Electronic Supplementary Information

Growth of CeO_2 nanocubes showing size-dependent optical and oxygen evolution reaction behaviors

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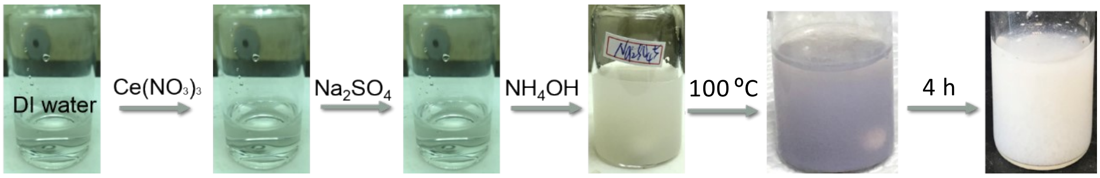

Fig. S1 Photographs taken in the synthesis of CeO_2 nanocubes.

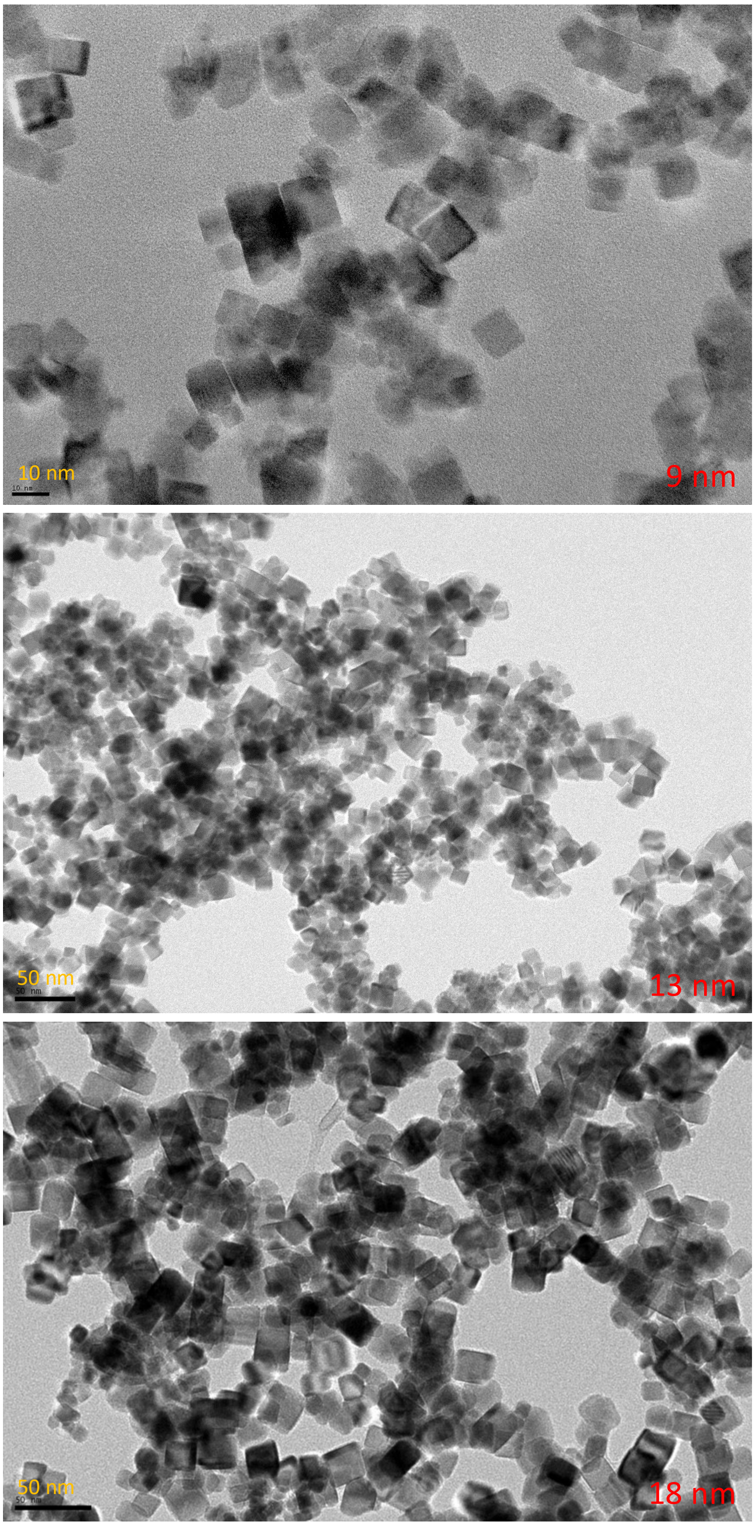

