Anisotropic Nanoporous Morphology of ZnO-Supported Co that Enhances Catalytic Activity

Christopher M. Coaty[†#], Adam Corrao[§±#], Victoria Petrova[†#], Taewoo Kim[‡], David P. Fenning[†ǂ‖‡], Peter Khalifah*[§±], Ping Liu*[†ǂ‖‡]

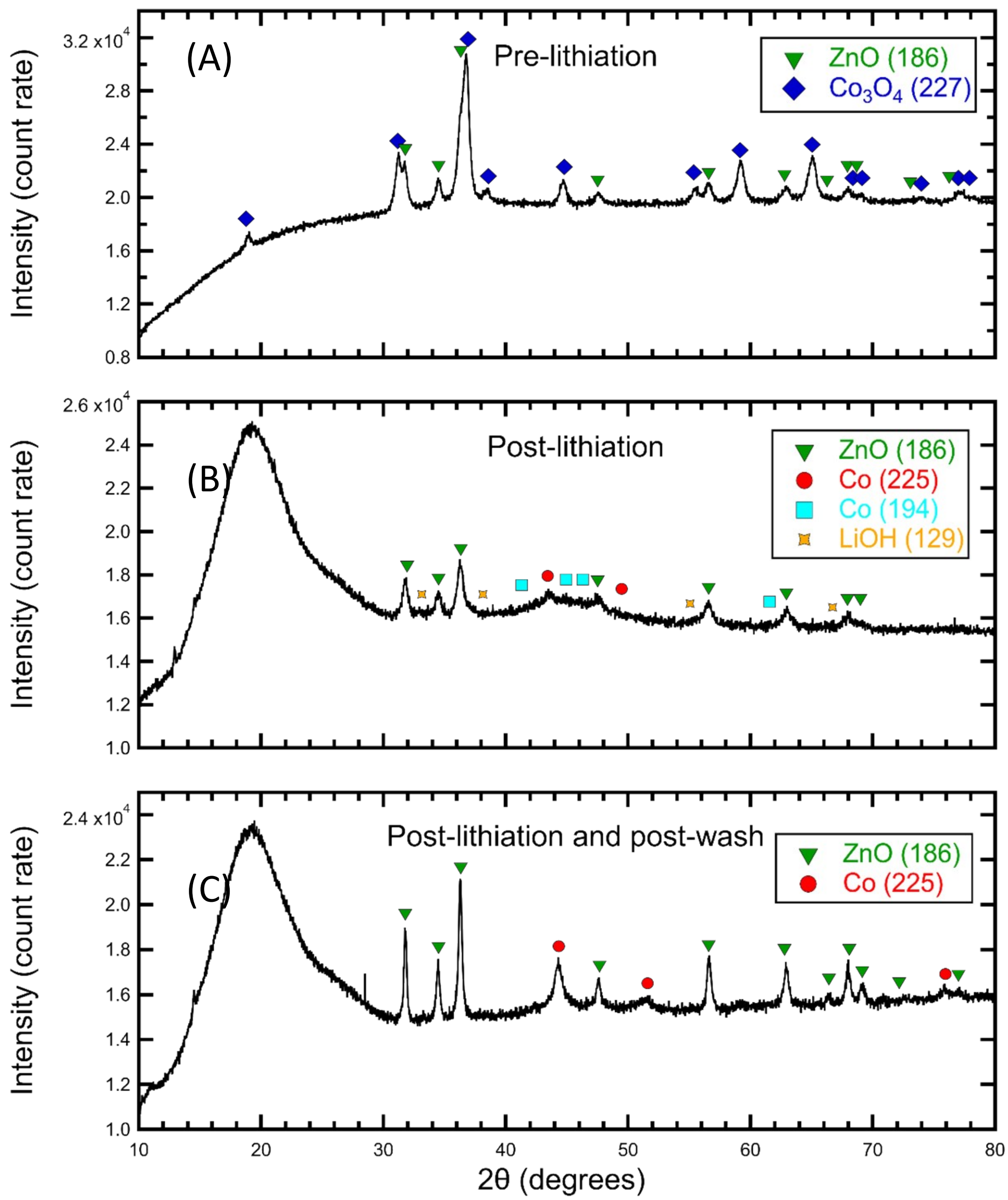


Figure S1. Phase identification results based on laboratory XRD patterns for (a) the pre-lithiation precursor mixture of ZnO and Co_3O_4, (b) the post-lithiation intermediate nanocomposite with a Li-containing phase, and (c) the post-lithiation and post-wash final NPo ZOC product.

