Supporting information for

**Anodic SnO$_2$ Porous Nanostructures with Rich Grain Boundaries for Efficient CO$_2$ Electroreduction to Formate**

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Fig. S1 (a, b) SEM images taken from the surface of SnO$_2$-AO$_8$ and SnO$_2$-AO$_{12}$, and (c, d) their corresponding pore size distribution graphs.
Fig. S2 SEM image taken from the cross-section of SnO$_2$-AO$_{10}$.
Fig. S3 High-resolution TEM image of SnO$_2$-AO$_{10}$ nanostructures.
Fig. S4 XRD patterns of Sn foil, SnO$_2$-A0$_8$ and SnO$_2$-A0$_{12}$ nanostructures.
Fig. S5 Polarization curves obtained on (a) Sn plate, (b) SnO\textsubscript{2}-AO\textsubscript{8}, and (c) SnO\textsubscript{2}-AO\textsubscript{12} in N\textsubscript{2} and CO\textsubscript{2} saturated 0.5 M KHCO\textsubscript{3} solution with a scan rate of 50 mV s\textsuperscript{-1}.
Fig. S6 Current density curves of samples recorded at -0.8 V vs. RHE in 0.5 M KHCO$_3$ with the CO$_2$ flow rate of 2 mL min$^{-1}$. 
**Fig. S7** Electrochemical Impedance Spectroscopy (EIS) analysis SnO$_2$-AO$_8$, SnO$_2$-AO$_{10}$ and SnO$_2$-AO$_{12}$ electrode in CO$_2$ saturated 0.5 M KHCO$_3$ solution. The inset is an equivalent circuit diagram for fitting the Nyquist plot. Note: the diameter of the semicircle for SnO$_2$-AO$_{10}$ is smaller than that of both SnO$_2$-AO$_8$ and SnO$_2$-AO$_{12}$, signifying that SnO$_2$-AO$_{10}$ exhibits the smallest charge-transfer resistance ($R_{ct}$). It is well accepted that the crystallinity of an electroactive material governs its electrical conductivity, which in turn affects significantly its electrocatalytic performance. Consequently, the lower activity of the other two SnO$_2$ nanostructures (i.e., SnO$_2$-AO$_8$ and SnO$_2$-AO$_{12}$) might be due to their poorer crystallinity (cf. **Fig.3d** & **Fig. S4**) which limits the electrical conductivity.
Fig. S8 H₂, CO, and HCOOH FE as a function of electrolysis time on Sn plate electrode at the potential from -0.7 to -1.2 V vs. RHE.
Fig. S9 GC Spectra of products detected on Sn plate at different potentials.
Fig. S10 $H_2$, CO, and HCOOH FE as a function of electrolysis time on SnO$_2$-AO$_8$ electrode at the potential from -0.7 to -1.2 V vs. RHE.
**Fig. S11** $\text{H}_2$, CO, and HCOOH FE as a function of electrolysis time on SnO$_2$-AO$_{10}$ electrode at the potential from -0.7 to -1.2 V vs. RHE.
Fig. S12 H$_2$, CO, and HCOOH FE as a function of electrolysis time on SnO$_2$-AO$_{12}$ electrode at the potential from -0.7 to -1.2 V vs. RHE.
Fig. S13 SEM image of SnO$_2$-AO$_{10}$ after CO$_2$RR at -0.8 V vs. RHE for 180 min. The yellow ellipses indicate the presence of macropores.
**Fig. S14** XRD patterns of SnO$_2$-AO$_{10}$ after CO$_2$RR under -0.8 V (vs RHE) for 180 min. Signals of both metallic Sn and SnO$_2$ were detected. The weak intensity is due to the scarcity of the sample that was collected after reaction. The strong peak at 22$^\circ$ arises from the carbon black.
**Fig. S15** Depth XPS analysis (sputtering rate: 0.72 nm/s, sputtering time: 300 s) of SnO$_2$-A0$_{10}$ after CO$_2$RR at -0.8 V vs. RHE for 180 min.
Table S1. Comparison of working potentials and FEs for CO, HCOOH and C1 of Sn-based CO₂RR from the literature and this work.

| Sn-based Catalysts          | Electrolyte       | Potential * (V vs. RHE) | FE max (%) | Reference |
|-----------------------------|-------------------|-------------------------|------------|-----------|
|                             |                   |                         | CO         | HCOOH     | CO+HCOOH  |               |
| SnO₂@Carbon                 | 0.1M NaHCO₃       | -1.19                   | NA         | 96.3      | NA        | 1            |
| SnO₂‐50                     | 0.5M KHCO₃        | -0.56V vs.SHE           | NA         | 56        | NA        | 2            |
| Graphene confined Sn quantum sheets | 0.1M NaHCO₃     | -1.16                   | NA         | 89        | NA        | 3            |
| Sn-pNW                      | 0.1M KHCO₃        | -0.8                    | 14         | 78        | 92        | 4            |
| Core/Shell Cu/SnO₂ Structure| 0.5M KHCO₃       | -0.7                    | 93         | NA        | NA        | 5            |
| Urchin-like SnO₂            | 0.5M KHCO₃       | -1.4                    | NA         | 62        | NA        | 6            |
| Mesoporous SnO₂             | 0.1M KHCO₃       | -0.8                    | 38         | ~40       | ~80       | 7            |
| SnO/C                       | 0.5M KHCO₃       | -0.66                   | 37         | NA        | NA        | 8            |
| Tin oxide NP                | 0.5 mol dm⁻³      | -0.4                    | NA         | 70        | NA        | 9            |
| porous Sn₀₂₉In₀₇₁            | 0.1M NaHCO₃       | -1.0                    | ~13        | 59.2      | ~72       | 10           |
| Sn/SnO₂ porous hollow fiber | 0.1M KHCO₃       | -0.95                   | ~10        | 82.1      | 93        | 11           |
| SnO₂/AgO₃                   | 0.1 M KHCO3      | -0.8                    | ~60        | 21.1      | 95        | 12           |
| CuSn-NW Air                 | 0.5M KHCO₃       | -1.0                    | NA         | 90.2      | NA        | 13           |
| CuSn-NW Air                 | 0.5M KHCO₃       | -0.9                    | NA         | 81.2      | NA        | 13           |
| SnO₂-AO₈                    | 0.5MKHCO₃        | -0.8                    | 15.7       | 55.8      | 71.5      | This work    |
| SnO₂-AO₈                    | 0.5MKHCO₃        | -1.0                    | 6          | 78        | 84        | This work    |
| SnO₂-AO₁₀                   | 0.5MKHCO₃        | -0.8                    | 22         | 72.9      | ~95       | This work    |
| SnO₂-AO₁₀                   | 0.5MKHCO₃        | -0.9                    | 15         | 76.4      | 91.4      | This work    |
| SnO₂-AO₁₂                   | 0.5MKHCO₃        | -0.8                    | 15.6       | 68.1      | 83.7      | This work    |
| SnO₂-AO₁₂                   | 0.5MKHCO₃        | -1.0                    | 5          | 81.7      | 87        | This work    |

Note: The potentials were converted to RHE scale based on the equation, \(E(\text{RHE}) = E(\text{Ag/AgCl}) + 0.0591 \times \text{pH} + 0.210 \text{V}\) or \(E(\text{RHE}) = E(\text{SCE}) + 0.0591 \times \text{pH} + 0.242 \text{V}\) by assuming the pH of CO₂-saturated 0.5 M and 0.1 M NaHCO₃ or KHCO₃ is 7.2 and 6.8, respectively. * the best value reported.

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