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Chainlike Mesoporous SnO₂ as a Well-Performing Catalyst for Electrochemical CO₂ Reduction / Bejtka, Katarzyna; Zeng, Juqin; Sacco, Adriano; Castellino, Micaela; Hernández, Simelys; Farkhondehfal, M. Amin; Savino, Umberto; Ansaloni, Simone; Pirri, Candido F.; Chiodoni, Angelica. - In: ACS APPLIED ENERGY MATERIALS. - ISSN 2574-0962. - ELETTRONICO. - 2:5(2019), pp. 3081-3091. [10.1021/acsaem.8b02048]

Availability:

This version is available at: 11583/2734428 since: 2020-01-14T10:27:19Z

Publisher:

American Chemical Society

Published

DOI:10.1021/acsaem.8b02048

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Supporting Information

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

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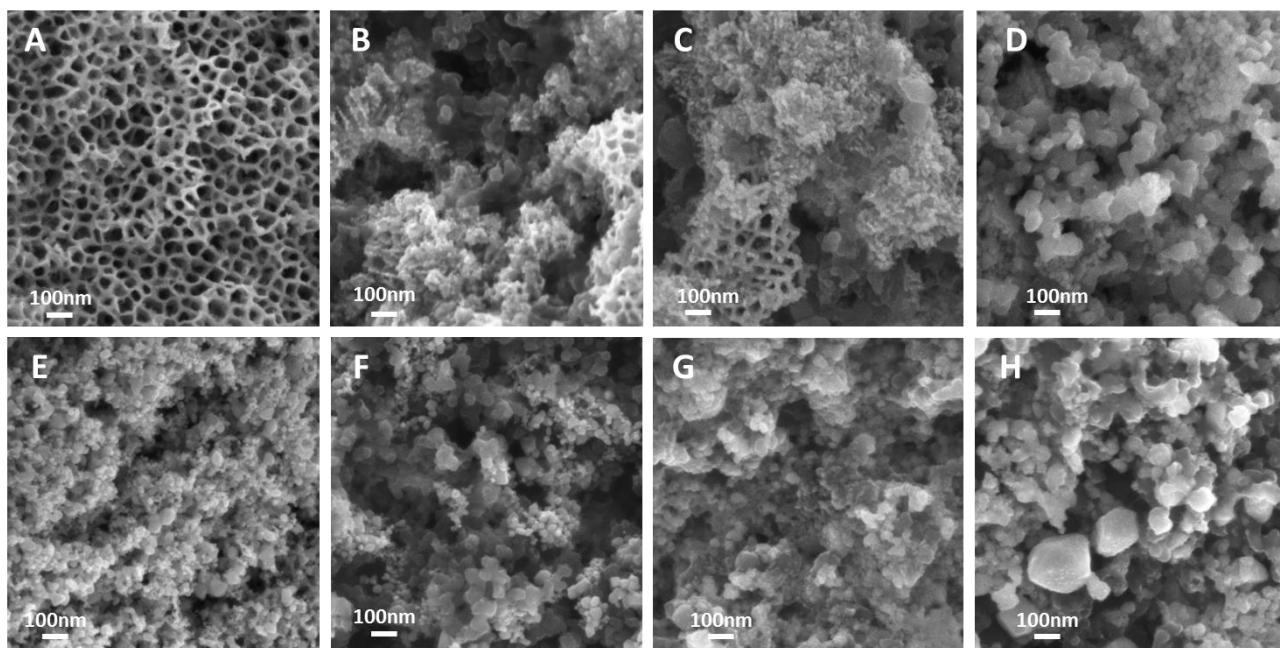


Figure S1 Top view FESEM images of the (a) as-grown SnO₂, (b) as-prepared electrode SnO₂-anod, (c) SnO₂-anod electrode reduced for 20min and (d) tested SnO₂-anod electrode, (e) commercial SnO₂, (f) as-prepared electrode SnO₂-comm, (g) SnO₂-comm electrode reduced for 20min and (h) tested SnO₂-comm electrode. All images are shown at the same magnification.

