Electronic Supplementary Information

Morphological evolution of cadmium oxide crystals showing color changes and facet-dependent conductivity behavior

Gautam Kumar,[a] Chong-Rui Chen,[a] Bo-Hao Chen,[ab] Jing-Wei Chen,[a] and Michael H. Huang*[a]

[a]*Department of Chemistry and Frontier Research Center on Fundamental and Applied Sciences of Matters, National Tsing Hua University, Hsinchu 300044, Taiwan*

E-mail: hyhuang@mx.nthu.edu.tw

[b]*National Synchrotron Radiation Research Center, Hsinchu 300092, Taiwan*

Gibbs free energy change calculation

$Cd(CH_3COO)_2 + 2OH^- \rightarrow Cd(OH)_2 + 2CH_3COO^-$ (1)

$Cd(OH)_2 \rightarrow CdO + H_2O$ (2)

Sum: $Cd(CH_3COO)_2 + 2OH^- \rightarrow CdO + 2CH_3COO^- + H_2O$ (3)

$Q = [CH_3COO^-]^2/[Cd(CH_3COO)_2][OH^-]^2$

For CdO stellated octahedra, $[CH_3COO^-] = 0.04$ M $[Cd(CH_3COO)_2] = 0.02$ M $[OH^-] = 0.04$ M $Q = 50.00$ M^{-1}

For CdO octahedra, $[CH_3COO^-] = 0.14$ M $[Cd(CH_3COO)_2] = 0.07$ M $[OH^-] = 0.14$ M $Q = 14.29$ M^{-1}

For CdO truncated octahedra, $[CH_3COO^-] = 0.18$ M $[Cd(CH_3COO)_2] = 0.09$ M $[OH^-] = 0.18$ M $Q = 11.11$ M^{-1}

For $Cd(OH)_2$ hexagonal plates, $[CH_3COO^-] = 0.24$ M $[Cd(CH_3COO)_2] = 0.12$ M $[OH^-] = 0.24$ M $Q = 8.33$ M^{-1}

$\Delta G = \Delta G^o + RT\ln Q$

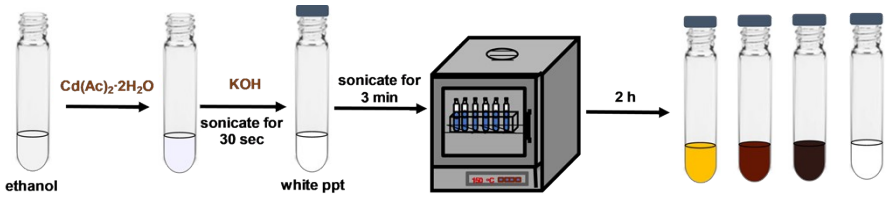
$\Delta G^o = -228.4$ kJ/mol for CdO $T = 423$ K $R = 8.31451$ J/K mol

$\Delta G = -214.6$ kJ/mol for stellated octahedra

$\Delta G = -219.0$ kJ/mol for octahedra

$\Delta G = -219.9$ kJ/mol for truncated octahedra

$\Delta G = -220.9$ kJ/mol for $Cd(OH)_2$ hexagonal plates



Shape	Ethanol (mL)	1 M $Cd(CH_3COO)_2·2H_2O$ (mL)	1 M KOH (mL)	Total volume (mL)	Reaction temperature (°C)	Reaction time (h)
CdO stellated octahedra	4.7	0.1	0.2	5	150	2
Shape	**Ethanol (mL)**	**0.5 M $Cd(CH_3COO)_2·2H_2O$ (mL)**	**0.5 M KOH (mL)**	**Total volume (mL)**	**Reaction Temperature (°C)**	**Reaction time (h)**
CdO octahedra	2.9	0.7	1.4	5	150	2
CdO truncated octahedra	2.3	0.9	1.8			
$Cd(OH)_2$ hexagonal plates	1.4	1.2	2.4			

Fig. S1 Reaction procedure and the reagent amounts used to synthesize CdO crystals and $Cd(OH)_2$ plates.

