

## Electronic Supplementary Information

### **Pore-Structure-Directed CO<sub>2</sub> Electroreduction to Formate on SnO<sub>2</sub>/C Catalysts**

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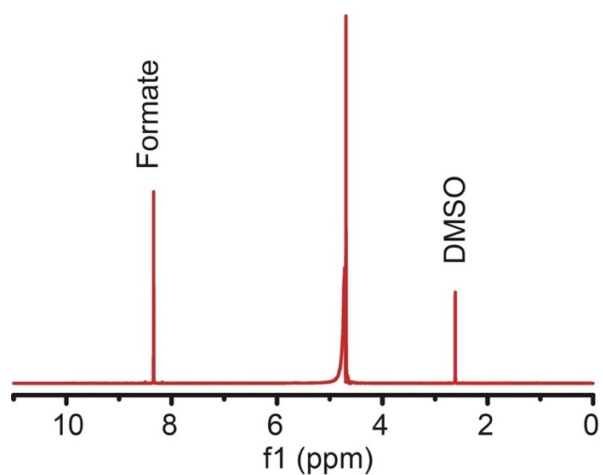
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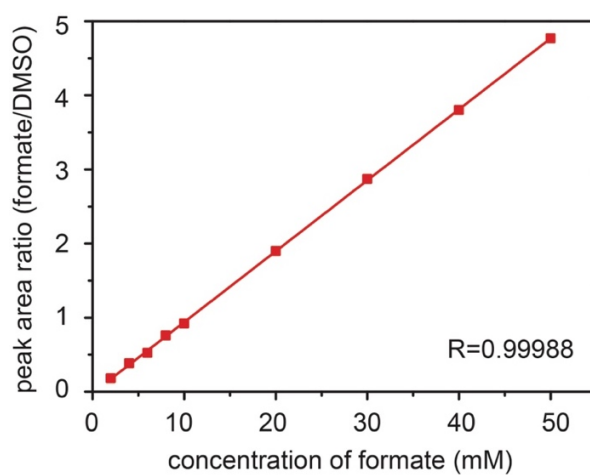
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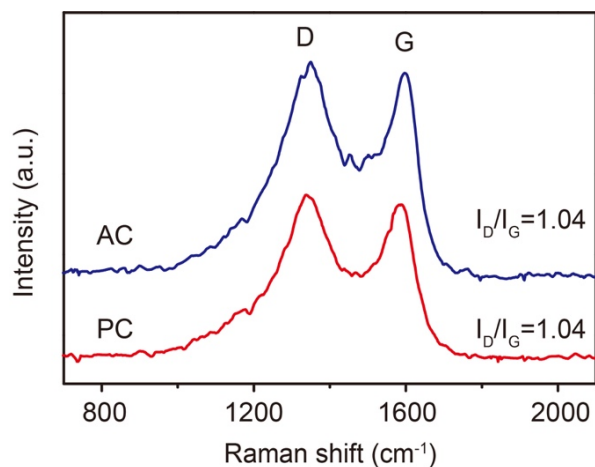
This file includes Fig. S1-S11 and Table S1-S2



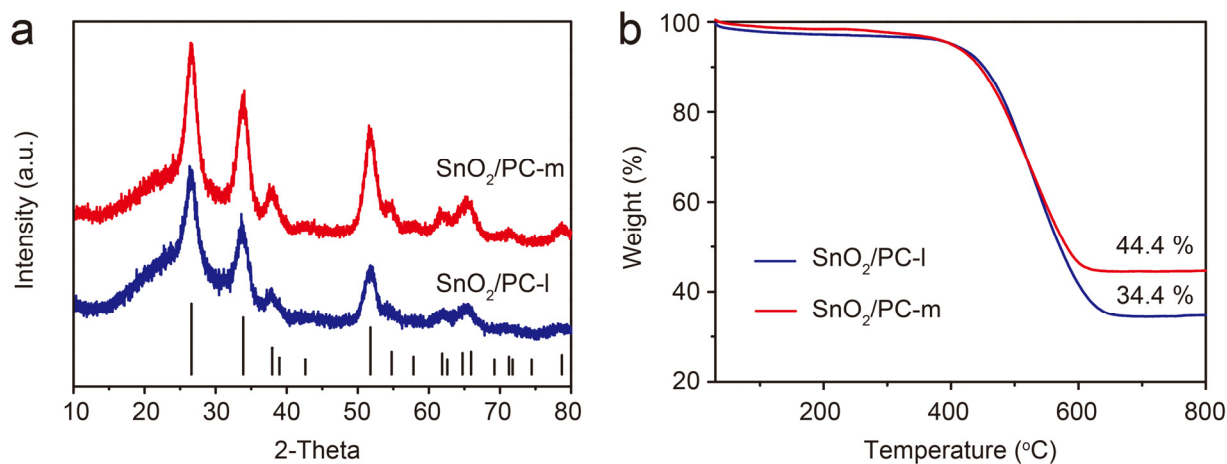
**Fig. S1** NMR spectrum of the cathodic electrolyte after 1 h of CO<sub>2</sub> reduction at -1.16 V.