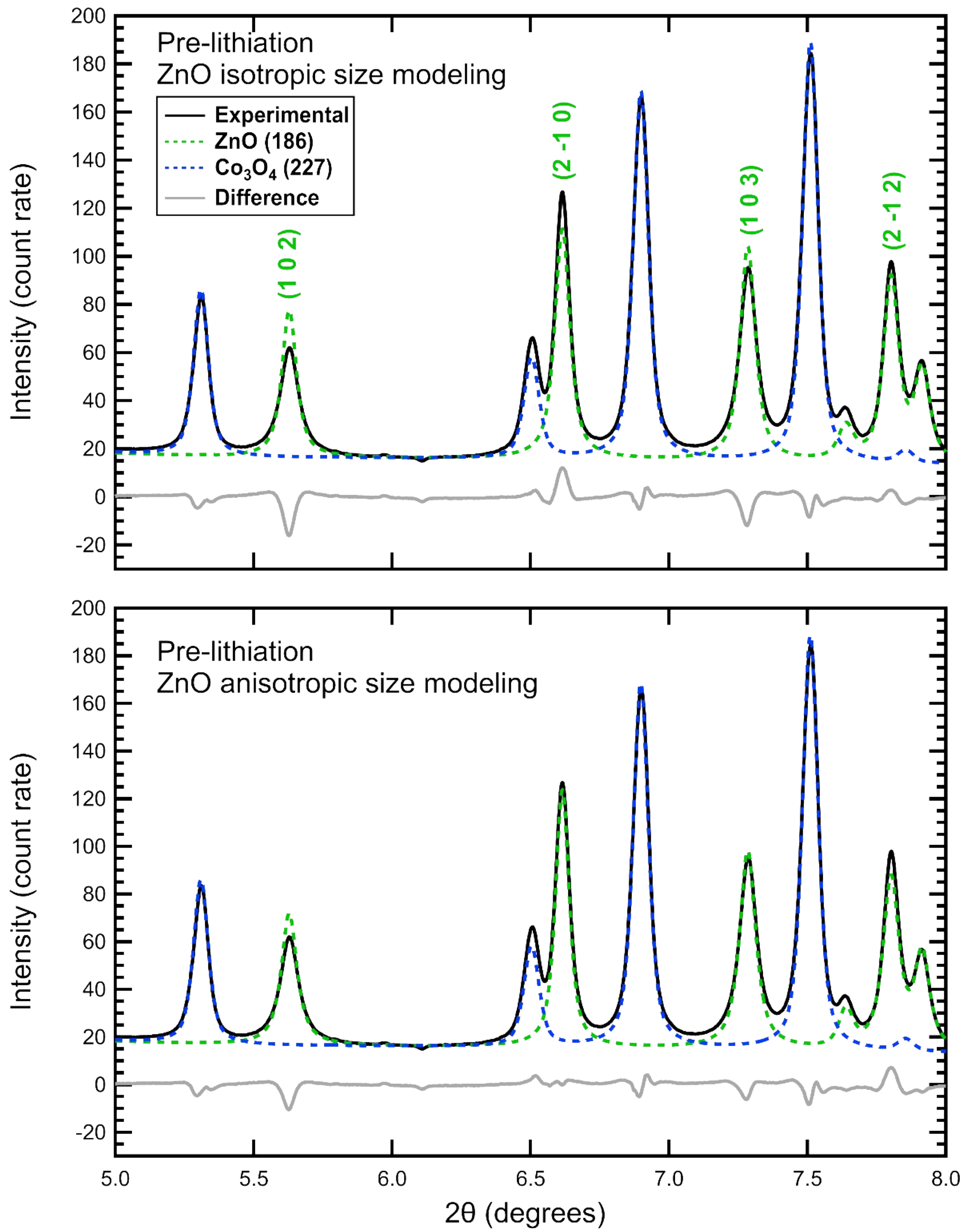


Figure S2. Comparisons of fit quality for XRD data of pre-lithiated sample for Rietveld refinements using isotropic size broadening (top, R_{wp} = 3.957) and anisotropic size broadening (bottom, R_{wp} = 3.363) for the ZnO phase.