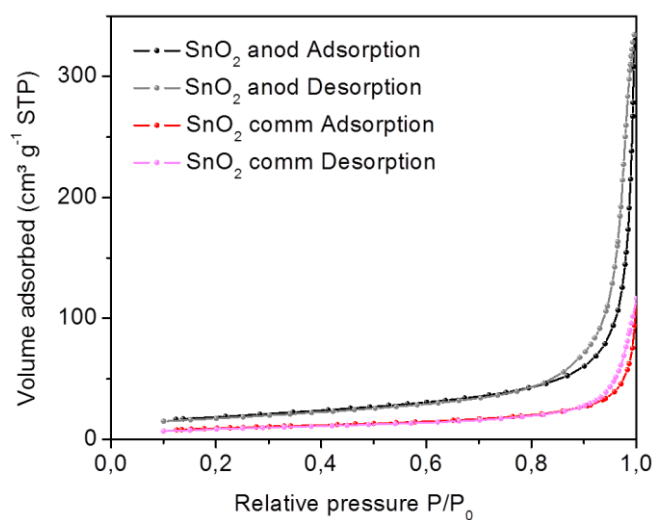


Figure S2 N₂ adsorption/desorption isotherms for SnO₂ prepared via anodic oxidation and commercial.

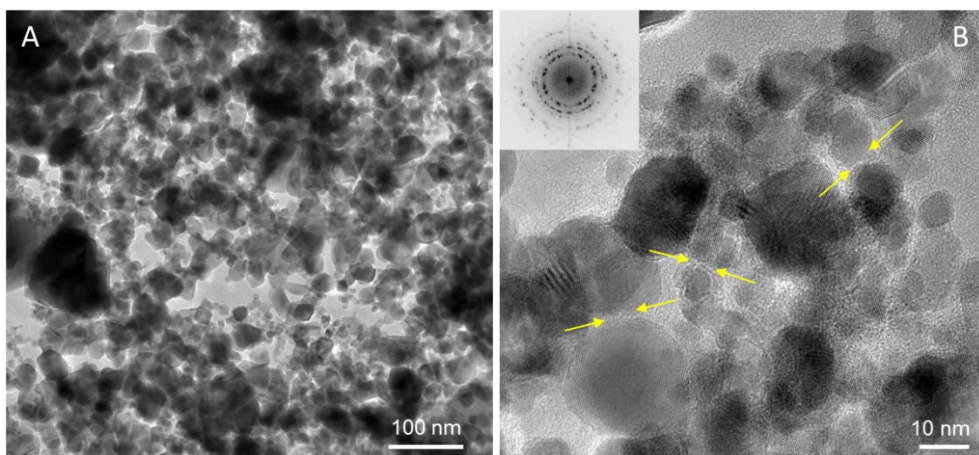


Figure S3 TEM image at two different magnification of the commercial SnO_2 . In the inset the FFT of picture (b) is also reported.

