

*Supporting Information*

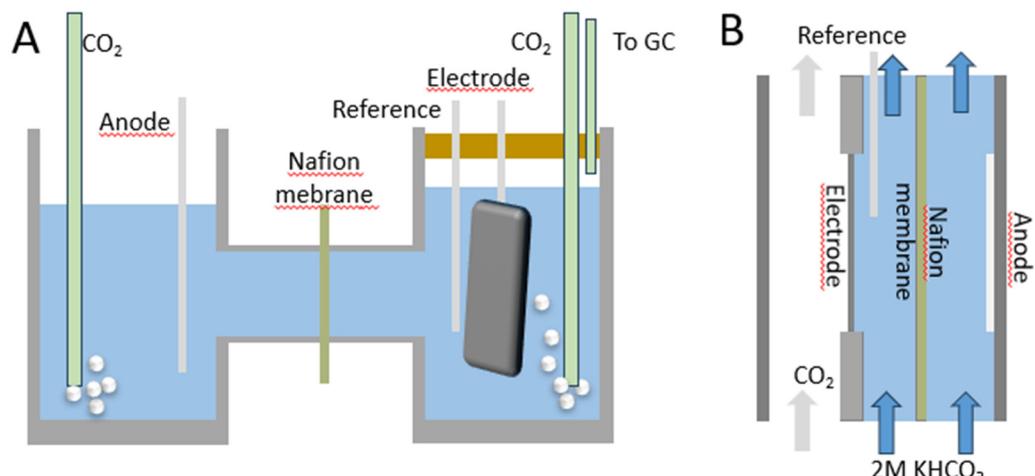
# Effects of Annealing Conditions on the Catalytic Performance of Anodized Tin Oxide for Electrochemical Carbon Dioxide Reduction