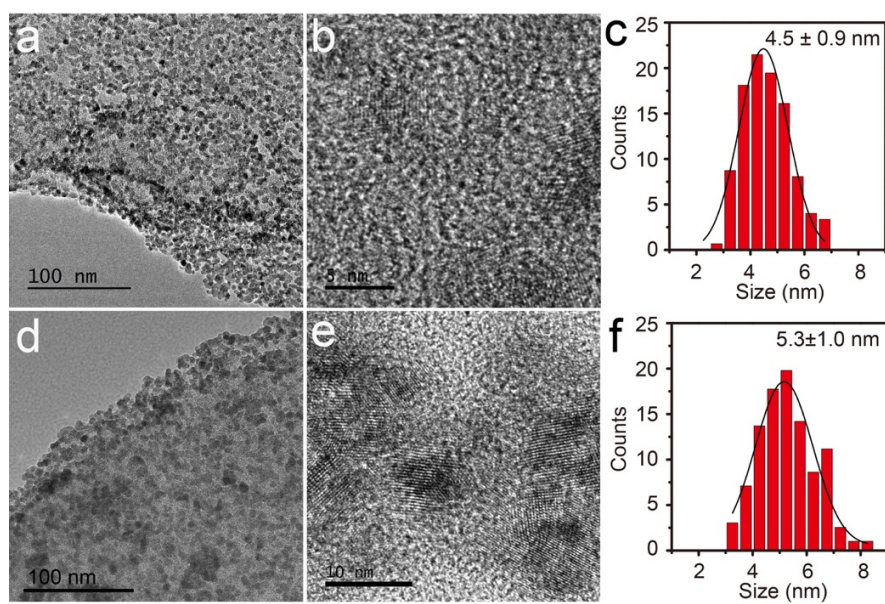
**Fig. S2** The calibration curve for formate with different concentrations.



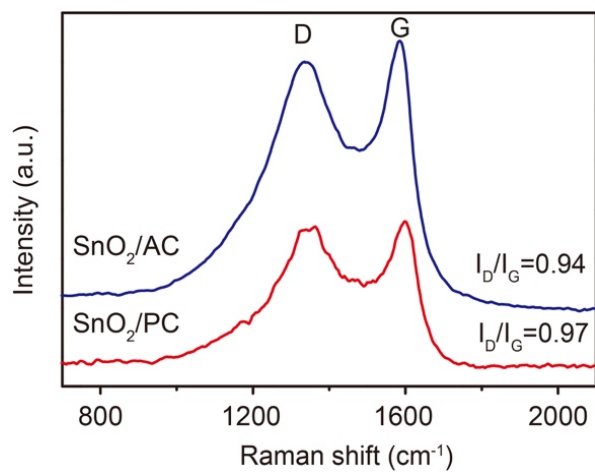
**Fig. S3** The Raman spectra for PC and AC.



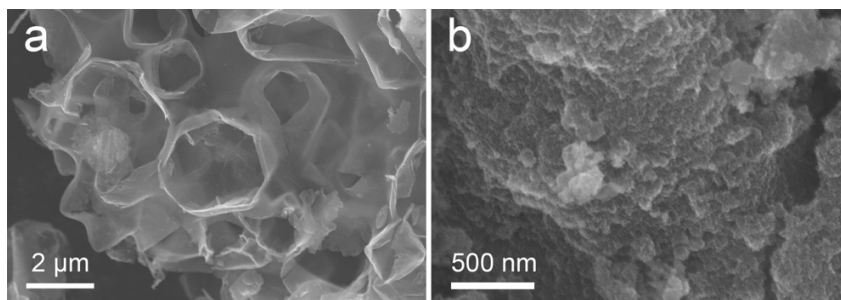
**Fig. S4** (a) XRD patterns and (b) TG curves of SnO<sub>2</sub>/PC with lower feeding amount of stannous chloride (0.02 mM, denoted as SnO<sub>2</sub>/PC-m) and higher feeding amount of stannous chloride (0.04 mM, denoted as SnO<sub>2</sub>/PC-l).