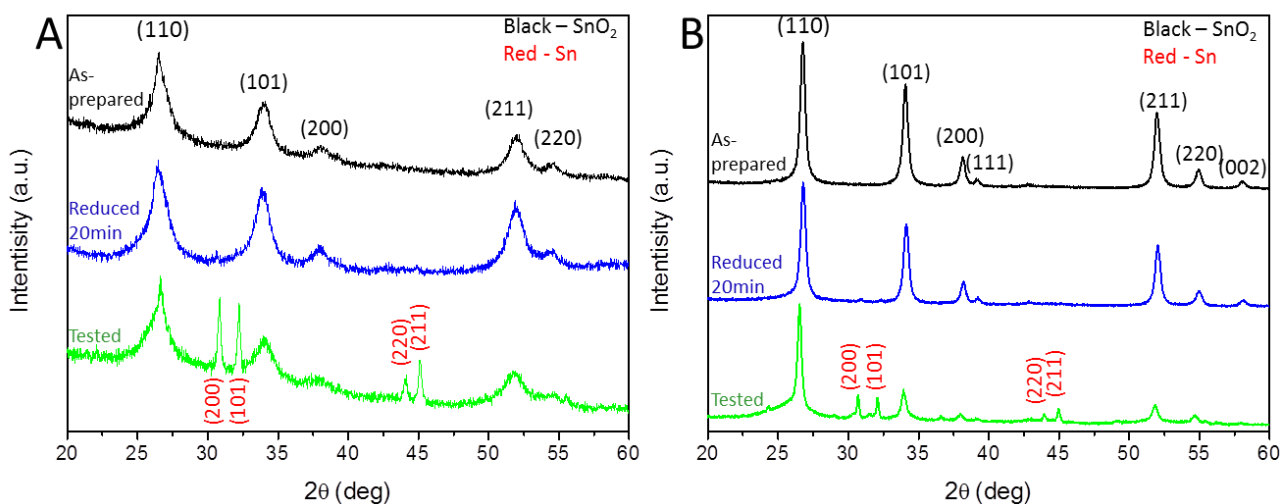


Figure S4 XRD patterns of (a) SnO_2 -anod and (b) SnO_2 -comm electrodes (as-prepared, reduced for 20min and tested).

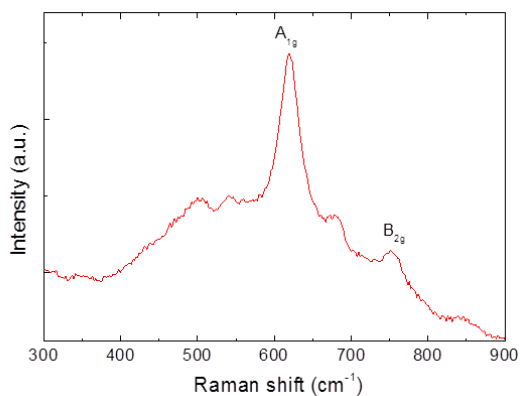


Figure S5 Raman spectrum of as-prepared SnO_2 -anod electrode.

