Supporting Information

In situ Formation of Cobalt Oxide Nanocubanes as Efficient Oxygen Evolution Catalysts

Gregory S. Hutchings,[1,‡] Yan Zhang,[1,‡] Jian Li,[2] Bryan T. Yonemoto,[1] Xinggui Zhou[2], Kake Zhu,[2,*] and Feng Jiao[1,*]

[1] Center for Catalytic Science & Technology (CCST), Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, USA.

[2] UNILAB, State Key Lab of Chemical Engineering, School of Chemical Engineering, East China University of Science and Technology, 130 Meilong road, Shanghai 200237, P. R. China.

*Correspondence to: jiao@udel.edu and kakezhu@ecust.edu.cn.

‡These authors contributed equally to this work.

Table of Contents

Crystal structure simulation

To determine the unit cell the peak positions were manually fit using the CMPR program[1] by starting from the unit cell and space group ($R\bar{3}m$) for presumably isostructural compounds reported by Le Bihan et al. and Yu et al.[2,3] After choosing the unit cell parameters we confirmed our cell thru a Le Bail fit of an analogous structure with a similar space group ($LiCoO_2$) using EXPGUI and GSAS.[4,5]

Table S1. Fitted unit cell parameters of as-made $Co(OH)(OCH_3)$ material.

Space Group	*a*	*b*	*c*	*α*	*β*	*γ*
$R\bar{3}m$	3.165 Å	3.165 Å	23.5 Å	90	90	120

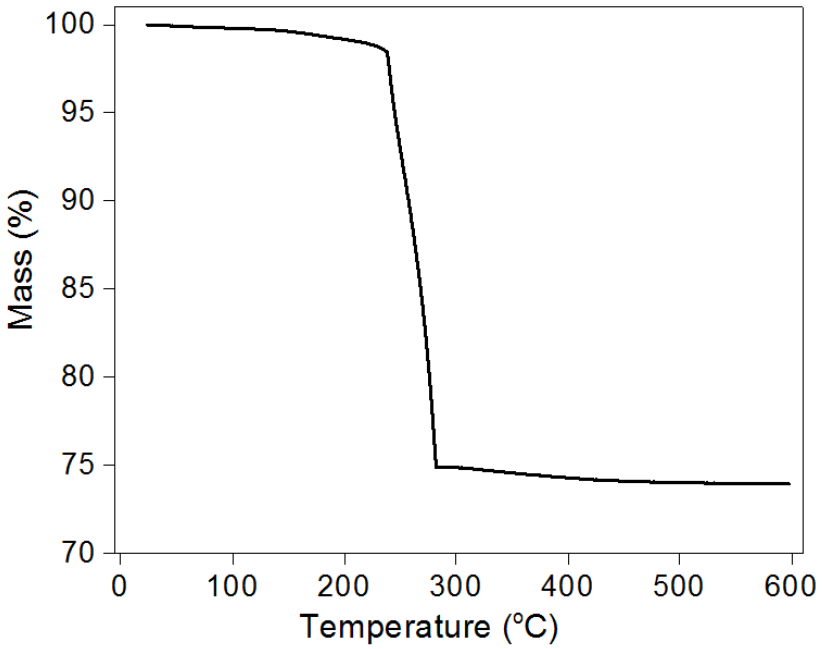

Figure S1. TGA result for as-made $Co(OH)(OCH_3)$. The end product was found to be Co_3O_4 and ~25% weight loss was observed during the heat treatment in air to 600°C, which is consistent with the expected weight loss of $Co(OH)(OCH_3)$ to Co_3O_4 conversion.