Fig. S2 Large-area TEM images of different-sized CeO_2 nanocubes.

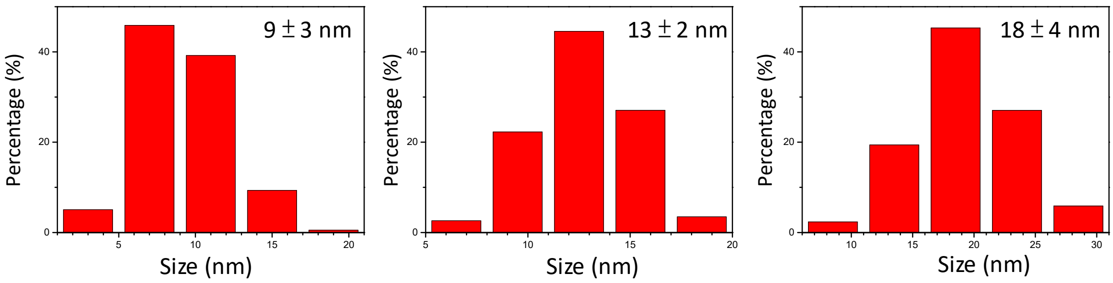

Fig. S3 Size distribution histograms of the synthesized CeO_2 nanocubes. Average sizes and their standard deviations are provided.

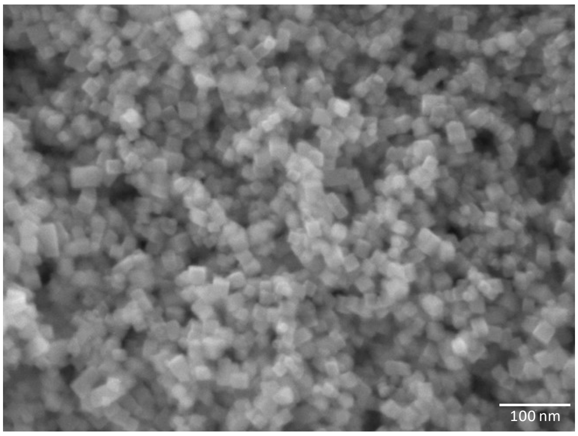

Fig. S4 SEM image of the synthesized 18 nm CeO_2 nanocubes.