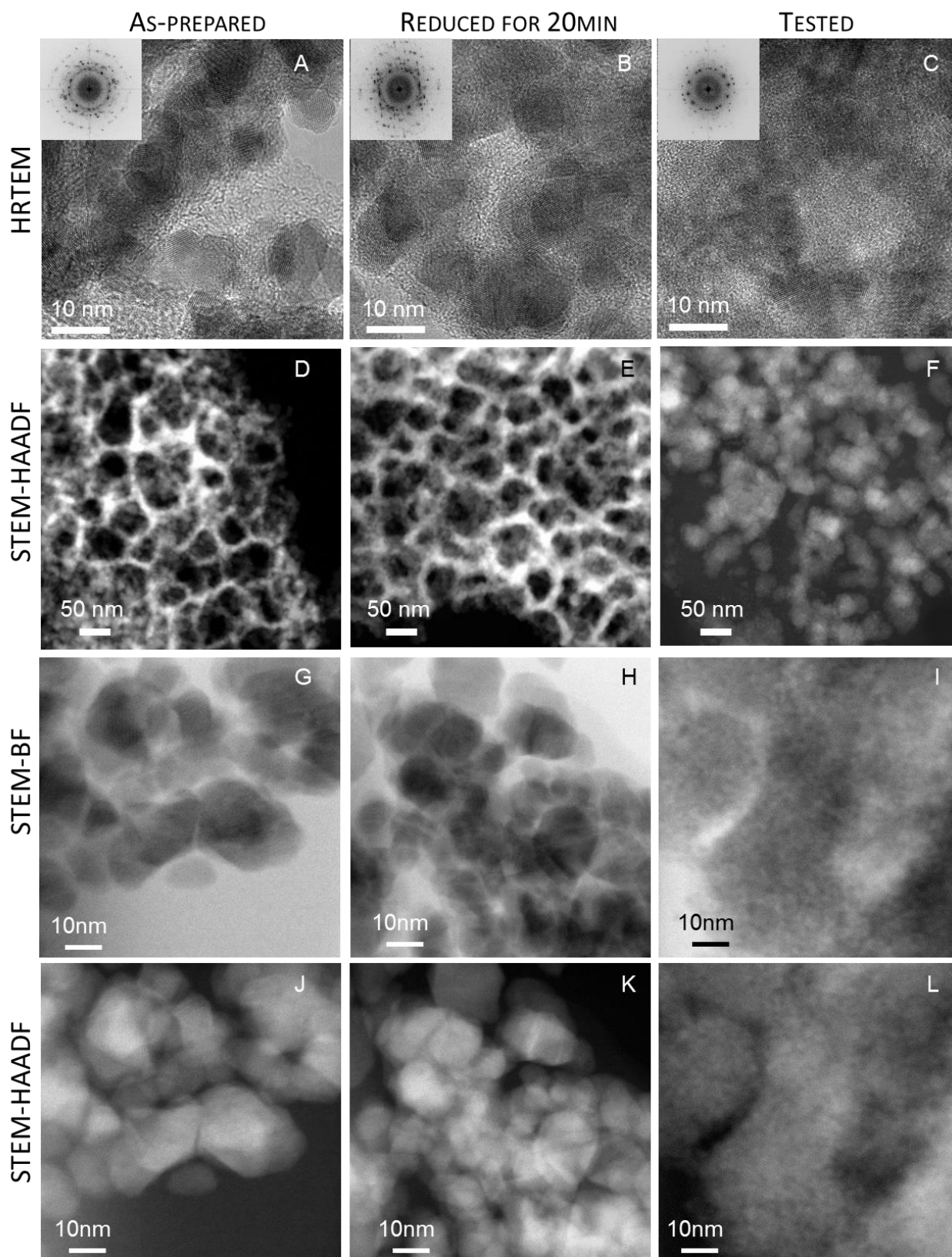


Figure S6 TEM study of the crystals evolution of the SnO₂-anod, including the as-prepared, reduced for 20 minutes and long term tested material. In the rows the following images are shown: HRTEM with FFT (of the shown area) in the inset, low magnification HAADF-STEM image, high magnification BF-STEM and HAADF-STEM.

The double-layer capacitance (C_{dl}) values of the SnO₂-comm, SnO₂-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} .

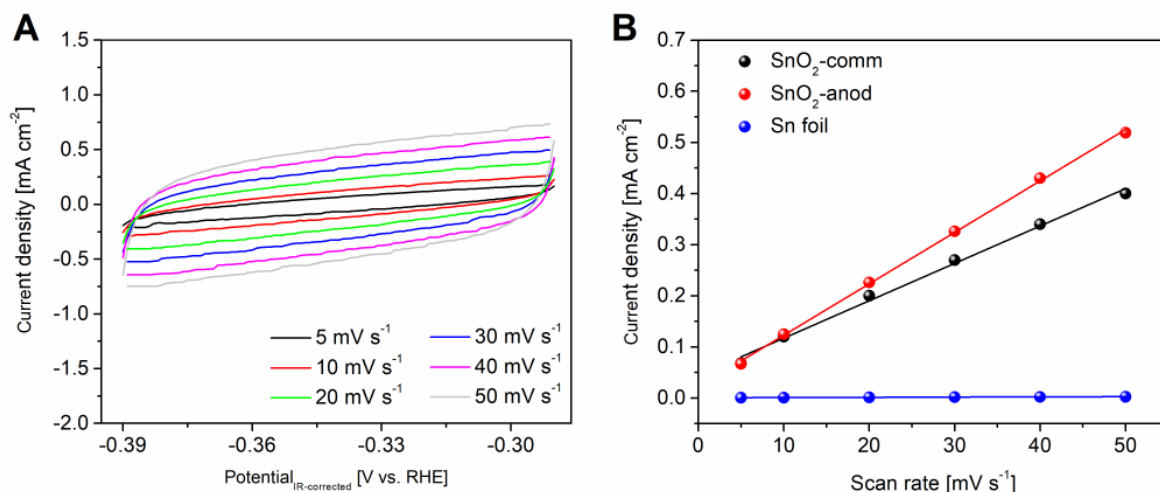


Figure S7 Determination of double-layer capacitance for various electrodes in CO₂-saturated 0.1 M KHCO₃: (a) representing CVs on SnO₂-anod electrode; (b) Capacitance values calculated from the slopes of current densities vs. scan rate.

