Chainlike Mesoporous SnO2 as a Well-Performing Catalyst for Electrochemical CO2 Reduction

Supporting Information

Chainlike Mesoporous SnO_2 as a Well-Performing Catalyst for Electrochemical CO_2 Reduction

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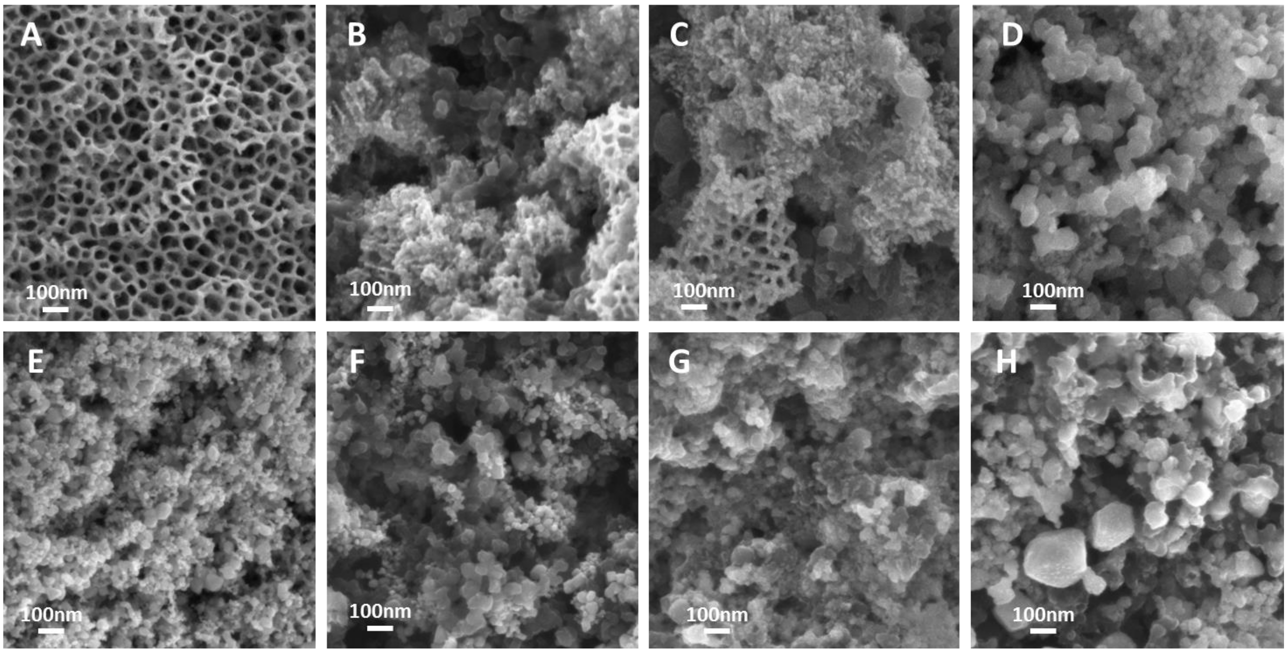

Figure S1 Top view FESEM images of the (a) as-grown SnO_2,(b) as-prepared electrode SnO_2-anod, (c) SnO_2-anod electrode reduced for 20min and (d) tested SnO_2-anod electrode, (e) commercial SnO_2, (f) as-prepared electrode SnO_2-comm, (g) SnO_2-comm electrode reduced for 20min and (h) tested SnO_2-comm electrode. All images are shown at the same magnification.