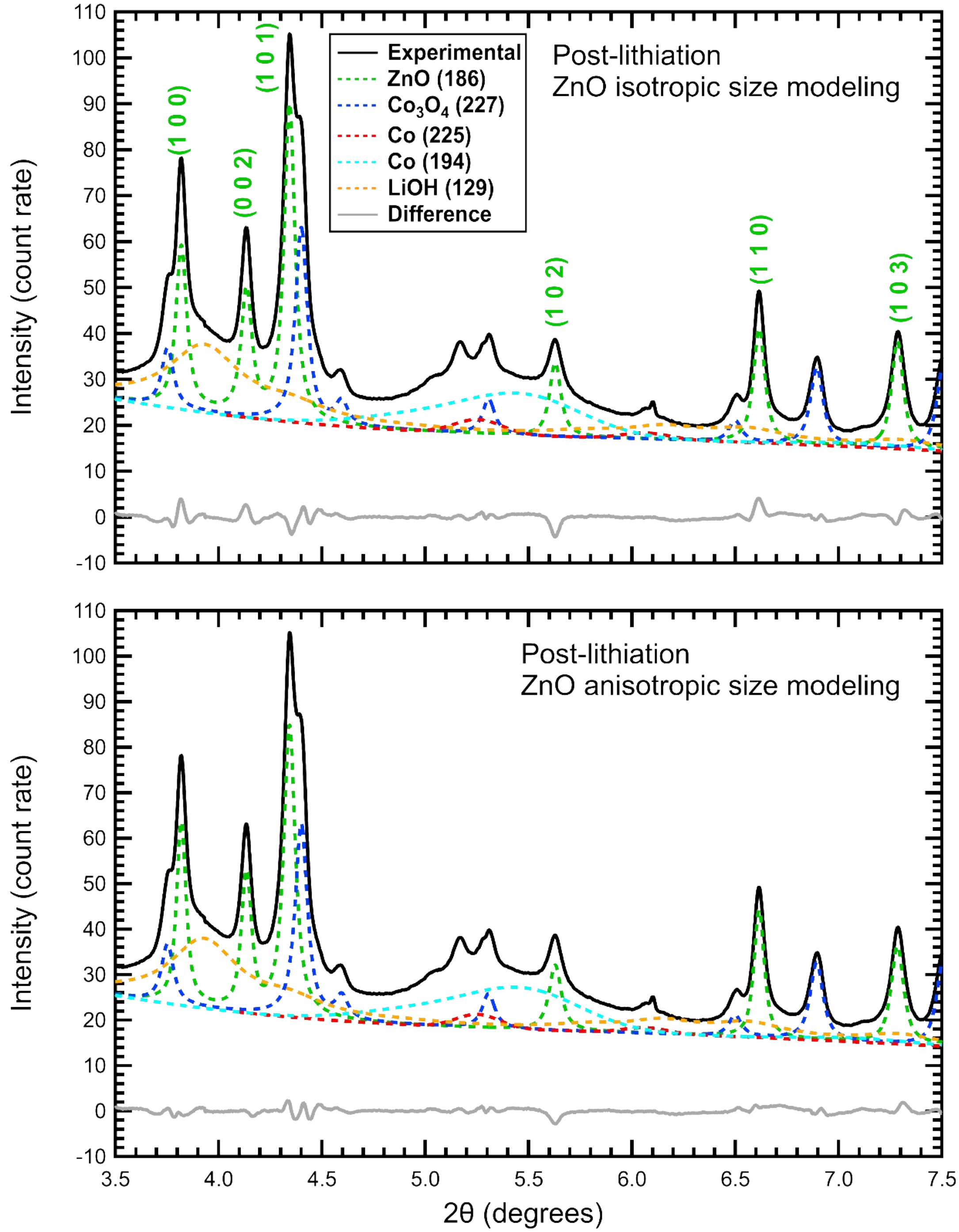


Figure S3. Comparisons of fit quality for XRD data of post-lithiated sample for Rietveld refinements using isotropic size broadening (top, R_{wp} = 2.029) and anisotropic size broadening (bottom, R_{wp} = 1.790) for the ZnO phase.