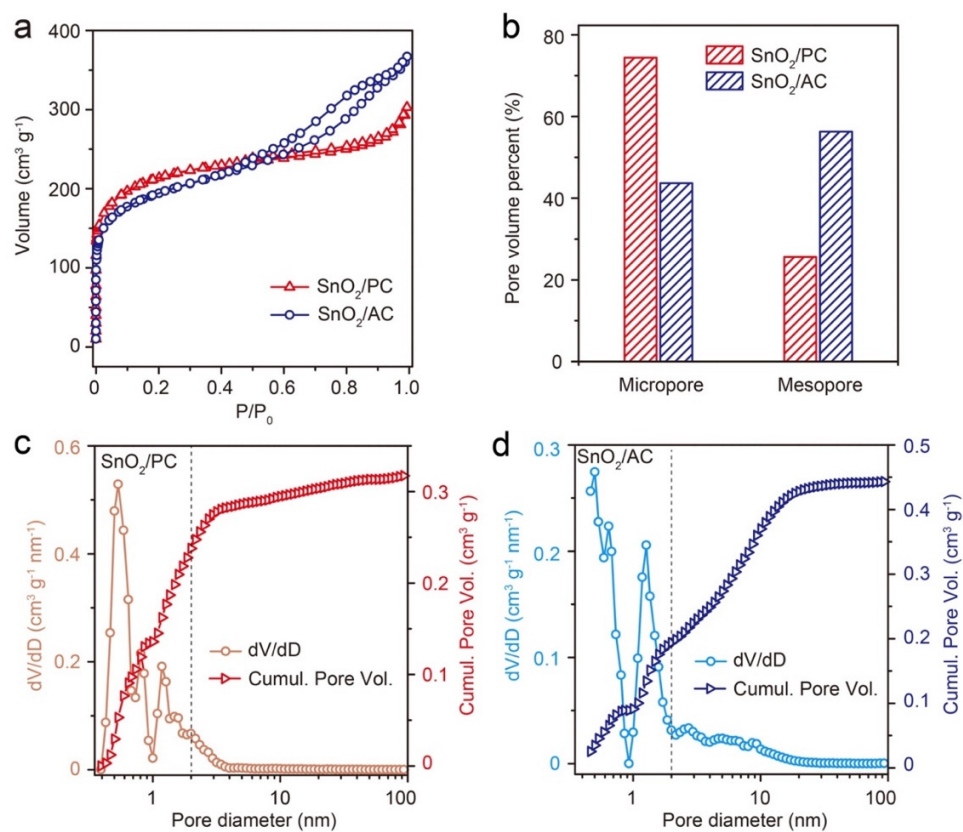
**Fig. S5** TEM images and size distributions of SnO<sub>2</sub>/PC with (a-c) lower feeding amount of stannous chloride (0.02 mM) and (d-f) higher feeding amount of stannous chloride (0.04 mM).



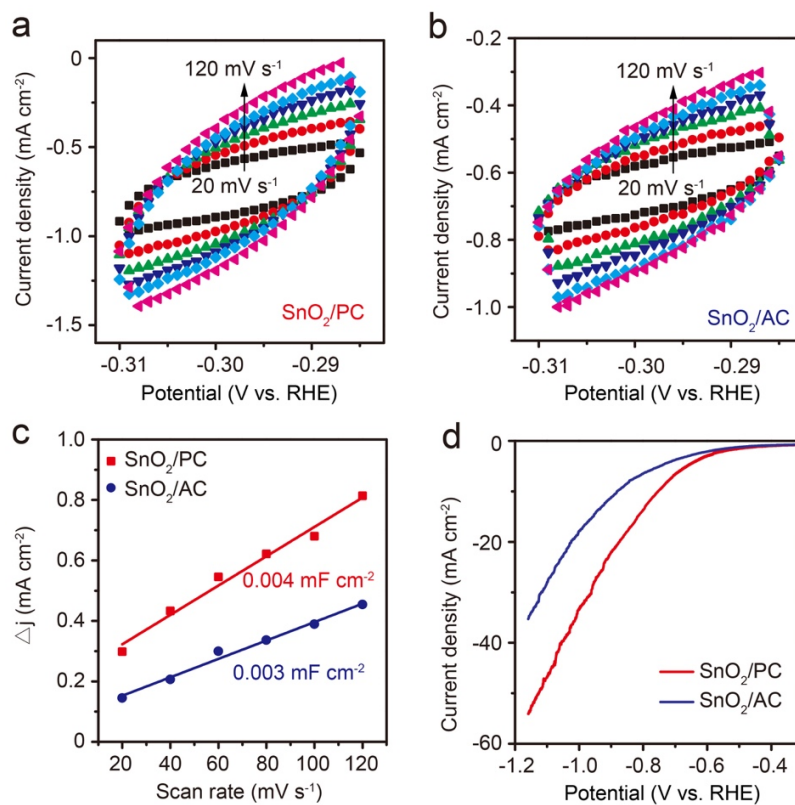
**Fig. S6** The Raman spectra for SnO<sub>2</sub>/PC and SnO<sub>2</sub>/AC.