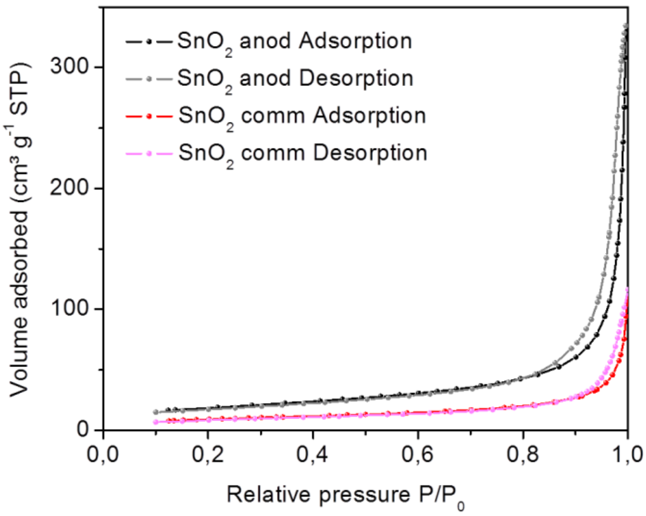

Figure S2 N_2 adsorption/desorption isotherms for SnO_2 prepared via anodic oxidation and commercial.

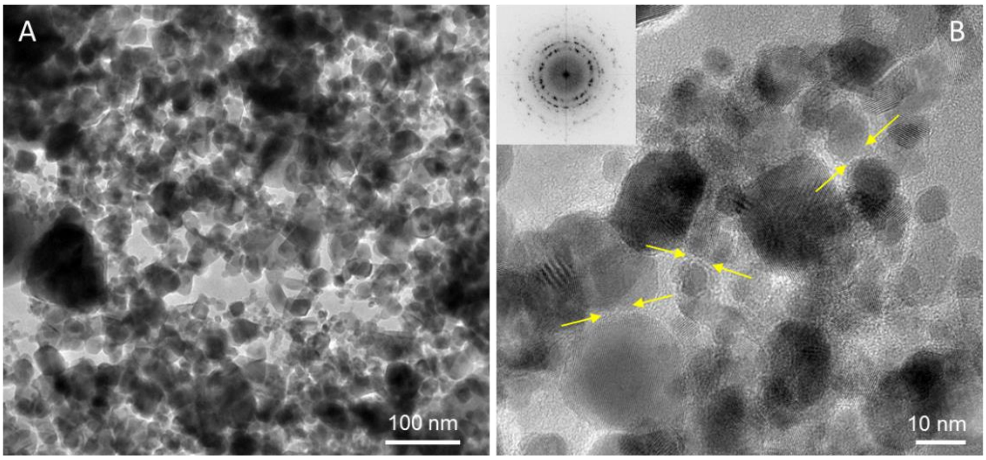

Figure S3 TEM image at two different magnification of the commercial SnO_2. In the inset the FFT of picture (b) is also reported.