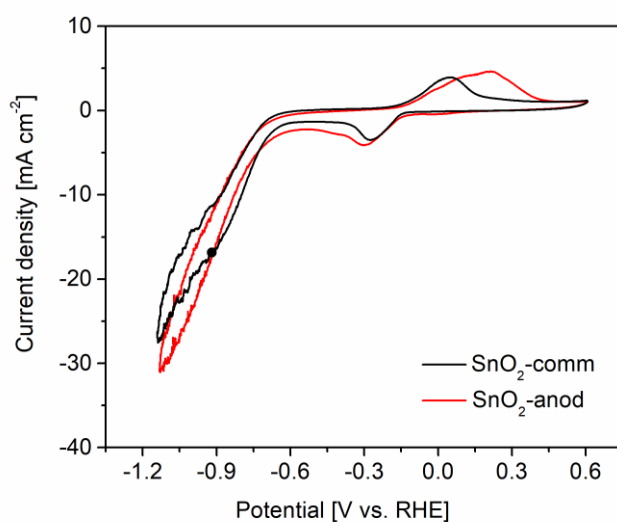


Figure S8 Comparison of the voltammograms of SnO₂-comm and SnO₂-anod in the CO₂-saturated electrolyte.

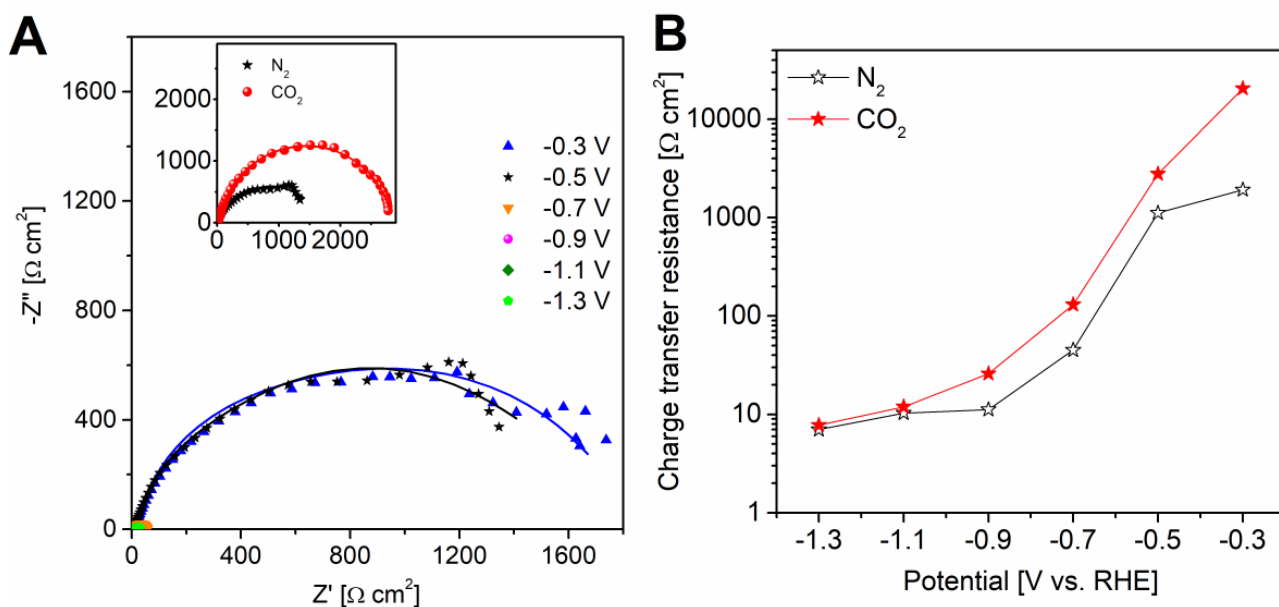


Figure S9 EIS analysis on a Sn foil electrode: (a) Nyquist plots obtained in N₂-saturated electrolyte (the points are experimental data, the lines are the curves calculated through fitting). In the inset, the two spectra acquired at -0.5 V in N₂- and CO₂-saturated solutions are shown. (b) Charge transfer resistances reported as a function of the potential.