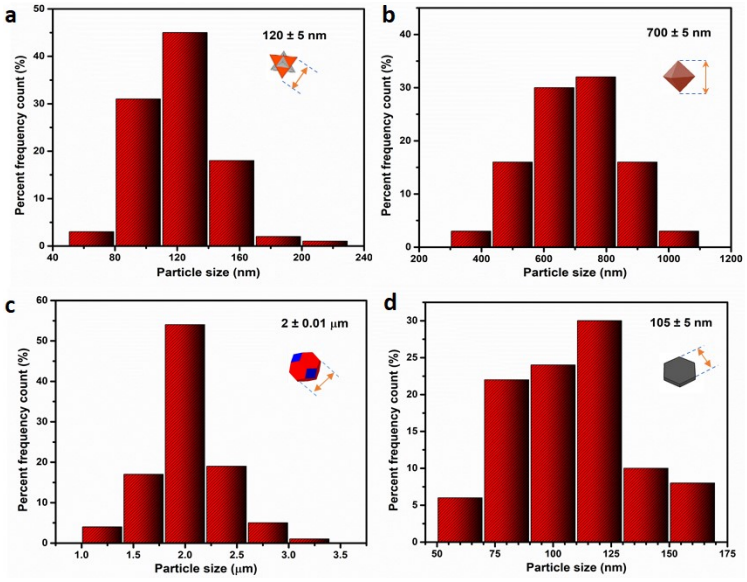


Fig. S2 Size distribution histograms of the synthesized CdO (a) stellated octahedra, (b) octahedra, (c) truncated octahedra, and (d) $Cd(OH)_2$ hexagonal plates.

Table S1 Crystallographic data of $Cd(OH)_2$.

Formula	H_2 Cd O_2
Molecular weight (g/mol)	146.42
Radiation source	Synchrotron NSRRC TPS19A
Wavelength (Å)	0.77489
Crystal system	Trigonal
Space group	*P* -3 m 1 (164)
Z	1
a (Å)	3.49615(8)
b (Å)	3.49615(8)
c (Å)	4.71465(11)
α	90.0
β	90.0
γ	120.0
Volume ($Å^3$)	49.9068(19)
Temperature (K)	Room temperature
2θ range (°)	7.0–69.75
d resolution (Å)	0.682
Total reflection number	85
limiting indices	$0 \leq h \leq 4$; $0 \leq k \leq 2$; $-6 \leq l \leq 6$
Rietveld Refinement program	GSAS II[1]
Rp	1.62%
wRp	2.14%
RF^2	3.68%