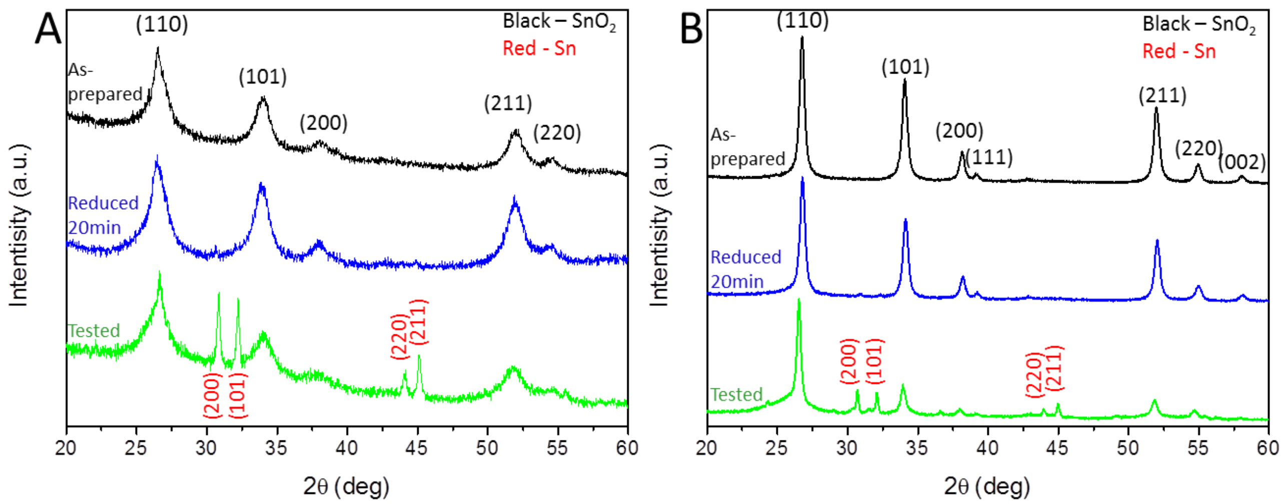

Figure S4 XRD patterns of (a) SnO_2-anod and (b) SnO_2-comm electrodes (as-prepared, reduced for 20min and tested).

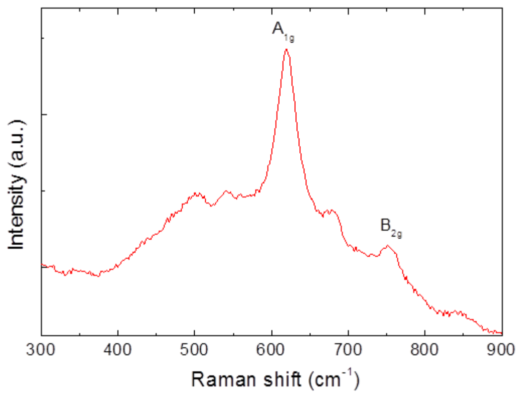

Figure S5 Raman spectrum of as-prepared SnO_2-anod electrode.