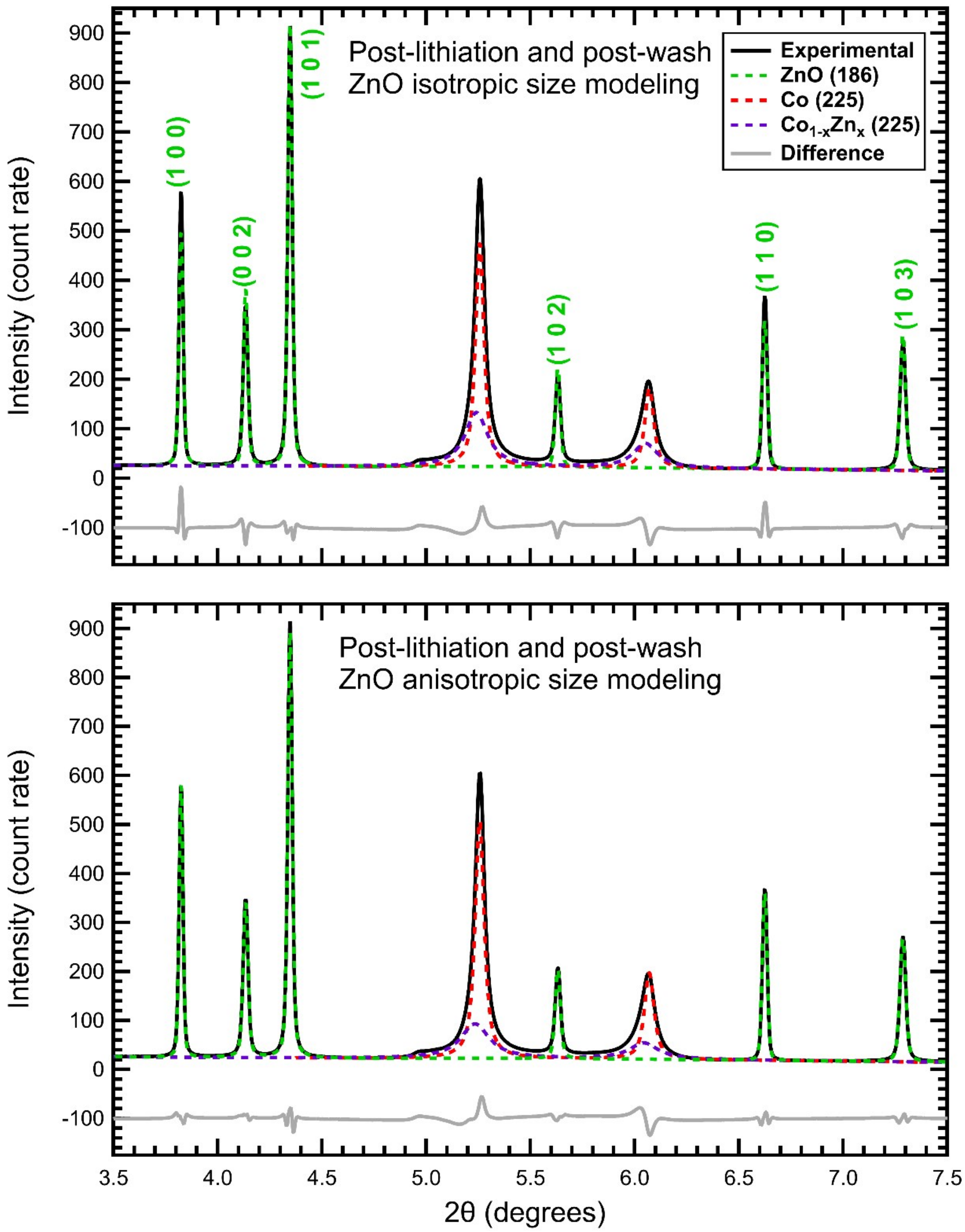


Figure S4. Comparisons of fit quality for XRD data of post-lithiated and post-washed sample for Rietveld refinements using isotropic size broadening (top, R_{wp} = 7.256) and anisotropic size broadening (bottom, R_{wp} = 6.240) for the ZnO phase.

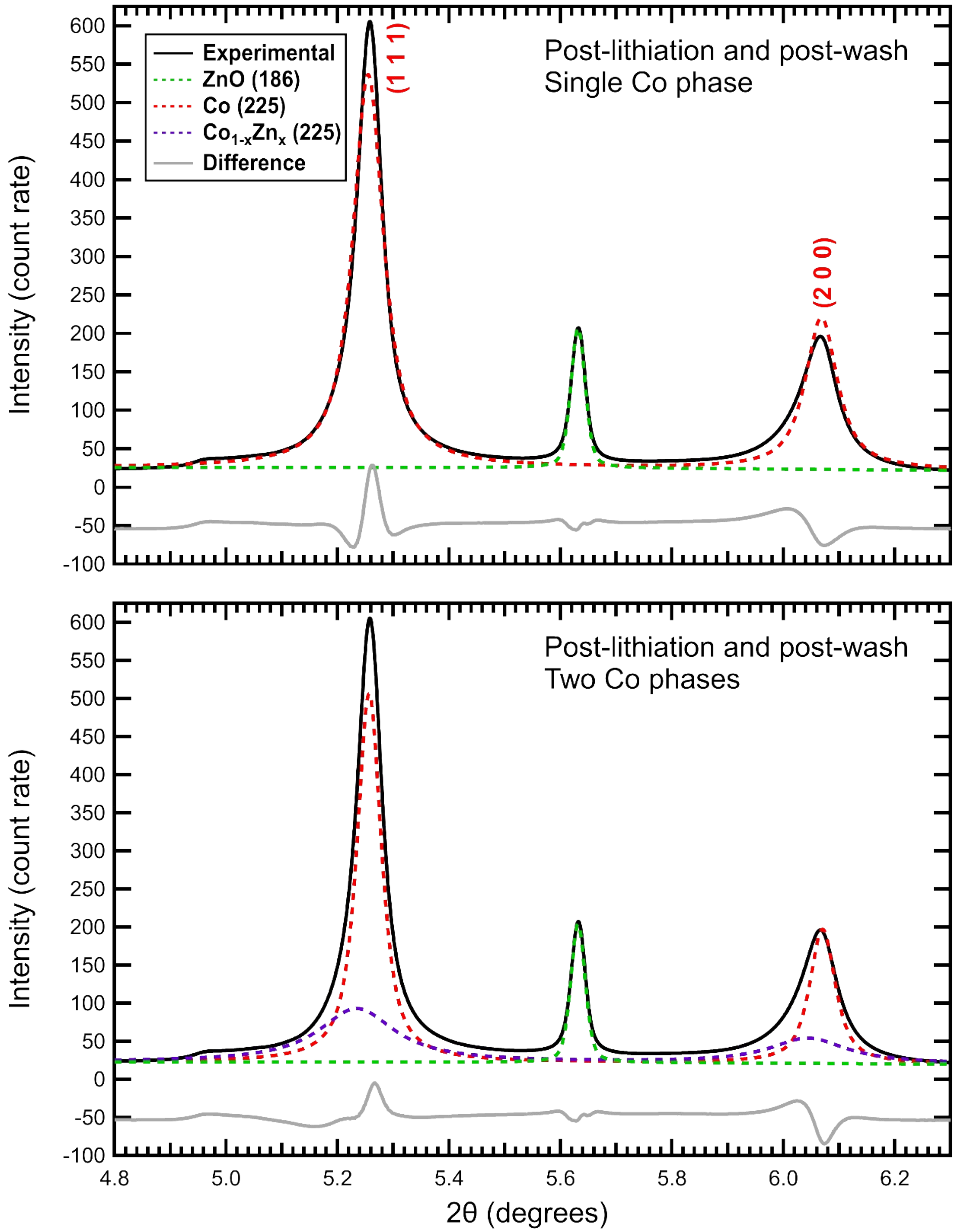
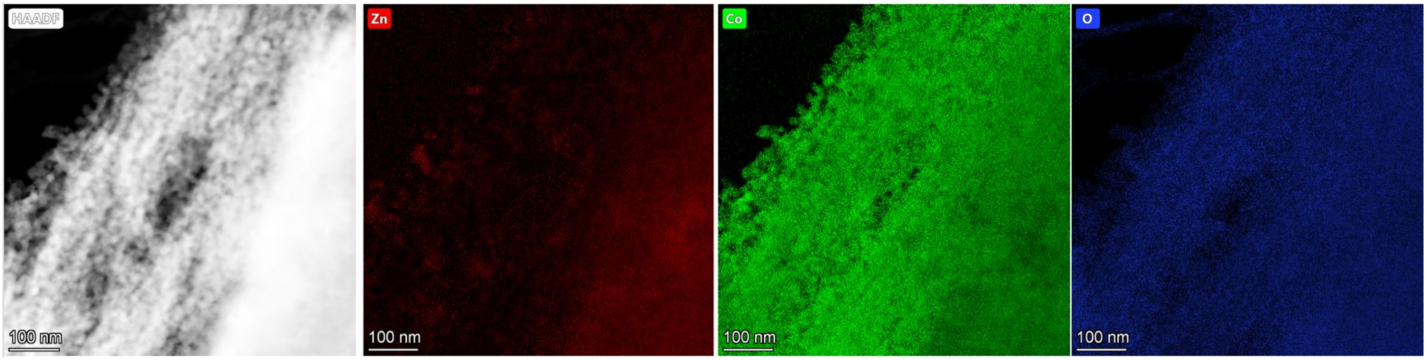