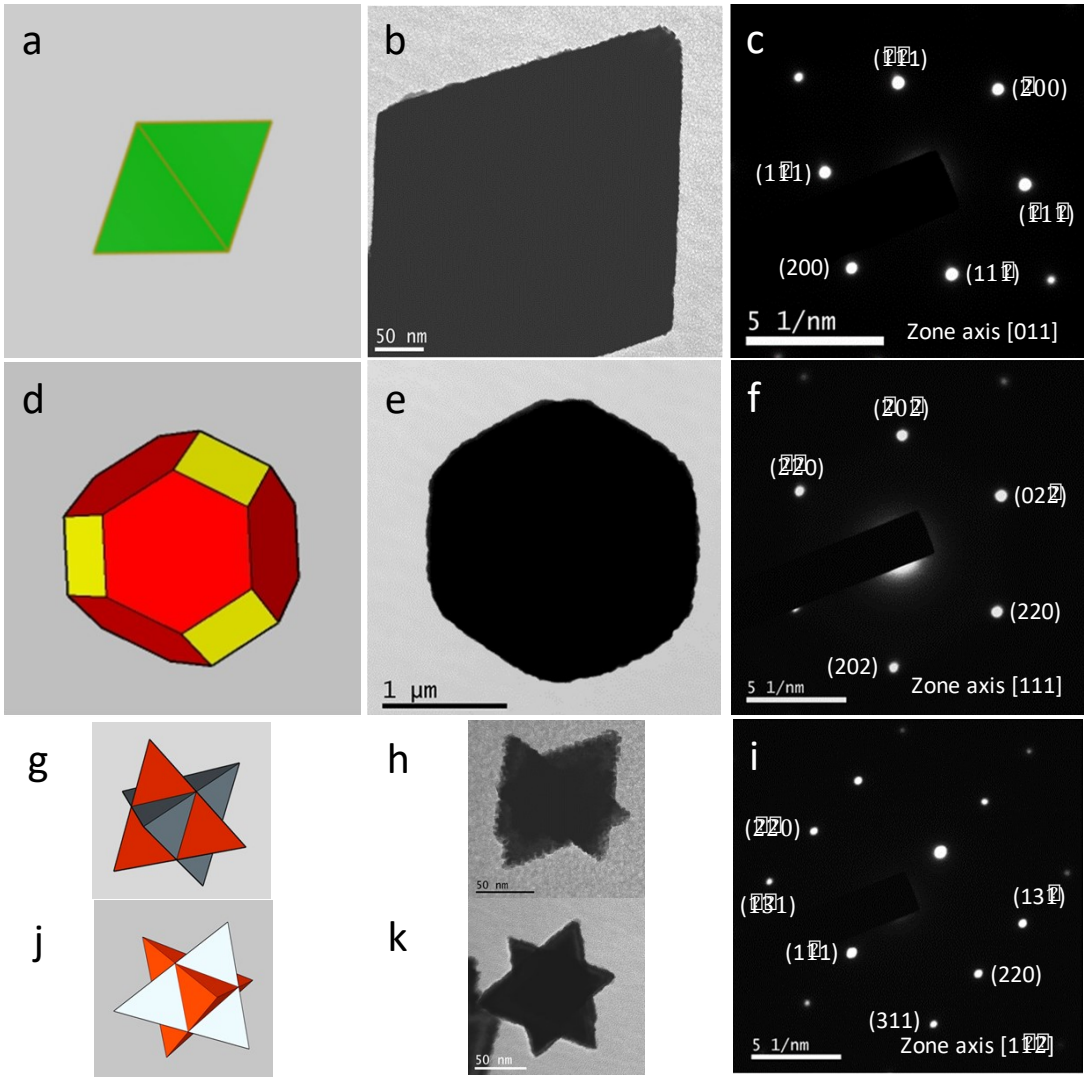


Fig. S3 TEM images, the corresponding SAED patterns, and models showing the particle orientations of CdO (a–c) octahedron, (d–f) truncated octahedron, and (g–i) stellated octahedron. Extended electron beam irradiation causes the stellated octahedron surfaces to become roughened. (j, k) Model and TEM image of another stellated octahedron.

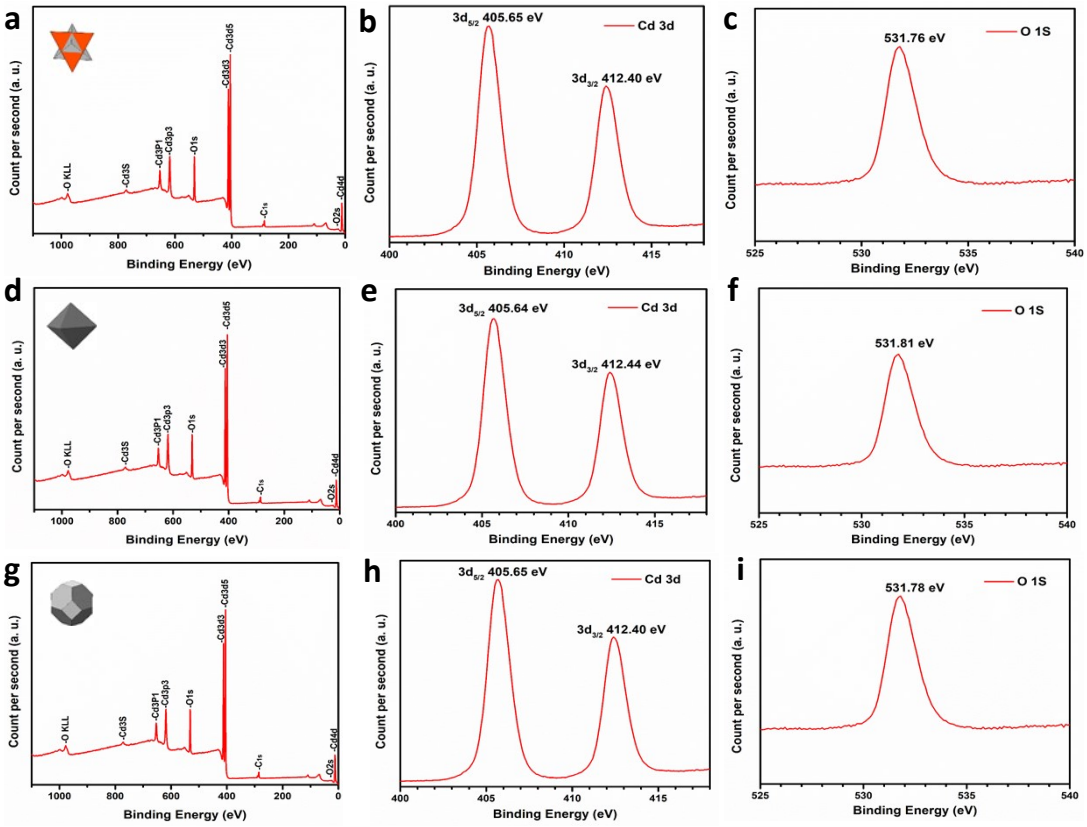


Fig. S4 (a–c) Full XPS spectrum of the CdO stellated octahedra and regions of Cd 3d and O 1s peaks. (d–f) Full XPS spectrum of CdO octahedra and regions of Cd 3d and O 1s peaks. (g–i) Full XPS spectrum of the CdO truncated octahedra and regions of Cd 3d and O 1s peaks.