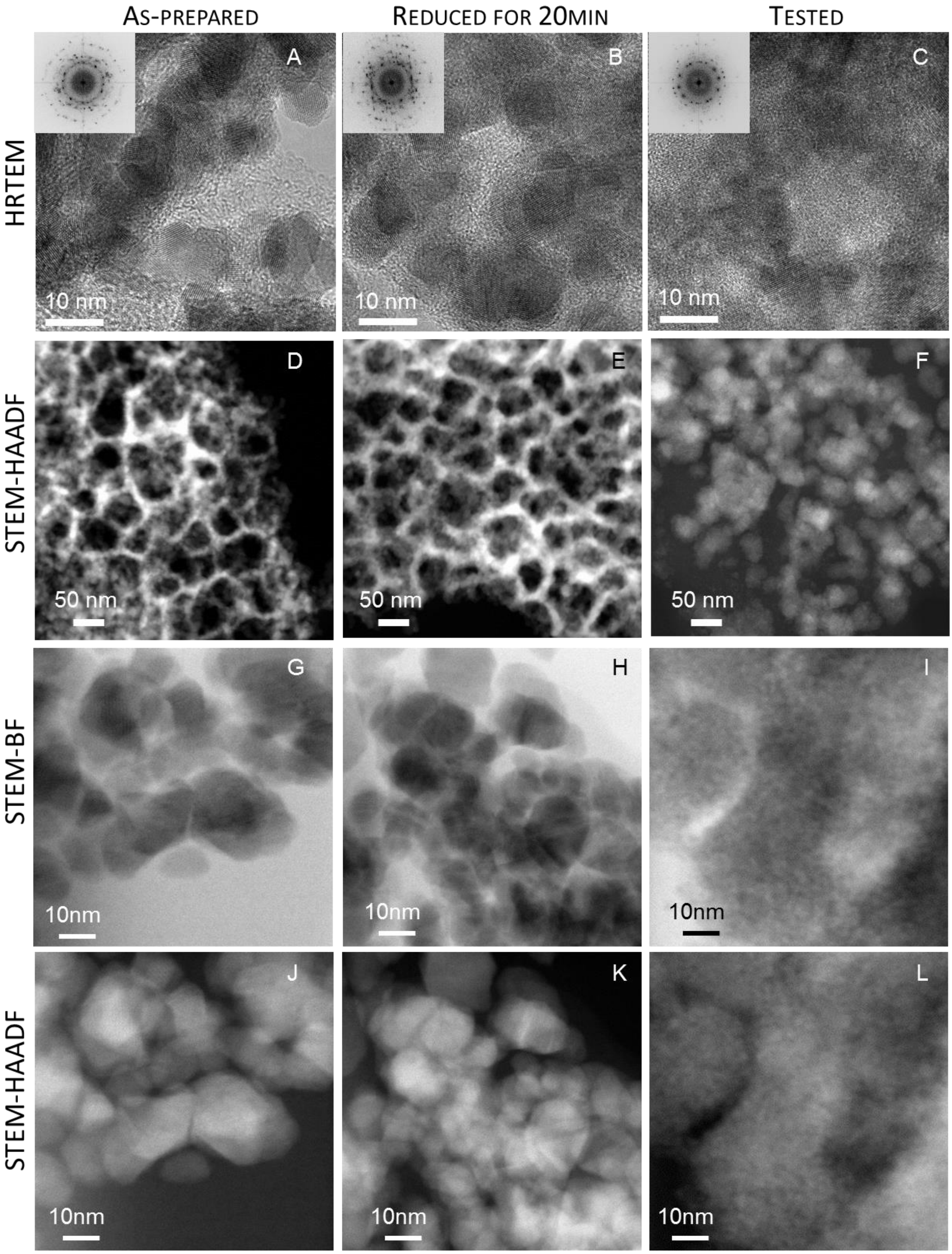

Figure S6 TEM study of the crystals evolution of the SnO_2-anod, including the as-prepared, reduced for 20 minutes and long term tested material. In the rows the following images are shown: HRTEM with FFT (of the shown area) in the inset, low magnification HAADF-STEM image, high magnification BF-STEM and HAADF-STEM.

The double-layer capacitance (C_{dl}) values of the SnO_2-comm, SnO_2-anod and Sn foil electrodes are evaluated by cyclic voltammetry (CV) at various scan rates in a potential range between -0.29 V and -0.39 V. The geometric current densities are plotted against the scan rates, and the slope of the linear fitting quantifies the double-layer capacitance C_{dl}.

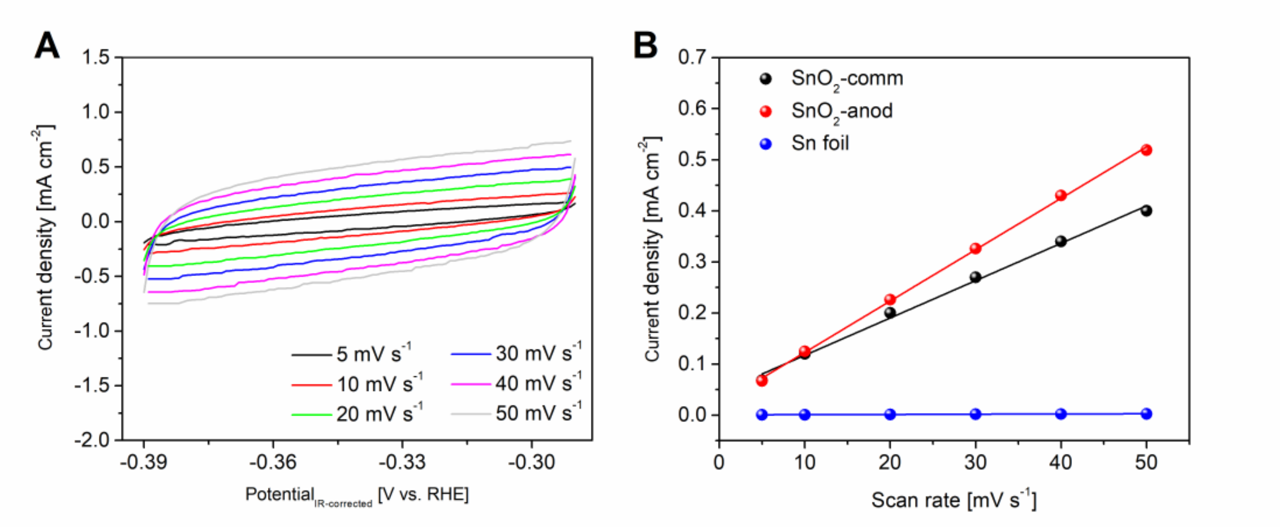

Figure S7 Determination of double-layer capacitance for various electrodes in CO_2-saturated 0.1 M KHCO3: (a) representing CVs on SnO_2-anod electrode; (b) Capacitance values calculated from the slopes of current densities vs. scan rate.

