represent standard diffraction peaks for CeO_2 based on ICDD PDF card 34-0394.

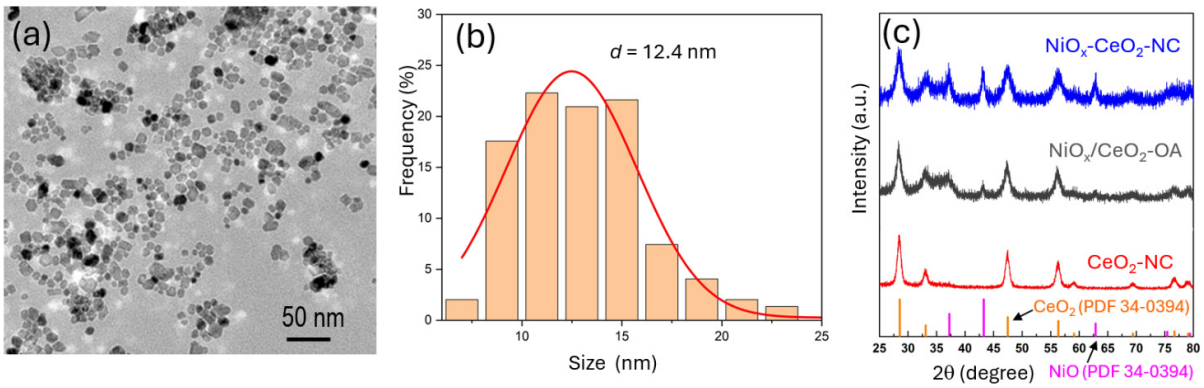

Figure S2. TEM image, particle size distribution, and XRD patterns of CeO_2-based NCs. (a) Low-magnification TEM image of CeO_2-NC; (b) particle size distribution of CeO_2-NC derived from (a); (c) XRD patterns of NiO_x–CeO_2-NC, NiO_x/CeO_2-OA, and CeO_2-NC. Vertical lines at the bottom of (c) indicate standard diffraction peaks for CeO_2 (ICDD PDF# 34-0394) and NiO (ICDD PDF# 47-1049).

5. References

[1] C. Li, Y. Luan, B. Zhao, A. Kumbhar, F. Zhang, and J. Fang, *MRS Adv.* **5,** 523-529 (2020).

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[3] P. Bharathan, C. Li, B. Zhao, A. Dennett, L. Zhang, and J. Fang, *J. Mater. Chem. A* **13,** 38290-38300 (2025).