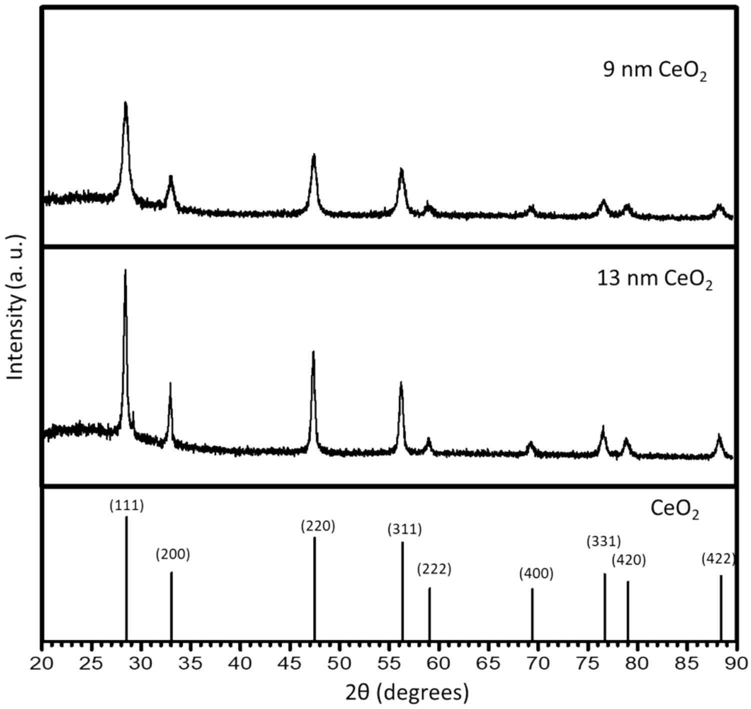

Fig. S5 XRD patterns of the 9 and 13 nm CeO_2 nanocubes and the standard XRD pattern of CeO_2. The 9 nm sample shows peak broadening due to the small particle sizes.

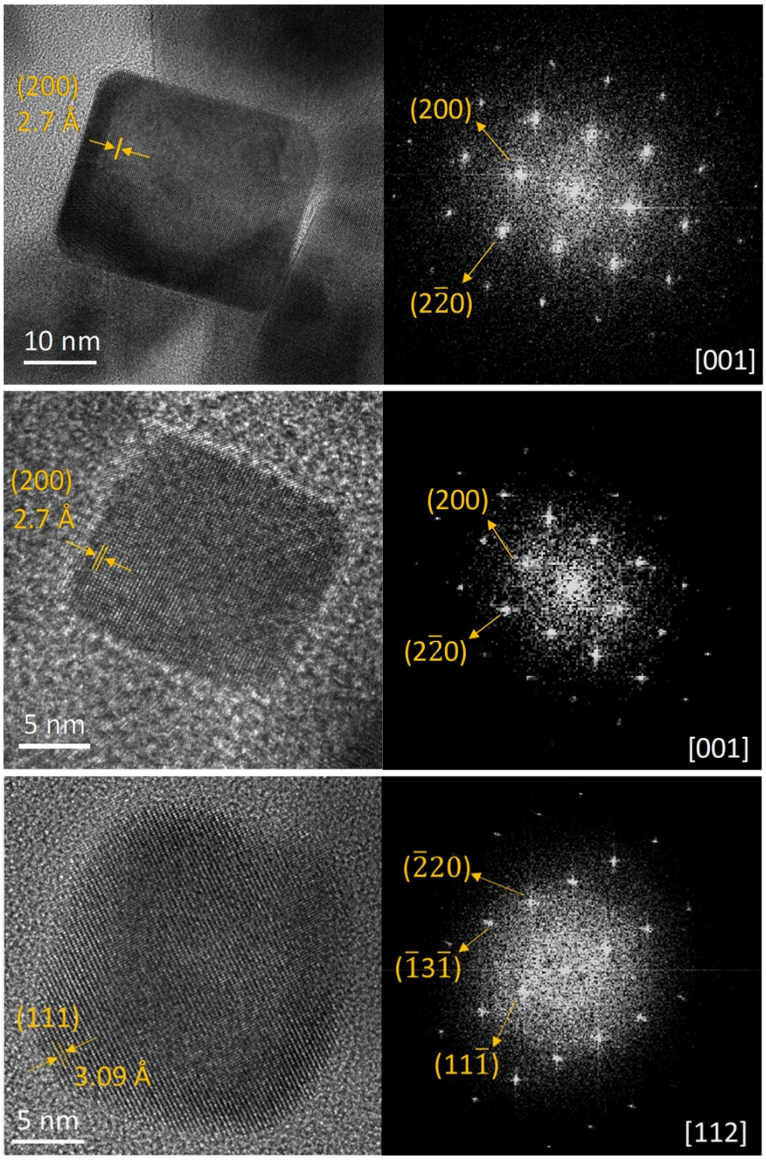

Fig. S6 Additional HR-TEM images of CeO_2 nanocubes from the 18 nm sample and the FFT patterns. Viewing directions are indicated.