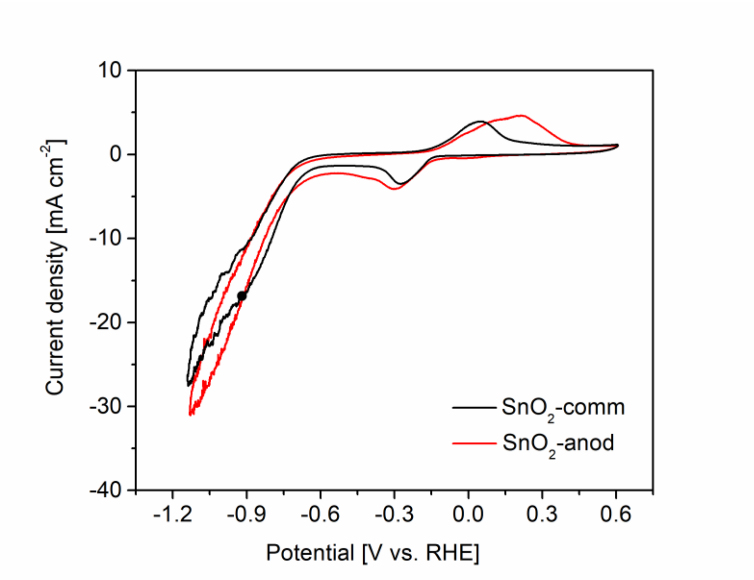

Figure S8 Comparison of the voltammograms of SnO_2-comm and SnO_2-anod in the CO_2-saturated electrolyte.