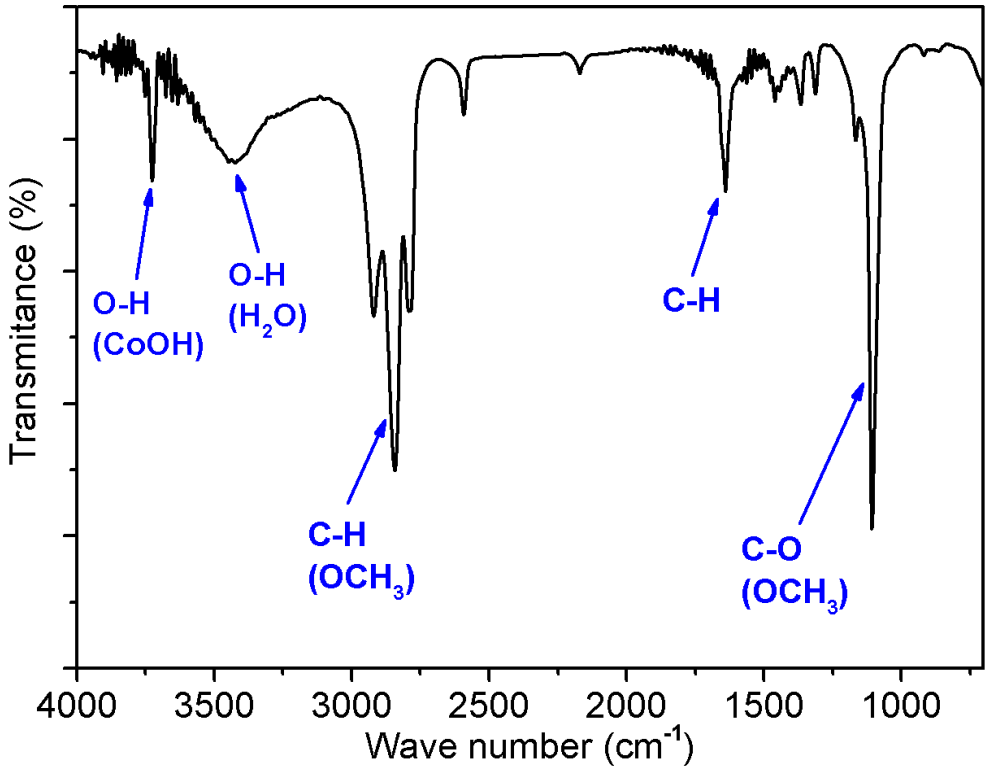

Figure S2. FTIR spectrum for as-made $Co(OH)(OCH_3)$. The spectrum agrees with previously published spectra for $Ni_xMg_{1-x}(OH)OCH_3$.[2,6]

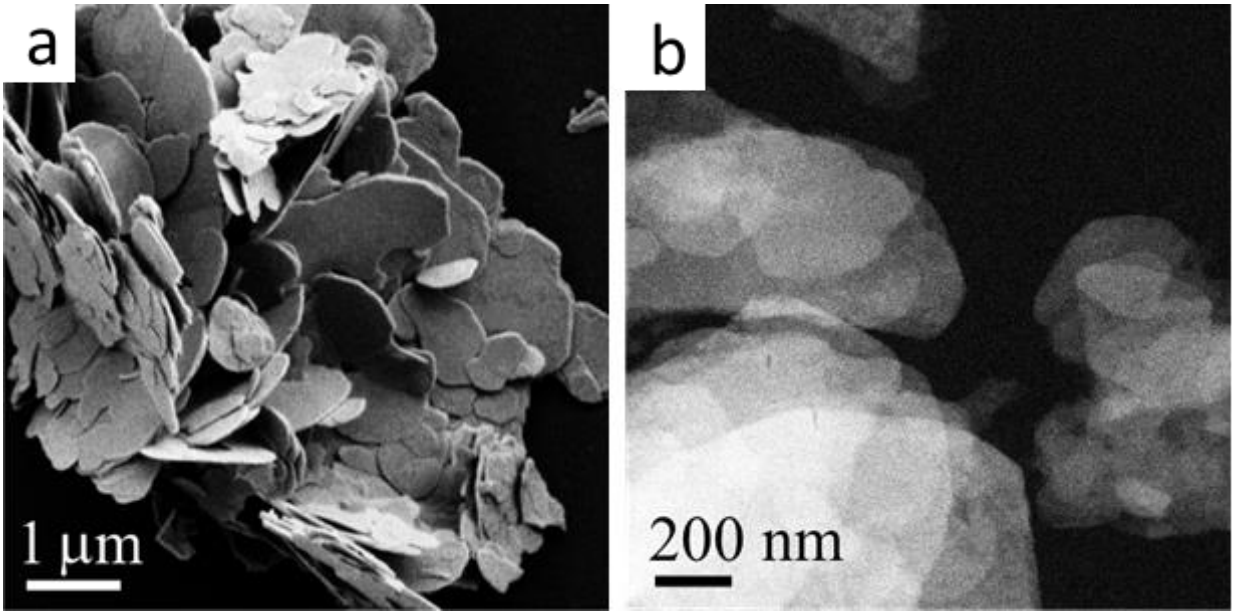

Figure S3. (a) SEM and (b) STEM images for layered $Co(OH)(OCH_3)$ after sonication in water.