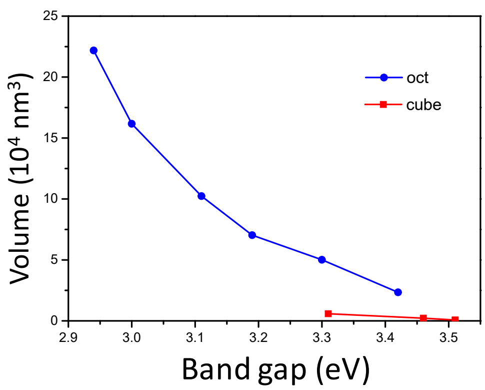

Fig. S7 Plot of particle volumes vs. band gaps of size-tunable CeO_2 octahedra and nanocubes.

$$E_c = E_{fb} + \frac{k_B T}{e} ln \frac{N_D}{N_C}$$

$$N_C = \frac{2(2\pi m^* k_B T)^{3/2}}{h^3}$$

E_{fb} : flat-band potential
k_B : Boltzmann's constant
T : temperature
e : electron charge (1.602×10^{-19} C)
N_C : effective density of states in the conduction band
N_D : donor concentration (electron density for n-type semiconductor such as CeO_2)
m^*: effective mass of the electrons ($0.4 \times 9.109 \times 10^{-31}$ kg)
h : Planck's constant

$$\frac{1}{C^2} = \frac{2}{e\varepsilon\varepsilon_o N_D} \left(E - E_{fb} - \frac{k_B T}{e}\right)$$

(Mott–Schottky equation)

E : applied potential
C : space charge capacitance of the semiconductor
ε : the dielectric constant (24.5 for CeO_2)
ε_o : permittivity of the vacuum (8.85×10^{-14} F cm^{-1})

Fig. S8 Mott–Schottky equation and other equations used to determine the conduction band energy E_c of CeO_2 nanocubes.

Table S1 (upper) Calculations to determine E_c for different CeO_2 nanocube samples. (lower) Calculations to determine E_v for different CeO_2 nanocube samples. The solution pH is 6.16, which is used to obtain E_c in RHE scale.

		$N_D = \frac{2}{e\varepsilon\varepsilon_o slope}$					
	E_{fb} (eV)	Slope (F^{-2} cm^4 V^{-1})	N_D (cm^{-3})	N_C	ln(N_D/N_C)	$k_B T$/e*ln(N_D/N_C)	E_c (vs. Ag/AgCl) (eV)
9 nm	–0.570	1.66×10^{10}	3.47×10^{20}	6.27×10^{24}	–9.80	–0.251	–0.821
13 nm	–0.630	2.60×10^{10}	2.21×10^{20}		–10.25	–0.263	–0.893
18 nm	–0.669	1.30×10^{10}	4.43×10^{20}		–9.56	–0.245	–0.914

	E (V vs. RHE) = E (V vs. Ag/AgCl) + 0.21 + (0.0591 × 6.16)			
	E_c (vs. Ag/AgCl) (eV)	E_c (vs. RHE) (eV)	Band gap (eV)	E_v (vs. RHE) (eV)
9 nm	–0.821	–0.25	3.57	3.32
13 nm	–0.893	–0.32	3.48	3.16
18 nm	–0.914	–0.34	3.45	3.11