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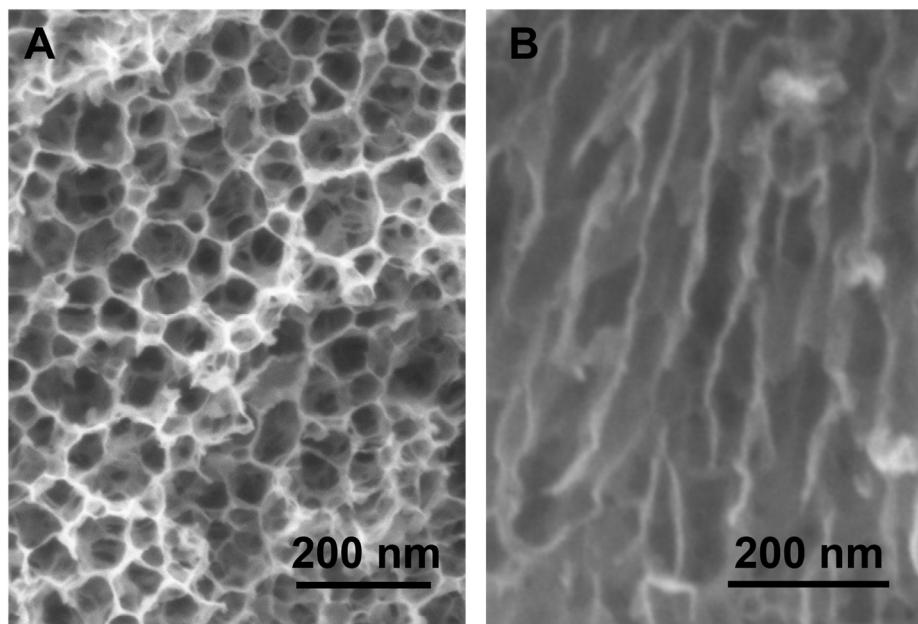
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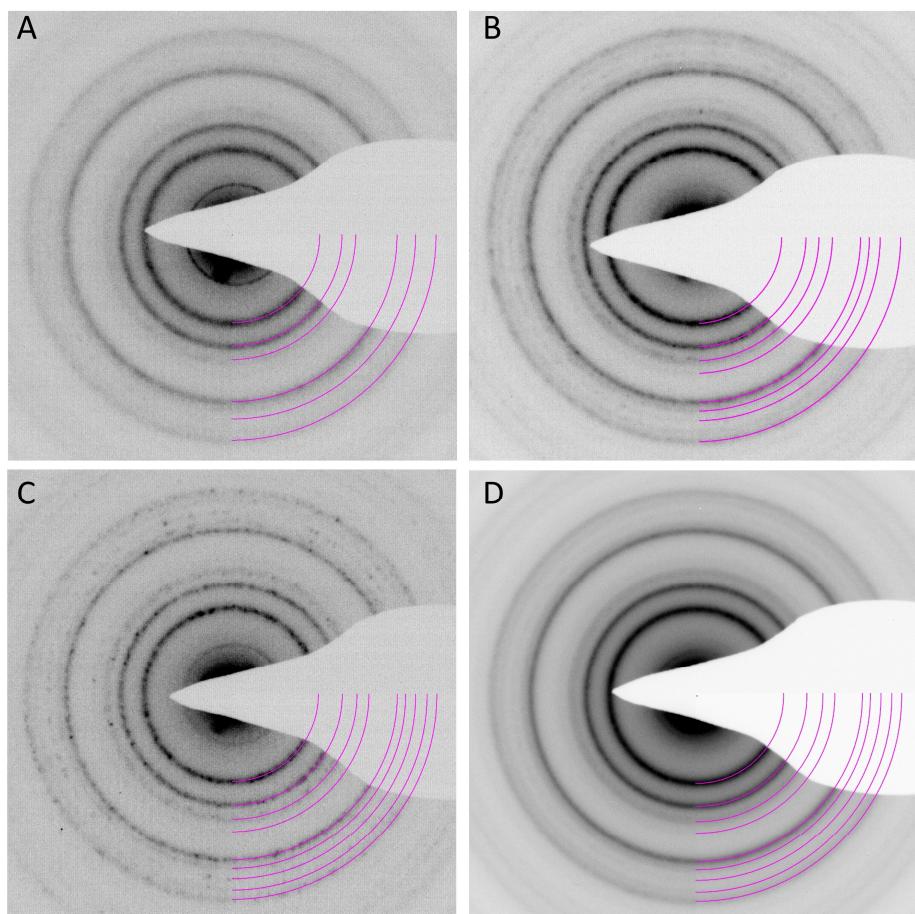
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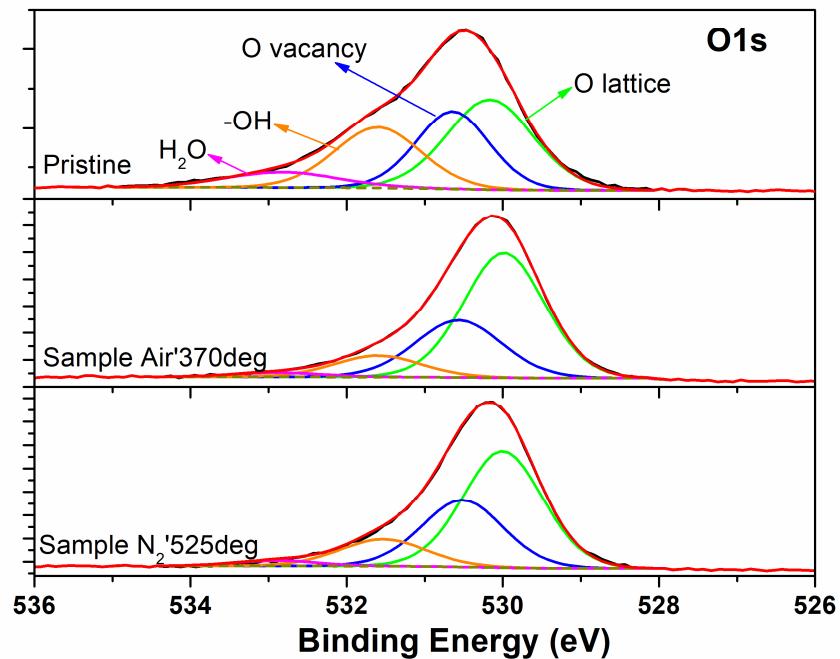
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**Figure S2.** FESEM images of pristine catalyst: (A) top view and (B) cross-section view.