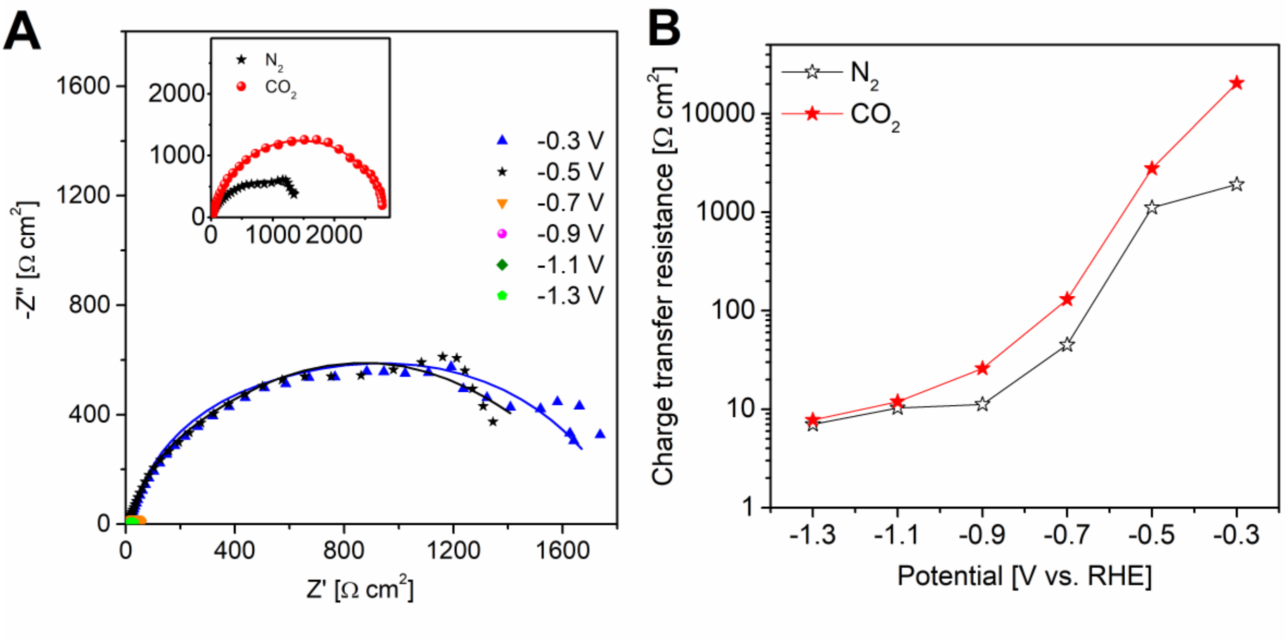

Figure S9 EIS analysis on a Sn foil electrode: (a) Nyquist plots obtained in N_2-saturated electrolyte (the points are experimental data, the clines are the curves calculated through fitting. In the inset, the two spectra acquired at -0.5 V in N2- and CO_2-saturated solutions are shown. (b) Charge transfer resistances reported as a function of the potential.

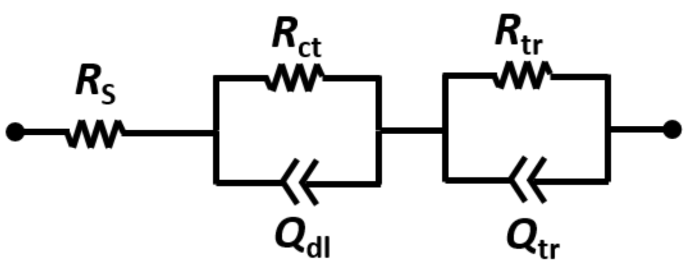

Figure S10 Equivalent circuit used for fitting of EIS data.

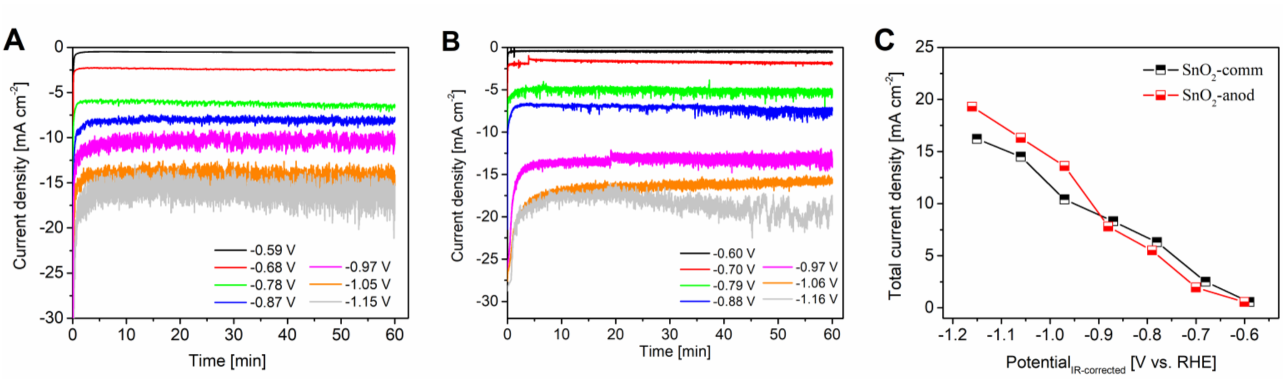

Figure S11 CA measurements carried out in CO_2-saturated 0.1 M $KHCO_3$ aqueous solution at different potentials: (a) SnO_2-comm; (b) SnO_2-anod; (c) Comparison of total current densities on SnO_2-comm and SnO_2-anod electrodes at various potentials.