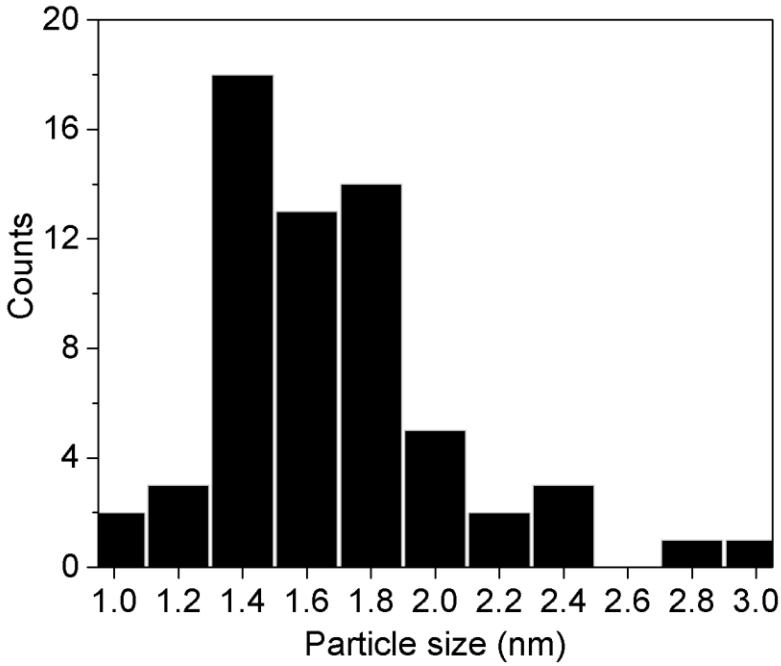

Figure S4. Particle size distribution of as-prepared cobalt oxide nanocubanes.

Table S2. Turnover frequencies (TOFs) for Co-based OER catalysts in photo-driven systems.

Catalyst material	TOF [a]	Sensitizer	Buffer solution with initial pH	Use a support?	Ref.
Cobalt oxide nanocubanes	**2.3×10^{-2}**	**$[Ru(bpy)_3]Cl_2$**	**$NaHCO_3$-$NaSiF_6$, pH = 5.8**	**N**	**This work**
6 nm Co_3O_4 nanoparticles	2.0×10^{-3}	$[Ru(bpy)_3]Cl_2$	$NaHCO_3$-$NaSiF_6$, pH = 5.8	N	This work
6 nm Co_3O_4 nanoparticles	1.3×10^{-3}	$[Ru(bpy)_3]Cl_2$	$NaHCO_3$-$NaSiF_6$, pH = 5.8	N	7
6 nm Mn doped Co_3O_4 nanoparticles	1.8×10^{-3}	$[Ru(bpy)_3]Cl_2$	$NaHCO_3$-$NaSiF_6$, pH = 5.8	N	7
$LaCoO_3$	2.7×10^{-3}	$[Ru(bpy)_3](ClO_4)_2$	Phosphate, pH = 7.0	N	8
Cubic $Li_2Co_2O_4$	1.0×10^{-3}	$[Ru(bpy)_3]Cl_2$	$NaHCO_3$ + $NaSiF_6$, pH = 5.8	N	9
Hollow Co_3O_4 microsphere	2.7×10^{-4}	$[Ru(bpy)_3]Cl_2$	$NaHCO_3$ + $NaSiF_6$, pH = 5.8	N	10
Mesoporous Co_3O_4	2.4×10^{-4}	$[Ru(bpy)_3]Cl_2$	$NaHCO_3$ + $NaSiF_6$, pH = 5.8	N	11
CoSBA (single site)	1.4×10^{-2}	$[Ru(bpy)_3]Cl_2$	$NaHCO_3$ + $NaSiF_6$, pH = 5.6	Y	12
Co-APO-5	2.3×10^{-3}	$[Ru(bpy)_3]Cl_2$	$NaHCO_3$ + $NaSiF_6$, pH = 6.0	Y	13
β-$Co(OH)_2$ anchored on zeolite Y	1.9×10^{-3}	$[Ru(bpy)_3]Cl_2$	$NaHCO_3$ + $NaSiF_6$, pH = 6.0	Y	14
3 nm Co_3O_4 nanoparticles /SBA-15	1.9×10^{-3}	$[Ru(bpy)_3]Cl_2$	$NaHCO_3$ + $NaSiF_6$, pH = 5.8	Y	15
KIT-6/Co_3O_4-HEX	4.0×10^{-4}	$[Ru(bpy)_3]Cl_2$	$NaHCO_3$ + $NaSiF_6$, pH = 5.8	Y	16
Co_3O_4 nanoparticles (20-50 nm)	4.9×10^{-5}	$[Ru(bpy)_3]Cl_2$	$NaHCO_3$ + $NaSiF_6$, pH = 6	N	17
$Co_4Se_3O_9Cl_2$	5.4×10^{-3}	$[Ru(bpy)_3]Cl_2$	$NaHCO_3$ + $NaSiF_6$, pH = 5.8	N	18
Fe_2O_3@NiO core-shell nanoparticles	6.0×10^{-4}	$[Ru(bpy)_3](ClO_4)_2$	Borate, pH = 8.0	N	19
Mn_2O_3	1.9×10^{-3}	$[Ru(bpy)_3]Cl_2$	Phosphate, pH = 7.0	N	20
$Co_3V_2O_8$	4.3×10^{-3}	$[Ru(bpy)_3]Cl_2$	Borate, pH = 8.5	N	21
Active MnO_x	4.8×10^{-5}	$[Ru(bpy)_3]Cl_2$	Phosphate, pH = 7.2	N	22
$[Co_4(H_2O)_2(VW_9O_{34})_2]^{10-}$	2.2×10^{-3}	$[Ru(bpy)_3]Cl_2$	Borate, pH = 9.0	N	23

