## From channeled to hollow CoO octahedrons: Controlled growth,

## structural evolution and energetic applications

Ming Cheng<sup>1, #</sup>, Sibin Duan<sup>2, #</sup>, Hongsheng Fan<sup>1</sup> and Rongming Wang<sup>2, \*</sup>

<sup>1</sup> Department of Physics, Beihang University, Beijing 100191, P. R. China

<sup>2</sup> School of Mathematics and Physics, University of Science and Technology Beijing, Beijing 100083, P. R. China

E-mail: rmwang@ustb.edu.cn

<sup>#</sup>These authors contribute equally.



Fig. S1 SEM image of an individual hollow CoO nanocrystal (NC), which shows an octahedral shape.

 Table S1
 The BET surface area of the three NCs

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Sample	Hollow CoO NCs	Channeled CoO NCs	Hollow CoO NCs		
BET (m²/g)	15.57	44.31	18.99		



**Fig. S2** (a-h) HRTEM images of the intermediates during the formation of hollow CoO NCs obtained at different times.



**Fig. S3** (a) and (b) are the TEM images of the channeled CoO NCs obtained at 240 °C. (d) and (e) are the TEM images of the sample evolved from the channeled CoO NCs after heated to 280 °C in solution. (c) and (f) are the corresponding FFT images of the NC in (b) and (e), repectively.



**Fig. S4** (a) TEM image of the nanoflowers obtained at a rapidly heating rate, (b) TEM image of the triangular plates obtained at a slowly heating rate.



**Fig. S5** TEM images of the channeled NCs obtained with adding different amount of TPP at 240 °C.



**Fig. S6** TEM images of the hollow product obtained with adding different amount of TPP at 280 °C.



**Fig. S7** CV curves of the hollow (a), channeled (c) and solid (e) CoO NCs electrodes at different scan rates. Galvanostatic charge-discharge curves of the hollow (b), channeled (d) and solid (f) CoO NCs electrodes at various current densities.



**Fig. S8** (a) Specific capacitance of the three NCs at different scan rates. (b) Specific capacitance of the three NCs at various current densities.



**Fig. S9** Measurement of the electrochemical double-layer capacitance ( $C_{dl}$ ). Cyclic voltammogram (CV) curves of electrodes consisting of the hollow CoO (a), channeled CoO (b) and solid CoO (c) in the double layer region at scan rates of 1, 2, 3, 4 and 5 mV/s in 1.0 M KOH aqueous electrolyte.



**Fig. S10** OER stability test of channeled CoO (a) and solid CoO (b) catalysts dispersed on glassy carbon electrode in 1M KOH electrolyte. Cycles were swept between 1.25 V and 1.65 V at 0.2 V/s. The anodic sweeps showed in the figures were measured from 1.25 V to 1.65 V at 0.005 V/s with IR compensation.



**Fig. S11** I-t curve of hollow and channeled CoO NCs at a constant overpotential of 0.39 V (1.62 V vs. RHE) measured in 1.0 M KOH solution.



**Fig. S12** (a) The curves of hydrogen generation volume as a function of time for the three NCs at 303K. (b), (c) and (d) are the hydrogen generation volume for the hollow, channeled and solid CoO NCs at different temperatures, repectively. (e) The hydrogen generation rates of the solid CoO NCs at different temperatures.

Temperature ——	Maximum hydrogen generation rates (mL min <sup><math>-1</math></sup> g <sup><math>-1</math></sup> )			
	Hollow CoO NCs	Channeled CoO NCs	Solid CoO NCs	
293 K	1449	1870	658	
303 K	3100	3450	1480	
313 K	5569	6260	3920	
323 K	10797	12594	9340	

## Table S2 Maximum $H_2$ Generation Rates of the three samples