## **Supporting Information**

## Revealing the role of aniline in assisting SnO<sub>2</sub> electrocatalytic CO<sub>2</sub> reduction to HCOOH: via the perspective of reaction pathway

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Fig. S1. Pictures of (a) H-type cell and (b) flow cell with an observable gas diffusion electrode.



Fig. S2. (a) XPS survey spectra of SnO<sub>2</sub>/OCNTs, SnO<sub>2</sub>/PDA<sub>0.25</sub>-OCNTs, SnO<sub>2</sub>/PDA<sub>0.5</sub>-OCNTs, SnO<sub>2</sub>/PDA<sub>0.75</sub>-OCNTs, and SnO<sub>2</sub>/PDA<sub>1</sub>-OCNTs. (b) Weight loss curves of SnO<sub>2</sub>/OCNTs, SnO<sub>2</sub>/PDA<sub>0.25</sub>-OCNTs, SnO<sub>2</sub>/PDA<sub>0.5</sub>-OCNTs, SnO<sub>2</sub>/PDA<sub>0.75</sub>-OCNTs, and SnO<sub>2</sub>/PDA<sub>1</sub>-OCNTs.



Fig. S3. TEM images of (a) OCNTs, (b) PDA<sub>0.25</sub>-OCNTs, (c) PDA<sub>0.5</sub>-OCNTs, (d) PDA<sub>0.75</sub>-OCNTs, and (e) PDA<sub>1</sub>-OCNTs. HR-TEM images of (a) OCNTs, (b) PDA<sub>0.5</sub>-OCNTs, (c) PDA<sub>1</sub>-OCNTs.



Fig. S4. (a) LSV curves obtained in 0.1 M KHCO<sub>3</sub> electrolytes saturated with  $N_2$ , (b) Faradaic efficiencies of  $H_2$ , (c) partial current densities of  $H_2$ , (d) Faradaic efficiencies of CO, (e) partial current densities of CO, and (f) current densities of total C1 products over as-prepared catalysts at different applied potentials.



Fig. S5. (a) N 1s XPS spectrum of t-PDA<sub>0.5</sub>-OCNTs. (b) Current densities and (c) Faradaic efficiencies of PDA<sub>0.5</sub>-OCNTs and t-PDA<sub>0.5</sub>-OCNTs at different applied potentials.



Fig. S6. (a) Stability tests of  $SnO_2/OCNTs$  at -1.29 V. TEM images of (b)  $SnO_2/PDA_{0.5}$ -OCNTs and (c)  $SnO_2/OCNTs$  after stability tests.



Fig. S7. *In-situ* FT-IR spectra of SnO<sub>2</sub>/OCNTs at different applied potentials.



Fig. S8. Current densities over (a)  $SnO_2/PDA_{0.5}$ -OCNTs and (b)  $SnO_2/OCNTs$  at different applied potentials. (c) Stability tests over  $SnO_2/PDA_{0.5}$ -OCNTs at -1.83 V in the flow cell with 1 M KHCO<sub>3</sub>.

Samples	N content (at.%)		
SnO <sub>2</sub> /OCNTs	/		
SnO <sub>2</sub> /PDA <sub>0.25</sub> -OCNTs	2.62		
SnO <sub>2</sub> /PDA <sub>0.5</sub> -OCNTs	3.49		
SnO <sub>2</sub> /PDA <sub>0.75</sub> -OCNTs	3.93		
SnO <sub>2</sub> /PDA <sub>1</sub> -OCNTs	6.64		

Table. S1. The contents of N elements of as-prepared catalysts by XPS

Table. S2. Contents of elements in the carriers

C content	
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Catalysts	Electrolytes	Potential at FE <sub>max</sub>	FE <sub>HCOOH</sub>	<i>ј</i> нсоон	Stability	
		(V vs. RHE)	(%)	(mA cm <sup>-2</sup> )	(h)	Ref.
SnO <sub>2</sub> /PDA <sub>0.5</sub> -CNTO	0.1 M KHCO <sub>3</sub>	-1.29	89	-32	36	This work
SnO <sub>2</sub> /PDA <sub>0.5</sub> -CNTO	1 M KHCO <sub>3</sub>	-1.83	95	-166	12	This work
Vo-rich SnO <sub>2</sub>	0.5 M KHCO <sub>3</sub>	-1.1	~ 60	-40	30	[54]
SnO <sub>2</sub> @N-CNW	0.5 M NaHCO <sub>3</sub>	-0.8	90	-13.5	20	[55]
NW-SnO <sub>2</sub>	0.5 M KHCO <sub>3</sub>	-1.0	87.4	-22	18	[56]
SnO <sub>2</sub> ⊃NC@EEG	0.1 M KHCO <sub>3</sub>	-1.2	81.2	-11	10	[57]
Sn/CN-0.1	0.1 M KHCO <sub>3</sub>	-0.9	96	-3.42	10	[58]
SnO <sub>2</sub> nanosheet	0.1 M KHCO <sub>3</sub>	-1.01	85	-12.75	/	[59]
mSnO <sub>2</sub> NTs-350	0.5 M KHCO <sub>3</sub>	-1.3	90	-9	12	[60]
VO-rich N-SnO <sub>2</sub> NS	0.1 M KHCO <sub>3</sub>	-0.9	83	~ -6.7	10	[61]
SnO <sub>2</sub> -CNT pH-11	0.5 M KHCO <sub>3</sub>	-0.77	76	~ -3.5	10	[62]
VO-SnO <sub>x</sub> /CF-40	0.1 M KHCO <sub>3</sub>	-1.0	86	-30	8	[63]
CNT#SnO <sub>2</sub> NDs	0.1 M KHCO <sub>3</sub>	-0.9	70	-5.3	24	[64]
SnO <sub>2</sub> /OC	0.1 M KHCO <sub>3</sub>	-1.0	75	-15	8	[65]
NRS-SnO	1 M KOH	-0.7	87	-330	/	[66]

Table. S3. Summary of the reported  $CO_2ER$  performance over  $SnO_2$ -based electrocatalysts