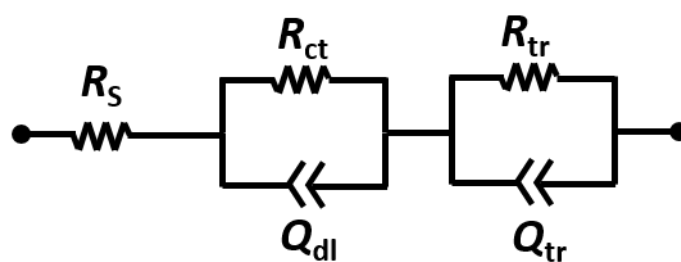


Figure S10 Equivalent circuit used for fitting of EIS data.

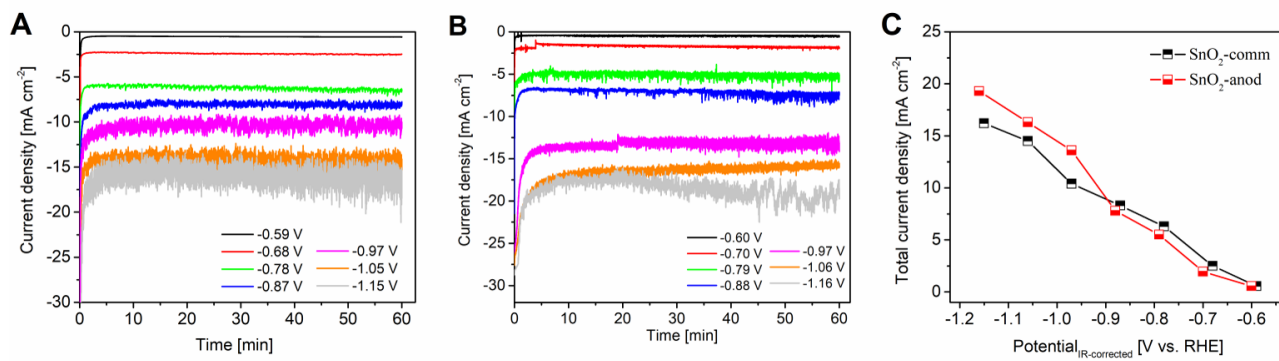


Figure S11 CA measurements carried out in CO₂-saturated 0.1 M KHCO₃ aqueous solution at different potentials: (a) SnO₂-comm; (b) SnO₂-anod; (c) Comparison of total current densities on SnO₂-comm and SnO₂-anod electrodes at various potentials.

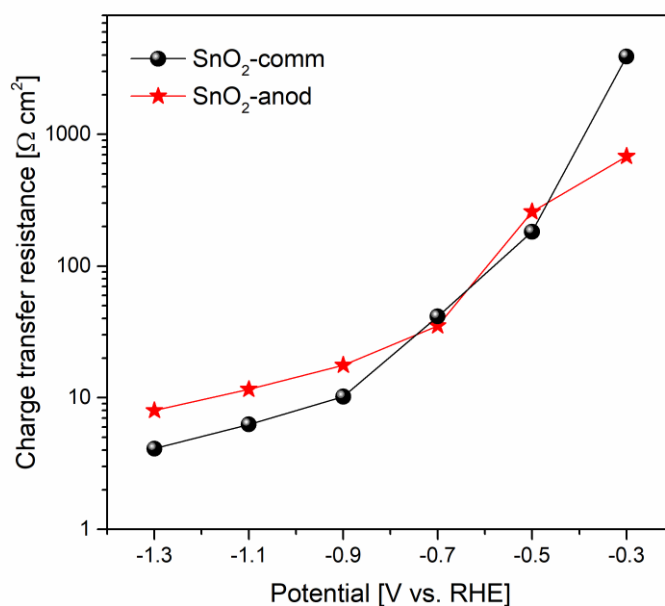


Figure S12 Comparison of charge transfer resistance obtained from EIS on SnO₂-comm and SnO₂-anod electrodes at various potentials.