**Figure S3.** Selected Area Electron Diffraction (SAED) patterns of all studied catalysts: (A) Pristine, (B) Air'-370deg, (C) Air'-525deg and (D) N2'-525deg. The rings in the images were obtained by Circular Hough transform diffraction analysis (A software tool for automated measurement of selected area electron diffraction patterns within Digital Micrograph [1]), and are superimposed on the SAED pattern, showing the position and size of the rings. These are polycrystalline SnO<sub>2</sub> (Tin Oxide, JCPDS 00-041-1445).



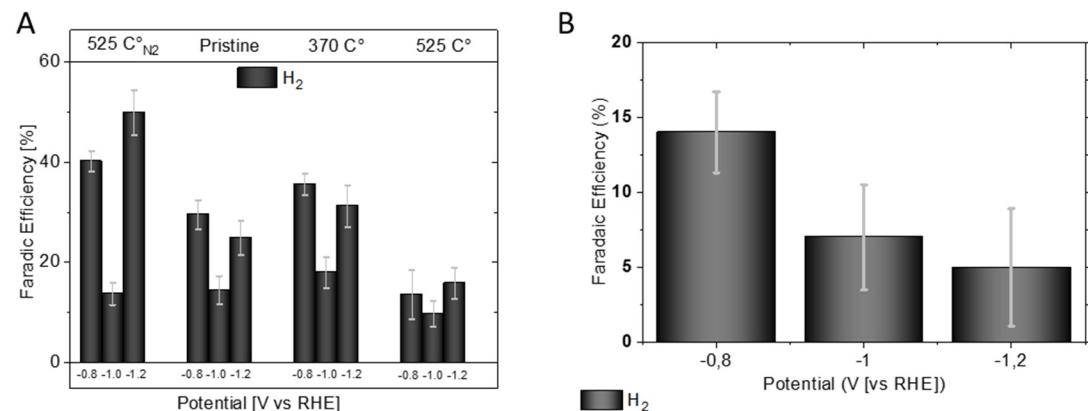
**Figure S4.** XPS O1s HR spectra for pristine, annealed in air at 370 °C and annealed in inert atmosphere at 525 °C.

**Table S1.** O 1s XPS peak deconvolution results for the four samples.

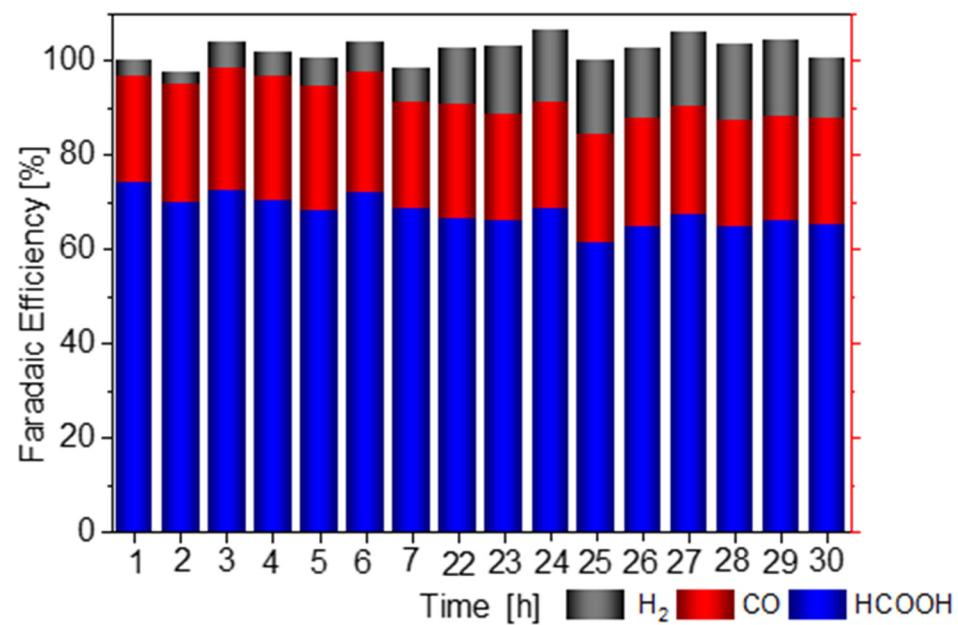
Samples	O1s XPS peak deconvolution results			
	Lattice O	O <sub>vac</sub>	-OH	H <sub>2</sub> O
Pristine	38.1	27.8	25.7	8.4
Air'370°C	58.5	28.5	10.7	2.3
Air'525°C	53.1	31.2	13.2	2.5
N <sub>2</sub> '525°C	54.9	27.4	14.3	3.4