Figure S5. Comparisons of fit quality for XRD data of post-lithiated and post-washed sample for Rietveld refinements using a single Co phase (top, R_{wp} = 7.291) and two Co phases (bottom, R_{wp} = 6.240) where the second Co phase ($Co_{1-x}Zn_x$) has 3% Zn substitution (x = 0.03).



Element	Atomic Fraction (%)	Atomic Error (%)	Mass Fraction (%)	Mass Error (%)	Fit error (%)
C	4.29	0.60	1.16	0.09	2.31
O	32.50	7.92	11.67	2.51	1.56
Co	**33.45**	6.43	44.25	6.83	0.65
Cu	7.91	1.52	11.29	1.74	0.30
Zn	**21.29**	4.10	31.25	4.83	0.67

Figure S6: EDX mapping on a TEM image of nanoporous ZOC shows well integrated dispersion of Zn, Co and O elements and quantification by atomic fraction in the table below confirms a Co:Zn ratio of approximately 1.5:1.

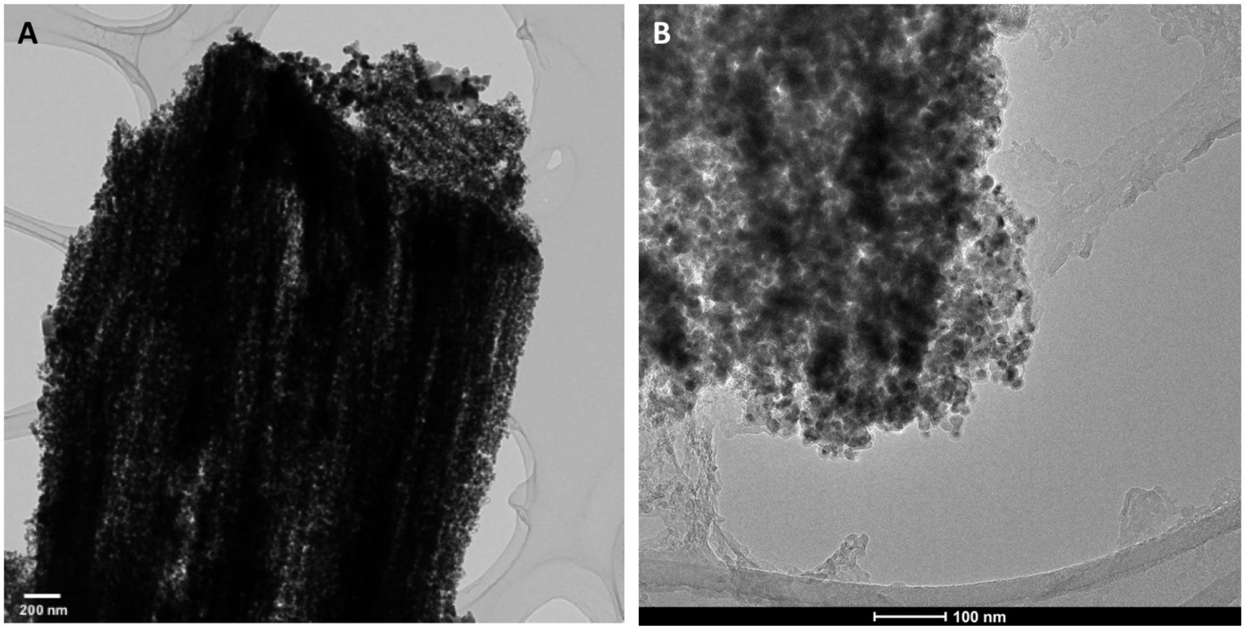


Figure S7 Low resolution TEM images clearly show the anisotropic shape of the ZOC particles. (A) has a scalebar of 200nm and (B) has a scalebar of 100nm.