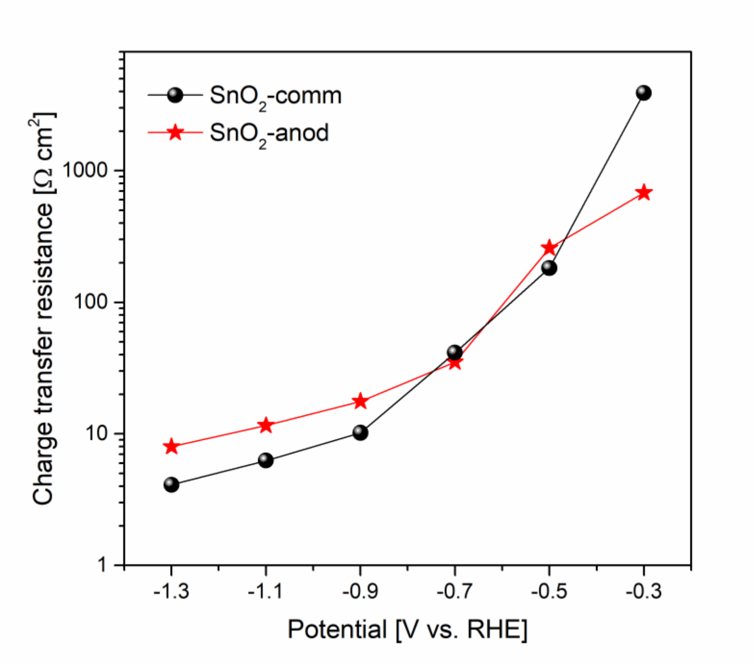

Figure S12 Comparison of charge transfer resistance obtained from EIS on SnO_2-comm and SnO_2-anod electrodes at various potentials.

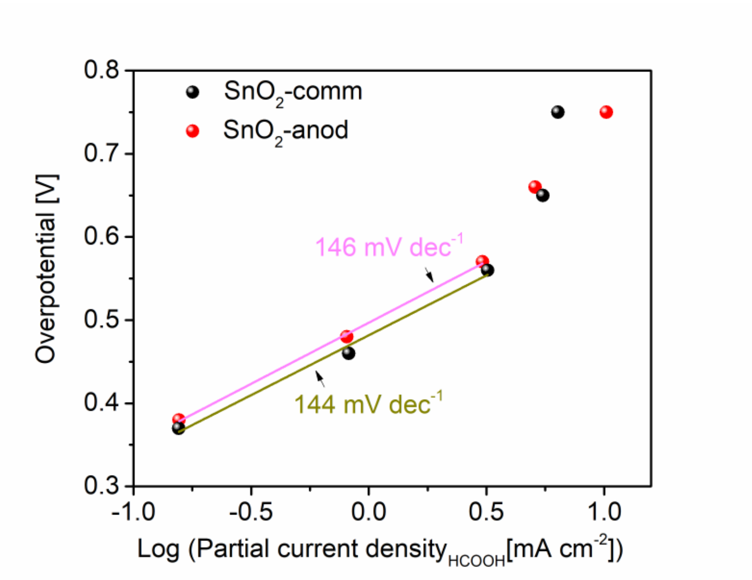

Figure S13 Tafel plot analysis for HCOOH production on SnO_2-comm and SnO_2-anod electrodes.

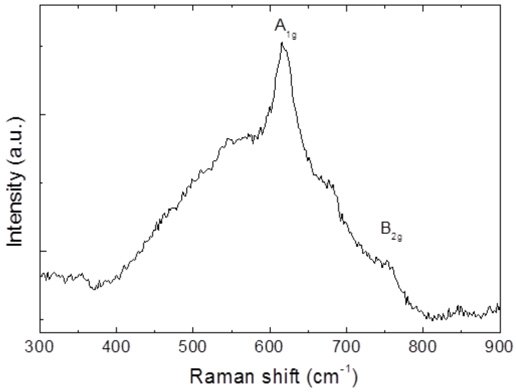

Figure S14 Raman spectrum of tested SnO_2-anod electrode.