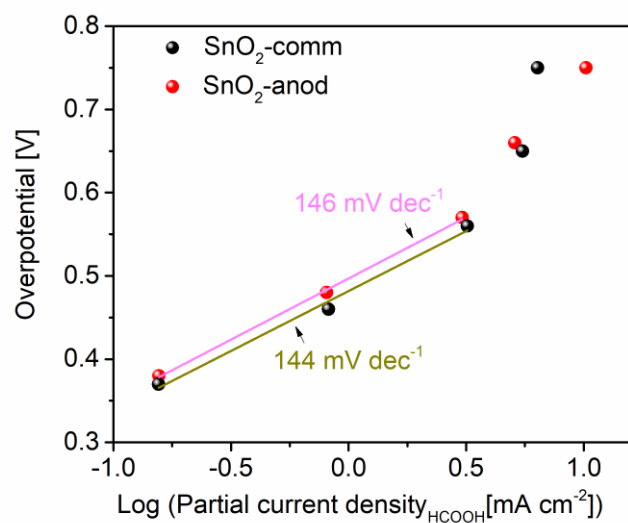


Figure S13 Tafel plot analysis for HCOOH production on SnO₂-comm and SnO₂-anod electrodes.

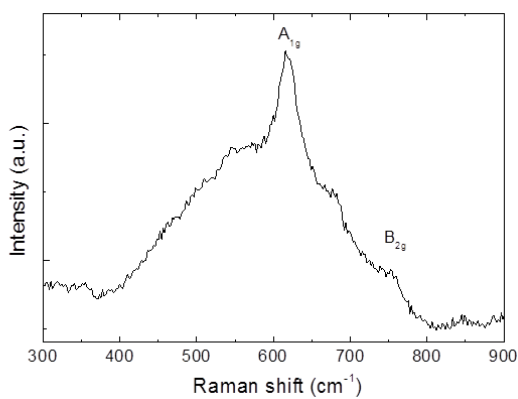


Figure S14 Raman spectrum of tested SnO₂-anod electrode.

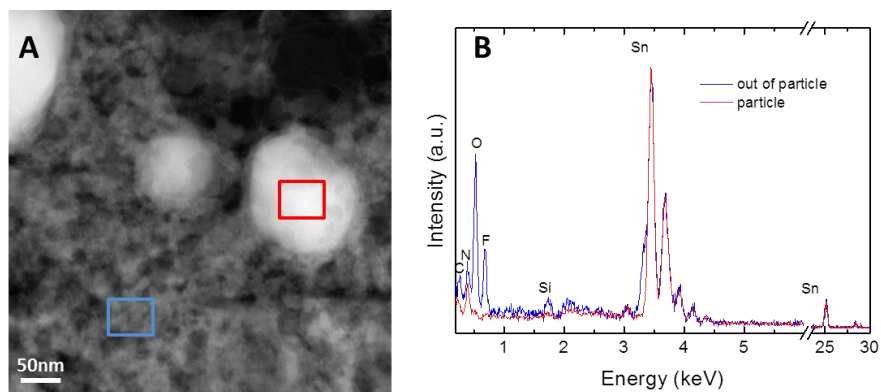


Figure S15 STEM image of the cross-section lamella of tested SnO₂-anod electrode (a) and EDX measurement performed locally in the particle and out of the particle (b).