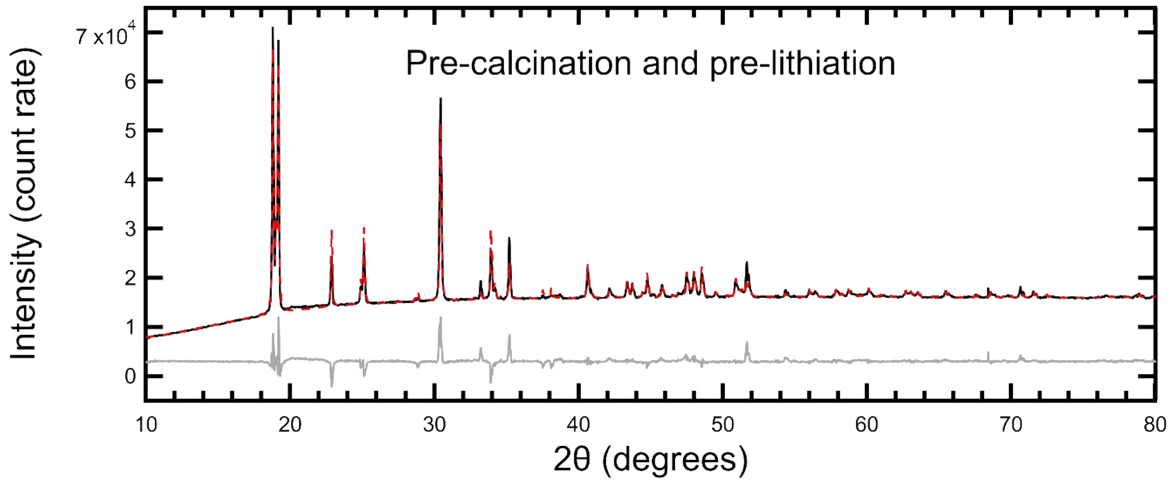


Figure S8. Rietveld fit (R_{wp} = 3.045) for a lab XRD pattern of the pre-calcination precursor, which was determined to be a single phase metal oxalate dihydrate, $Co_{1-x}Zn_x(C_2O_4)(H_2O)_2$, containing both Co and Zn ions mixed at an atomic scale. The Co:Zn ratio could not be directly quantified from diffraction studies, though *x* is presumed to be 0.5 based on the assumption of the complete incorporation of Co and Zn ions used in the synthesis of this phase.

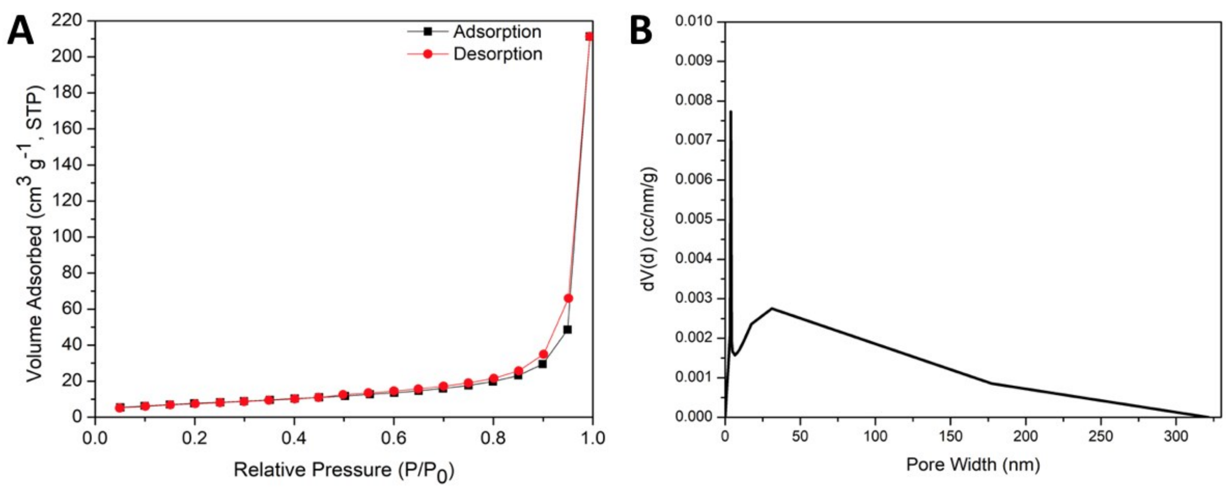


Figure S9. BET surface area and porosity data for ZOC. (A) Nitrogen adsorption-desorption isotherm; (B) BJH pore size distribution.