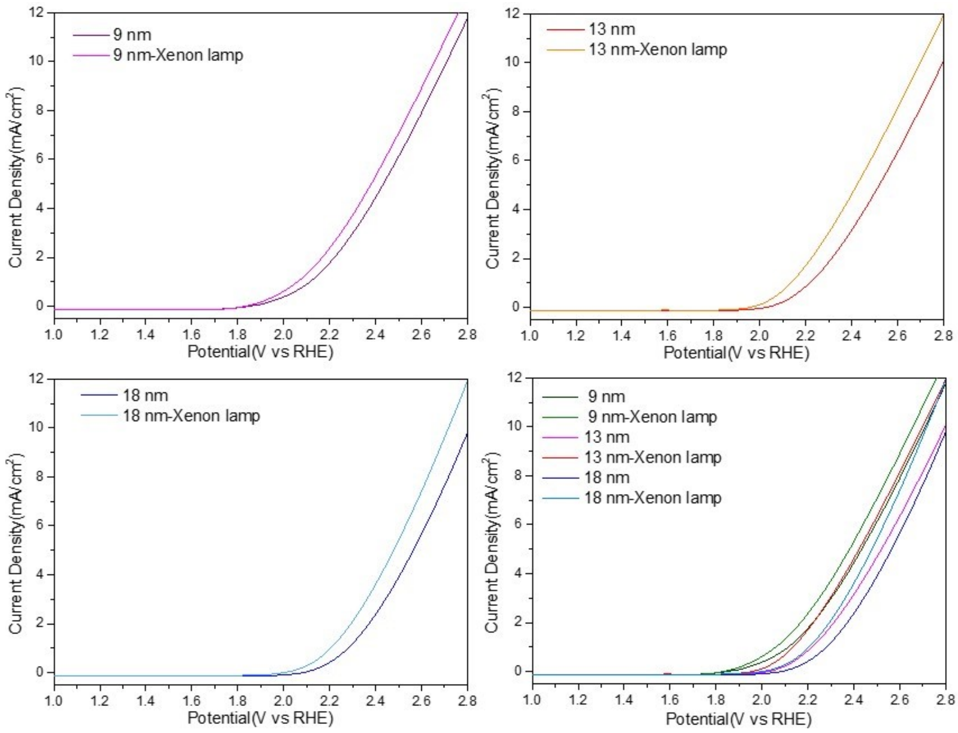

Fig. S9 Linear sweep voltammetry curves of size-tunable CeO_2 nanocubes before and upon light illumination.

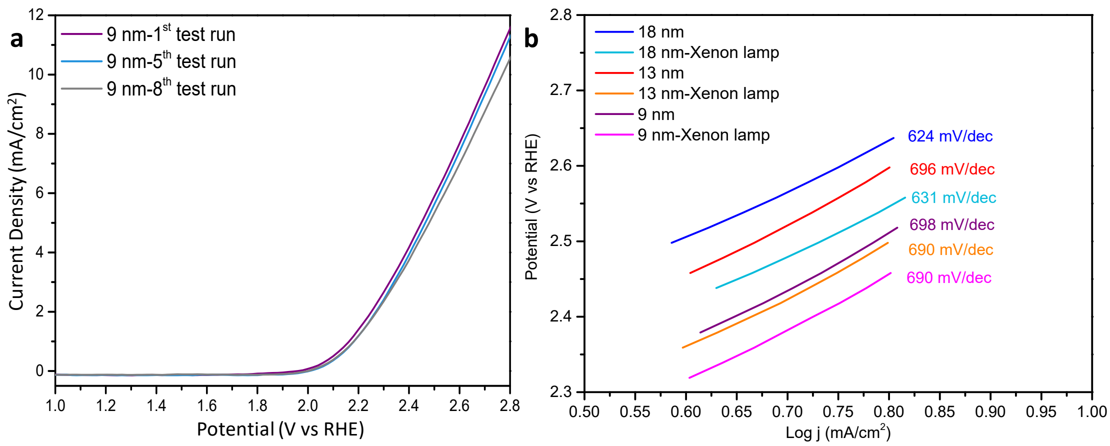

Fig. S10 (a) Reproducibility test of the measured LSV curves for the 9 nm CeO_2 sample. (b) Tafel plot for the different CeO_2 samples with and without light illumination.