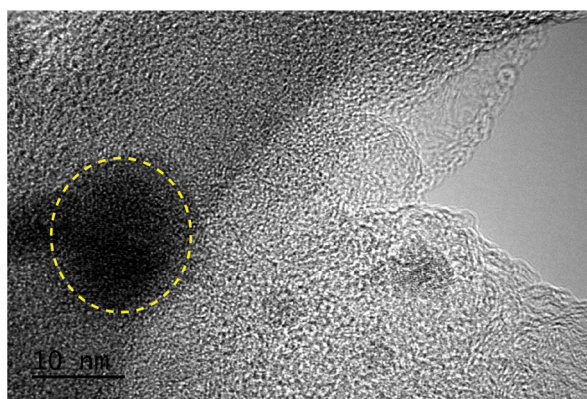
**Fig. S7** SEM images of (a) SnO<sub>2</sub>/PC and (b) SnO<sub>2</sub>/AC.



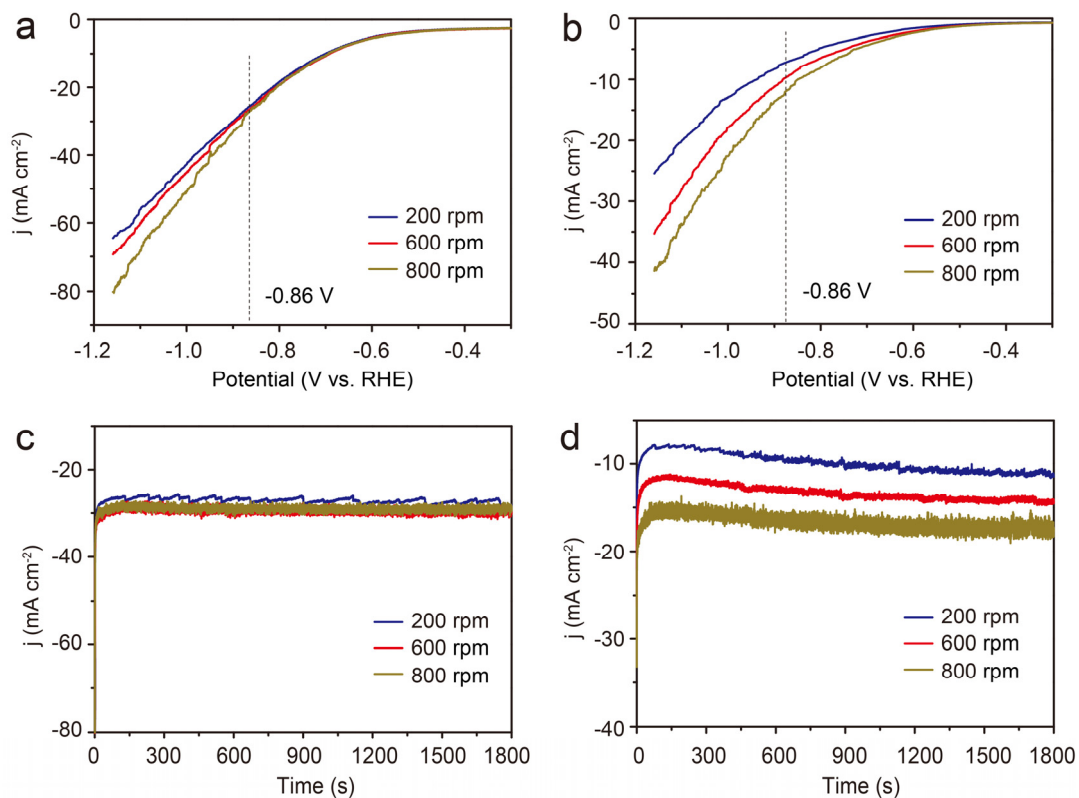
**Fig. S8** (a) Nitrogen sorption isotherms and (b) micropore and mesopore volume distribution for SnO<sub>2</sub>/PC and SnO<sub>2</sub>/AC; (c) pore size distribution for SnO<sub>2</sub>/PC and (d) pore size distribution for SnO<sub>2</sub>/AC.