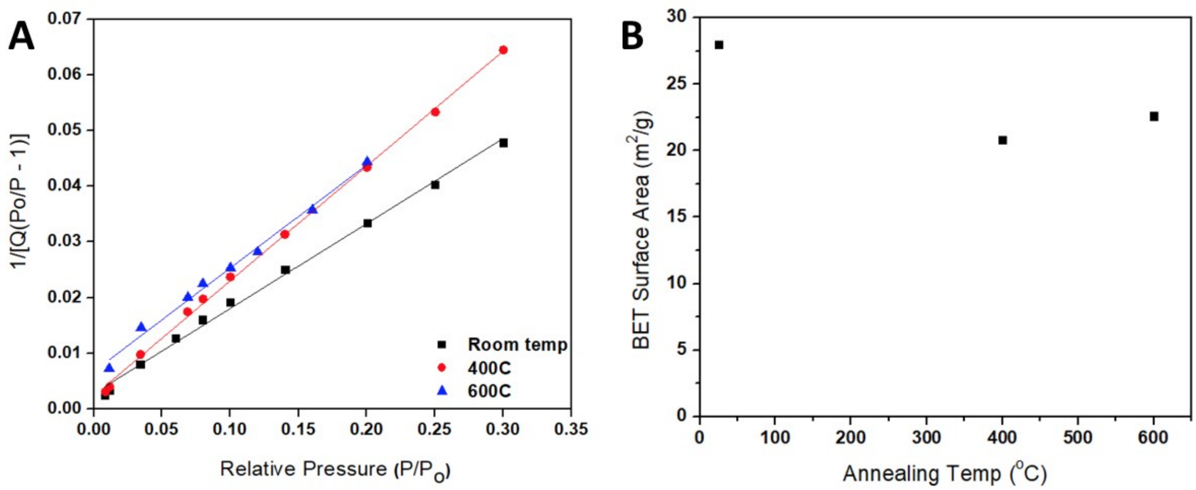


Figure S10. Nitrogen adsorption isotherms used to calculate BET surface area for ZOC at room temperature, 400C and 600C (A) as well as their corresponding trend in surface area (B).

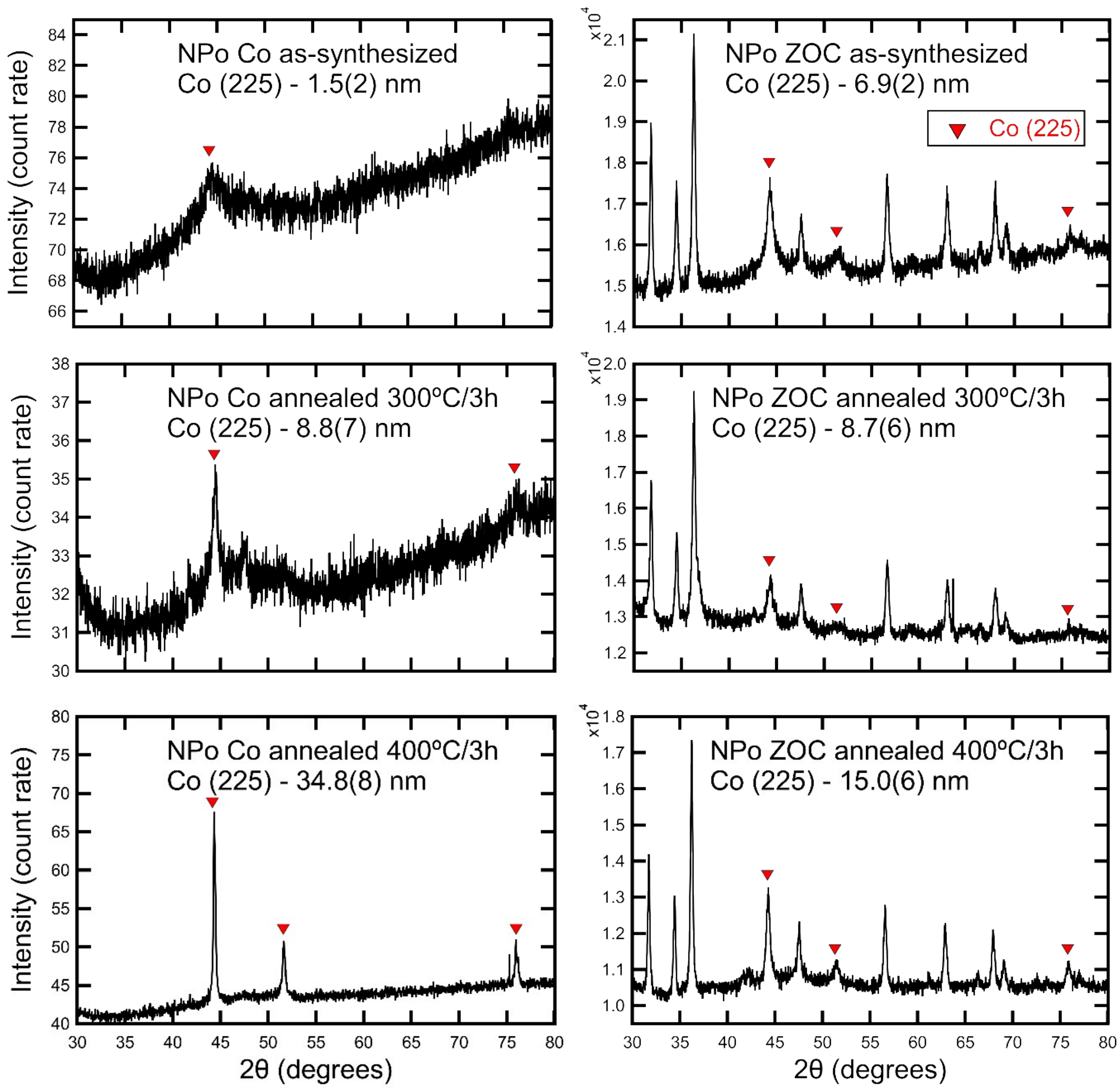


Figure S11. Comparisons of XRD data of (left) nanoporous Co metal and (right) nanoporous ZnO-supported Co, both shown for the as-synthesized samples (top), after annealing at 300 °C for 3 hours (middle), and after annealing at 400 °C for 3 hours (bottom). The enhanced resistance to coarsening of the hybrid Co-ZnO sample relative to pure nanoporous Co is reflected in its smaller particle size at 400 °C (15.0 *vs.* 34.8 nm).