**Table S2.** Comparison of Electrocatalytic Performance of Tin-Based Catalysts for CO<sub>2</sub> Reduction to Formic Acid / formate and CO.

Electrocatalysts	Electrolyte	FE <sub>CO<sub>2</sub></sub> RR [%]	Applied potential [V vs. RHE]	Current density [mA cm <sup>-2</sup> ]	Stability [h]	Ref
Mesoporous SnO <sub>x</sub> Nanoparticles	2 M KHCO <sub>3</sub>	95	-1.2	72	30	This work
Wavy SnO <sub>2</sub>	0.5 M KHCO <sub>3</sub>	91	-1.0	22 S	18	[2]
Mesoporous SnO <sub>2</sub> nanosheets	0.5 M KHCO <sub>3</sub>	90	-1.3	8.3	12	[3]
Porous SnO <sub>2</sub> /CC	0.5 M NaHCO <sub>3</sub>	95	-1.6 (V vs. Ag/AgCl)	45	24	[4]
Porous SnO <sub>2</sub> nanosheets	0.5 M KHCO <sub>3</sub>	92.4	-0.7	NA	10	[5]
Ultra-small SnO <sub>2</sub> NPs	1 M KHCO <sub>3</sub>	80	-1.21	145	NA	[6]
Ultrathin SnO <sub>2</sub> QWs	0.1 M KHCO <sub>3</sub>	87.3	-1.156	13.7	7	[7]
Pt atom/SnO <sub>2</sub>	0.1 M KHCO <sub>3</sub>	82.1 ± 1.4	-1.2	12.9	8	[8]
In-SnO <sub>2</sub> NWs	0.5 M KHCO <sub>3</sub>	85	-1.04	6.02	12	[9]
Mn-doped SnO <sub>2</sub>	0.1 M KHCO <sub>3</sub>	91.6	-1.03	21.2	8	[10]
VO-rich N-SnO <sub>2</sub> NS	0.1 M KHCO <sub>3</sub>	>90	-0.9	6.7	10	[11]
SnO <sub>2</sub> @N-CNW	0.5 M NaHCO <sub>3</sub>	90	-0.8	25	20	[12]
NC-SnO <sub>2</sub> @CC	0.5 M KHCO <sub>3</sub>	93	-0.7	44.3	24	[13]
SnO <sub>2</sub> /Sn	0.5 M KHCO <sub>3</sub>	93 ± 1	-1.0	28.7	9	[14]
SnO <sub>2</sub> /Py-CNTO	0.1 M KHCO <sub>3</sub>	96	-1.29	27.5	32	[15]



**Figure S5.** FE of H<sub>2</sub> of: A) H-cell experiments and B) flow cell experiments.



**Figure S6.** Stability test complete FE distribution at sampling time.

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