[a] Calculated based on all the Co atoms in the catalyst. The unit is [per second per cobalt atom].

Table S3. EXAFS fitting parameters corresponding to the fit in Fig. 4c.[a]

Path	S_0^2	R	N	σ^2	ΔE_0	R_f
Co-O	0.78 (0.05)	1.903 (0.008)	**6**	0.001 (0.0001)	-2.4 (1.1)	2.0%
Co-Co		2.854 (0.008)	5.8 (0.6)	0.002 (0.0003)		

[a] Uncertainties in parentheses. Bold values are fixed (only the coordination number of Co-O). Restraints were applied to keep all σ^2 values in physically meaningful range without arbitrarily fixing these values. The amplitude reduction factor (S_0^2) was found to be in close agreement with values used in previous work on small phosphate-derived cobalt oxide nanostructures.[24,25] The fitting range is $1 \leq k \leq 10$, $1 \leq R \leq 4$.

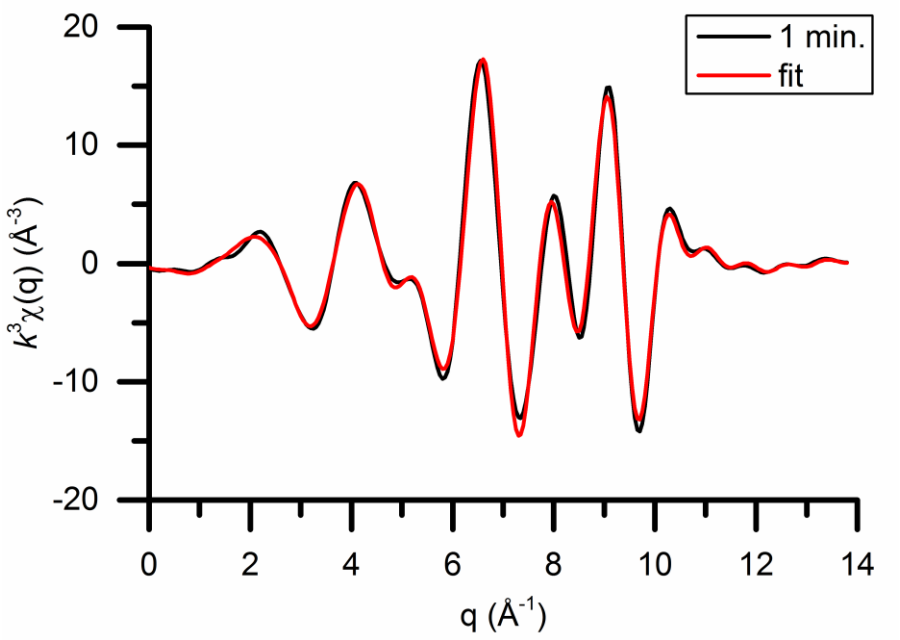

Figure S5. Real part of the *q*-space representation of the EXAFS fit to the 1 min. post-reaction sample.