Table S1 Comparison of electrocatalytic performance for reducing CO₂ 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
SnO ₂ 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

References

- (1) Hu H., Gui L., Zhou W., Sun J., Xu J., Wang Q., He B., Zhao L. Partially reduced Sn/SnO₂ porous hollow fiber: A highly selective, efficient and robust electrocatalyst towards carbon dioxide reduction. *Electrochimica Acta* **2018**, 285, 70-77.
- (2) Li F., Chen L., Knowles G.P., MacFarlane D.R., Zhang J. Hierarchical Mesoporous SnO₂ Nanosheets on Carbon Cloth: A Robust and Flexible Electrocatalyst for CO₂ Reduction with High Efficiency and Selectivity, *Angew. Chem. Int. Ed.* **2017**, 56, 505-509.
- (3) Li Y., Qiao J., Zhang X., Lei T., Girma A., Liu Y., Zhang J. Rational Design and Synthesis of SnO_x Electrocatalysts with Coralline Structure for Highly Improved Aqueous CO₂ Reduction to Formate. *ChemElectroChem* **2016**, 3, 1618 – 1628.
- (4) Zhao C.C., Wang J.L. Electrochemical reduction of CO₂ to formate in aqueous solution using electro-deposited Sn catalysts. *Chem. Eng. J.* **2016**, 293, 161–170.
- (5) Wang Q., Dong H., Yu H. Fabrication of a novel tin gas diffusion electrode for electrochemical reduction of carbon dioxide to formic acid. *RSC Adv.* **2014**, 4, 59970–59976.
- (6) Lee S., Ocon J.D., Son Y., Lee J. Alkaline CO₂ Electrolysis toward Selective and Continuous HCOO⁻ Production over SnO₂ Nanocatalysts. *J. Phys. Chem. C* **2015**, 119, 4884–4890.
- (7) Zhang, S., Kang, P., Meyer, T.J. Nanostructured Tin Catalysts for Selective Electrochemical Reduction of Carbon Dioxide to Formate. *J. Am. Chem. Soc.* **2014**, 136, 1734–1737.
- (8) Won D.H., Choi C.H., Chung J.H., Chung M.W., Kim E.H., Woo S.I. Rational Design of a Hierarchical Tin Dendrite Electrode for Efficient Electrochemical Reduction of CO₂. *ChemSusChem* **2015**, 8, 3092–3098.
- (9) Surya Prakash G.K., Viva F.A., Olah G.A. Electrochemical reduction of CO₂ over Sn-Nafion coated electrode for a fuel-cell-like device. *J. Power Sources* **2012**, 223, 68–73.
- (10) Yu J., Liu H., Song S., Wang Y., Tsiakaras P. Electrochemical reduction of carbon dioxide at nanostructured SnO₂/carbon aerogels: The effect of tin oxide content on the catalytic activity and formate selectivity. *Appl. Catal A, General* **2017**, 545, 159–166.
- (11) Kumar B., Atla V., Brian J.P., Kumari S., Nguyen T.Q., Sunkara M., Spurgeon J.M. Reduced SnO₂ Porous Nanowires with a High Density of Grain Boundaries as Catalysts for Efficient Electrochemical CO₂-into-HCOOH Conversion. *Angew. Chem. Int. Ed.* **2017**, 56, 3645 –3649.
- (12) Zhang B., Guo Z., Zuo Z., Pan W., Zhang J. The Ensemble Effect of Nitrogen Doping and Ultrasmall SnO₂ Nanocrystals on Graphene Sheets for Efficient Electroreduction of Carbon Dioxide. *Appl. Catal B. Environ.* **2018**, 239, 441–449.

- (13) Fu Y., Li Y., Zhang X., liu Y., Zhou X., Qiao J. Electrochemical CO₂ reduction to formic acid on crystalline SnO₂ nanosphere catalyst with high selectivity and stability. *Chinese Journal of Catalysis* **2016**, 37, 1081–1088.
- (14) Ge H., Gu Z., Han P., Shen H., Al-Enizi A. M., Zhang L., Zheng G. J. Mesoporous Tin Oxide for Electrocatalytic CO₂ Reduction. *Colloid Interface Sci.* **2018**, 531, 564-569.