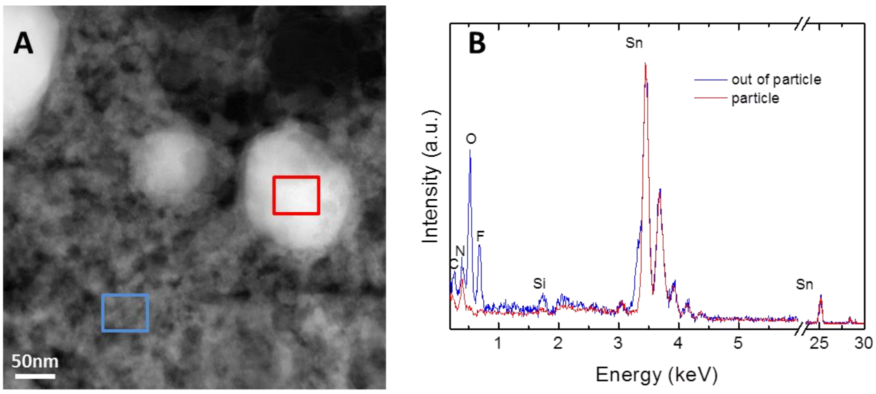

Figure S15 STEM image of the cross-section lamella of tested SnO_2-anod electrode (a) and EDX measurement performed locally in the particle and out of the particle (b).

Table S1 Comparison of electrocatalytic performance for reducing CO_2 to formic acid / formate on tin-based catalysts.

Electrode	Electrolyte	Maximum Faradic Efficiency [%]	Total current (mA cm^{-2})	Ref
Sn/SnO_2 porous hollow fiber	0.1 M $KHCO_3$	82% @-1.,6 V (vs. SCE)	28,6	1
SnO_2 nanosheets/Carbon cloth	0.5 M $NaHCO_3$	87% @ −1.6 V (vs. Ag/AgCl)	48,6	2
SnO_x NPs	0.5 M $KHCO_3$	87% @ −1.6 V (vs. SHE)	14,0	3
Electro deposited Sn	0.1 M $KHCO_3$	91% @ −1.4 V (vs. SCE)	15,0	4
Sn particles	0.5 M $KHCO_3$	73% @ −1.8 V (vs. Ag/AgCl)	13,5	5
SnO_2 nanopowder	0.5 M NaOH	68% @-0.6 V (vs. RHE)	3,5	6
SnO_2/graphene	0.1 M $NaHCO_3$	94% @-1.8 V (vs. SCE)	10,2	7
SnO_2/carbon black	0.1 M $NaHCO_3$	86% @-1.8 V (vs. SCE)	5,4	7
Sn dendrite	0.1 M $KHCO_3$	72% @-1.36 V (vs. RHE)	17,1	8
Sn - Nafion	0.5 M $NaHCO_3$	70% @-1.6 V (vs. NHE)	27,0	9
SnO_2/carbon aerogel	1.0 M $KHCO_3$	76% @ −0.96 V (vs. RHE)	23,5*	10
SnO_2 Porous NWs	0.1 M $KHCO_3$	80% @ -0.8 V (vs. RHE)	6,0	11
SnO_2 NPs	0.1 M $KHCO_3$	58% @ -0.8 V (vs. RHE)	2,4	11
SnO_2 at N-rGO	0.5 M $NaHCO_3$	78% @ -0.8 V (vs. RHE)	21,3	12
SnO_2 nanospheres	0.5 M $KHCO_3$	56% @ -1.1 V (vs. RHE)	6,0*	13
Mmesoporous SnO_2	0.1 M $KHCO_3$	40% @ -0.8 V (vs. RHE)	5.0	14
		40% @ -1.4 V (vs. RHE)	21.3	14
Chain-like mesoporous SnO_2	0.1 M $KHCO_3$	82% @ -1.06 V (vs. RHE)	16,3	This work
		80% @ -1.15 V (vs. RHE)	19.3	This work
SnO2 nanopowder	0.1 M $KHCO_3$	43% @ -1.15 V (vs. RHE)	16.2	This work
		67% @ -0.87 V (vs. RHE)	8.3	This work

* estimated on the basics of information given in the paper

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