References:

(1) Toby, B. H. *J. Appl. Crystallogr.* **2005**, *38*, 1040-1041.
(2) Yu, M. J.; Zhu, K. K.; Liu, Z. C.; Xiao, H. P.; Deng, W.; Zhou, X. G. *Appl. Catal. B: Environ.* **2014**, *148*, 177-190.
(3) Lebihan, S.; Guenot, J.; Figlarz, M. *J. Solid State Chem.* **1976**, *17*, 15-25.
(4) Toby, B. H. *J. Appl. Crystallogr.* **2001**, *34*, 210-213.
(5) Larson, A. C.; Von Dreele, R. B. *Los Alamos National Laboratory Report LAUR* **2000**, 86-748.
(6) Xiao, H. P.; Liu, Z. C.; Zhou, X. G.; Zhu, K. K. *Catal. Commun.* **2013**, *34*, 11-15.
(7) Zhang, Y.; Rosen, J.; Hutchings, G. S.; Jiao, F. *Catal. Today* **2014**, *225*, 171-176.
(8) Yamada, Y.; Yano, K.; Hong, D.; Fukuzumi, S. *PCCP* **2012**, *14*, 5753-5760.
(9) Gardner, G. P.; Go, Y. B.; Robinson, D. M.; Smith, P. F.; Hadermann, J.; Abakumov, A.; Greenblatt, M.; Dismukes, G. C. *Angew. Chem. Int. Ed.* **2012**, *51*, 1616-1619.
(10) Zhao, J.; Zou, Y.; Zou, X.; Bai, T.; Liu, Y.; Gao, R.; Wang, D.; Li, G.-D. *Nanoscale* **2014**, *6*, 7255-7262.
(11) Rosen, J.; Hutchings, G. S.; Jiao, F. *J. Am. Chem. Soc.* **2013**, *135*, 4516-4521.
(12) Ahn, H. S.; Yano, J.; Tilley, T. D. *Energy Environ. Sci.* **2013**, *6*, 3080-3087.
(13) Armandi, M.; Hernandez, S.; Vankova, S.; Zanarini, S.; Bonelli, B.; Garrone, E. *ACS Catal.* **2013**, *3*, 1272-1278.
(14) Del Pilar-Albaladejo, J.; Dutta, P. K. *ACS Catal.* **2014**, *4*, 9-15.
(15) Grzelczak, M.; Zhang, J.; Pfrommer, J.; Hartmann, J.; Driess, M.; Antonietti, M.; Wang, X. *ACS Catal.* **2013**, *3*, 383-388.
(16) Yusuf, S.; Jiao, F. *ACS Catal.* **2012**, *2*, 2753-2760.
(17) Liu, H. F.; Patzke, G. R. *Chem. Eur. J.* **2014**, *9*, 2249-2259.
(18) Rabbani, F.; Svengren, H.; Zimmermann, I.; Hu, S. C.; Laine, T.; Hao, W. M.; Akermark, B.; Akermark, T.; Johnsson, M. *Dalton Trans.* **2014**, *43*, 3984-3989.
(19) Du, X. Q.; Wei, J.; Zhao, J. L.; Han, R. X.; Ding, Y. *Chem. Eur. J.* **2014**, *9*, 2745-2750.
(20) Menezes, P. W.; Indra, A.; Littlewood, P.; Schwarze, M.; Gobel, C.; Schomacker, R.; Driess, M. *ChemSusChem* **2014**, *7*, 2202-2211.
(21) Zhao, Y. K.; Liu, Y. D.; Du, X. Q.; Han, R. X.; Ding, Y. *J. Mater. Chem. A* **2014**, *2*, 19308-19314.
(22) Indra, A.; Menezes, P. W.; Zaharieva, I.; Baktash, E.; Pfrommer, J.; Schwarze, M.; Dau, H.; Driess, M. *Angew. Chem. Int. Ed.* **2013**, *52*, 13206-13210.
(23) Lv, H. J.; Song, J.; Geletii, Y. V.; Vickers, J. W.; Sumliner, J. M.; Musaev, D. G.; Kogerler, P.; Zhuk, P. F.; Bacsa, J.; Zhu, G. B.; Hill, C. L. *J. Am. Chem. Soc.* **2014**, *136*, 9268-9271.
(24) Risch, M.; Khare, V.; Zaharieva, I.; Gerencser, L.; Chernev, P.; Dau, H. *J. Am. Chem. Soc.* **2009**, *131*, 6936-6937.
(25) Kanan, M. W.; Yano, J.; Surendranath, Y.; Dinca, M.; Yachandra, V. K.; Nocera, D. G. *J. Am. Chem. Soc.* **2010**, *132*, 13692-13701.