Table S1. Lattice parameters (Å), phase fractions (weight %), and crystallite sizes (nm) calculated from Rietveld refinements for lab XRD patterns of nanoporous ZnO-Co annealed from 300 – 600 °C.

Sample	Phases (space group)	Lattice parameters (Å)	Phase Fractions (wt. %)	Crystallite size (nm)
Nanoporous ZnO-Co **as-synthesized**	ZnO (186)	$a = b = 3.2521(3)$ $c = 5.2064(5)$	54(3)	19.9(3)
	Co (225)	$a = b = c = 3.5441(6)$	46(3)	**6.9(2)**
Nanoporous ZnO-Co annealed **300°C/3h**	ZnO (186)	$a = b = 3.2518(3)$ $c = 5.2051(5)$	55(3)	19.9(3)
	Co (225)	$a = b = c = 3.5442(9)$	21(3)	**8.7(6)**
	CoO (225)	$a = b = c = 4.245(3)$	4(2)	16(6)
	Co_3O_4 (227)	$a = b = c = 8.101(3)$	20(3)	6.7(6)
Nanoporous ZnO-Co annealed **400°C/3h**	ZnO (186)	$a = b = 3.2517(3)$ $c = 5.2034(4)$	65(2)	26(1)
	Co (225)	$a = b = c = 3.5412(4)$	31(2)	**15.0(6)**
	CoO (225)	$a = b = c = 4.282(2)$	4(1)	24(8)
Nanoporous ZnO-Co annealed **500°C/3h**	ZnO (186)	$a = b = 3.2529(3)$ $c = 5.2042(5)$	66(1)	26(1)
	Co (225)	$a = b = c = 3.5436(3)$	30(1)	**21.3(7)**
	CoO (225)	$a = b = c = 4.265(2)$	4(1)	31(10)
Nanoporous ZnO-Co annealed **600°C/3h**	ZnO (186)	$a = b = 3.2527(4)$ $c = 5.2046(7)$	60(2)	25(2)
	Co (225)	$a = b = c = 3.5444(4)$	31(2)	**20.5(8)**
	CoO (225)	$a = b = c = 4.264(1)$	9(2)	25(5)

Table S2. Gas composition over time from catalytic testing with the NPo ZOC.

Time (min.)	H_2 (mol %)	CO_2 (mol %)	CO (mol %)	CH_4 (mol %)	H_2 (ppm)	CO_2 (ppm)	CO (ppm)	CH_4 (ppm)
0	0	0	0	0	0	0	0	0
60	66	32.6	1.2	0.3	20063	9899	360	85
120	65.1	20	2.8	12.2	53147	16635	2329	10120
180	66.4	19.3	2.9	11.4	52965	15405	2316	9073
240	66.7	21	2.8	9.5	47045	14818	1966	6729
300	67.3	19.1	3	10.6	50724	14403	2274	7905
360	70.3	19.5	2.6	7.6	51369	14282	1880	5550

Table S3. Reactant gas mixture flow rate (mL/min), production of H_2 and CO_2 (ppm) for both the standard ZOC catalyst and the NPo ZOC catalyst, and factor of increased H_2 and CO_2 production for the NPo ZOC catalyst.

Reactant Gas Mixture Flow Rate (mL/min)	NPo ZOC H_2 Production (ppm)	NPo ZOC CO_2 Production (ppm)	Standard ZOC H_2 Production (ppm)	Standard ZOC CO_2 Production (ppm)	Factor of increased H_2 production (NPo ZOC / Standard ZOC)	Factor of increased CO_2 production (NPo ZOC / Standard ZOC)
50	2364.99	714.18	628.16	539.3547	3.76	1.32
80	420.88	400.73	122.95	202.6407	3.42	1.98
110	280.41	254.84	41	73.3644	6.84	3.47
160	118.46	118.62	30.3	69.298	3.92	1.71
210	30.31	51.6272	N/A	N/A	N/A	N/A

Table S4. Positions and *d*-spacings for unindexed peaks in the XRD data from the pre-lithiation precursor mixture of ZnO and Co_3O_4.

2θ Position (deg.)	*d*-spacing (Å)
1.64250	6.51293
1.98609	5.38629
2.62000	4.08323
3.25585	3.28595
3.28863	3.25320
3.50686	3.05081

Table S5. Positions and *d*-spacings for unindexed peaks in the XRD data from the post-lithiated hybrid nanocomposite sample.

2θ Position (deg.)	*d*-spacing (Å)
3.20000	3.34329
4.99940	2.14036
5.15084	2.07747
6.02908	1.77507
6.07870	1.76060
8.54158	1.25352
8.92742	1.19945