**Fig. S9** CVs of (a) SnO<sub>2</sub>/PC and (b) SnO<sub>2</sub>/AC at different scan rates from 20 to 120 mV s<sup>-1</sup>; (c) Plots of current density as a function of scan rate and (d) LSV curves normalized by ECSA of SnO<sub>2</sub>/PC and SnO<sub>2</sub>/AC.



**Fig. S10** TEM image of SnO<sub>2</sub>/PC after 10 h electrolysis.



**Fig. S11** LSV of the CO<sub>2</sub> electroreduction under different rotation speed for (a) SnO<sub>2</sub>/PC and (b) SnO<sub>2</sub>/AC; Current versus time curve under different rotation speed of (c) SnO<sub>2</sub>/PC and (d) SnO<sub>2</sub>/AC in CO<sub>2</sub>-saturated 0.5 M KHCO<sub>3</sub> aqueous solution at applied potential of -0.86 V for 0.5 h.

**Table S1** BET surface area and pore volume of PC, SnO<sub>2</sub>/PC, AC and SnO<sub>2</sub>/AC.

Sample	PC	SnO <sub>2</sub> /PC	AC	SnO <sub>2</sub> /AC
BET surface area (m <sup>2</sup> /g)	1268	788	1185	714
Pore volume (m <sup>2</sup> /g)	0.73	0.47	0.98	0.57



**Table S2** Comparison of the electrocatalytic performance for reducing CO<sub>2</sub> to formate on different catalysts and electrolytes.

Catalysts	Electrolyte	E (V) <sup>[a]</sup>	$j^{\text{total}}$ (mA cm <sup>-2</sup> ) <sup>[b]</sup>	FE <sub>formate</sub> <sup>[c]</sup>	Ref.
<b>SnO<sub>2</sub>/porous C</b>	0.5 M KHCO <sub>3</sub>	-0.86 vs. RHE	32	92%	This work
<b>Sn GDE<sup>[d]</sup></b>	0.5 M KHCO <sub>3</sub>	-1.8 vs. Ag/AgCl	13.45	73%	1
<b>Sn GDE</b>	0.5 M KHCO <sub>3</sub>	-1.8 vs. Ag/AgCl	22.2	78.6%	2
<b>Sn foil</b>	0.1 M KHCO <sub>3</sub>	-1.8 vs. Ag/AgCl	2.5	91%	3
<b>Sn foil</b>	0.5 M KHCO <sub>3</sub>	-2.0 vs. SCE	28	63.5%	4
<b>SnO<sub>2</sub></b>	0.5 M NaOH	-0.6 vs. RHE	3.5	67.6%	5
<b>Sn/SnO<sub>x</sub>/Ti foil</b>	0.5M NaHCO <sub>3</sub>	-0.7 vs. RHE	~2	~38%	6
<b>Sn-Carbon Nanofiber</b>	0.5 M KHCO <sub>3</sub>	-0.8 vs. RHE	17.74	62%	7
<b>SnO<sub>2</sub>/graphene</b>	0.1 M NaHCO <sub>3</sub>	-1.8 vs. SCE	10.2	93.6%	8
<b>SnO<sub>x</sub>/carbon black</b>	0.1 M NaHCO <sub>3</sub>	-1.16 vs. RHE	5.4	86%	8
<b>Electrodeposited Sn</b>	0.1 M KHCO <sub>3</sub>	-1.4 vs. SCE	15	91%	9
<b>Sn dendrite</b>	0.1 M KHCO <sub>3</sub>	-1.36 vs. RHE	17.1	71.6%	10
<b>Sn foam</b>	0.1 M NaHCO <sub>3</sub>	-2.0 vs. Ag/AgCl	23.5	90%	11
<b>Sn/Nafion GDE</b>	0.5 M NaHCO <sub>3</sub>	-1.6 vs. NHE	27	70%	12
<b>Porous Sn Nanowires</b>	0.1 M KHCO <sub>3</sub>	-0.8 vs. RHE	6	80.1%	4
<b>Ag-Sn core-shell Nanoparticles</b>	0.5 M NaHCO <sub>3</sub>	-0.8 vs. RHE	19.5	80%	13

[a] applied potential at the maximum FE<sub>formate</sub>; [b] Total current density at the maximum FE<sub>formate</sub>; [c] Maximum FE<sub>formate</sub>; [d] Gas diffusion electrode.

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