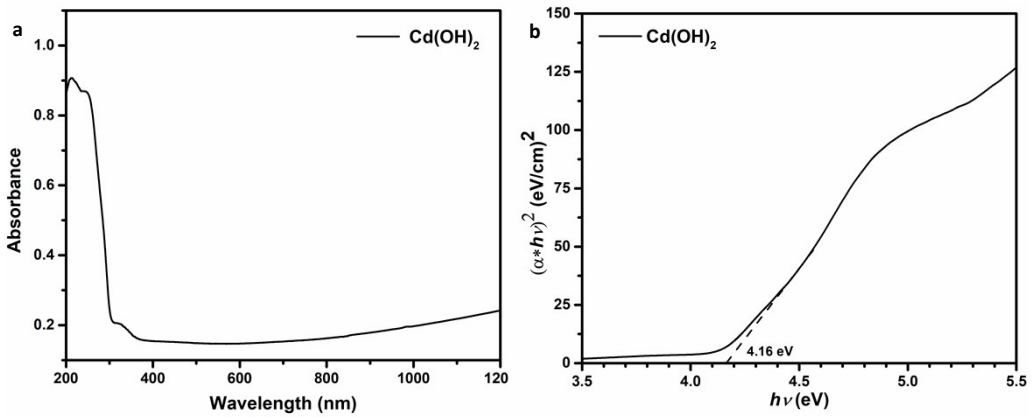


Fig. S5 (a) Diffuse reflectance spectrum of $Cd(OH)_2$ hexagonal plates and (b) the corresponding Tauc plot.

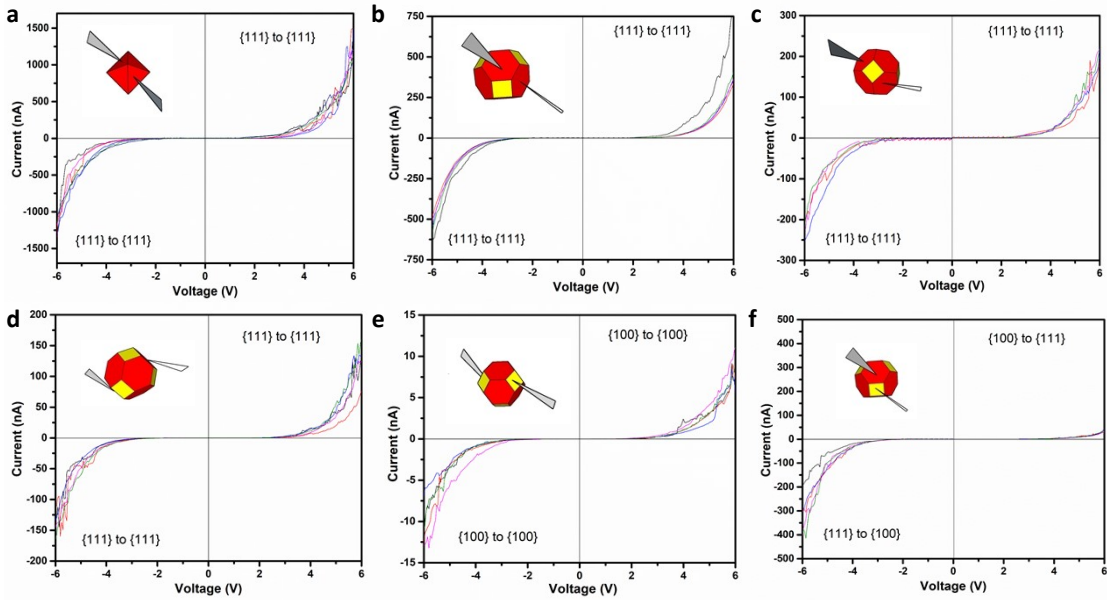


Fig. S6 Measured *I–V* curves with tungsten probes contacting (a) a CdO octahedron, (b) adjacent {111} faces of a CdO truncated octahedron, (c) proximal {111} faces of a truncated octahedron, (d) opposite {111} faces of a truncated octahedron, (e) opposite {100} faces of a truncated octahedron, and (f) {111} and {100} faces of a truncated octahedron.

Reference

1 B. H. Toby, R. B. Von Dreele, GSAS-II: the genesis of a modern open-source all purpose crystallography software package. *J. Appl. Crystallogr.,* 2013, **46**, 544–549.