Supporting Information

Identification of a new substrate effect that enhances the electrocatalytic activity of dendritic tin in CO_2 reduction

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Figure S1. SEM images of electrodeposited dendritic Sn catalysts on Pt and Cu foil substrates obtained by the potentiostatic method at a constant potential of -6 V vs. Ag/AgCl for 60 s.



Figure S2. Cyclic voltammograms obtained in N_2 saturated 0.5 M NaHCO₃ aqueous solution for (a, c, e, g) dendritic Sn on metal substrates over a potential range where double-layer charging and discharging are occurring. (b, d, f, h) display the double-layer capacitance behaviour of the dendritic Sn on metal substrates.



Figure S3. EDX elemental mapping of dendritic Sn on metal substrates.



Figure S4. XRD powder patterns for a bare Sn foil (substrate material).



Figure S5. Cyclic voltammograms obtained with dendritic (a) Sn/Pt, (b) Sn/Cu, (c) Sn/Sn and (d) Sn/In electrodes in CO_2 and N_2 saturated 0.5 M NaHCO₃ aqueous electrolyte solution at scan rates over the range of 30 to 100 mV s⁻¹.

Semi-quantitative estimation of the local pH and CO₂ concentration during electrolysis.



Figure S6. A simplified electrode geometry adopted for the estimation of surface pH and CO₂ concentration at a dendritic Sn/M electrode.

During electrolysis, both the HER and CO_2RR processes change the surface pH and CO_2 concentration, will both having an impact on the CO_2RR performance of the Sn/M electrode. Overall reactions are given in Eqns S1 and S2 for the bicarbonate medium and S3 and S4 for the phosphate buffer cases:

$$HCO_{3}^{-} + e^{-} \rightleftharpoons \frac{1}{2}H_{2} + CO_{3}^{2-}$$
 (S1)

$$CO_2 + 2e^- + HCO_3^- \rightleftharpoons HCOO^- + CO_3^{2-}$$
 (S2)

$$H_2 PO_4^- + e^- \rightleftharpoons \frac{1}{2} H_2 + HPO_4^{2-}$$
 (S3)

$$CO_2 + 2e^- + H_2PO_4^- \rightleftharpoons HCOO^- + HPO_4^{2-}$$
 (S4)

For simplicity, the CO formation reaction is not considered since it is much less significant in comparison with the formate formation reaction.

To calculate the surface concentrations, the electrode geometry needs be known. However, due to the complexity of the electrode geometry, performing a rigorous calculation is difficult. Therefore, the simplified, but meaningful geometry for a porous electrode (Figure S6) was used. The model was further simplified by making the following assumptions:

(1) Hydration of CO_2 to form H_2CO_3 is negligibly slow, while other coupled homogeneous reactions involving CO_2 species and acid-base reactions are fast (reversible).

- (2) Electron transfer reactions (Eqns S1-S4) only occur inside the pores, which is a reasonable assumption due to the much large surface area associated with this portion of the electrode.
- (3) The CO_2RR (to formate) only occurs at Sn, while the HER only occurs at M.
- (4) When X > L (where X is the distance from the surface of the substrate electrode and L is the thickness of the Sn layer), the concentration of each species remains at its bulk value since the solution is stirred during electrolysis.
- (5) Inside the pore, the mass transport associated with HCO₃⁻ or H₂PO₄⁻ is governed by linear diffusion if only the HER is considered.
- (6) CO₂ consumed on the surface of Sn (the wall of the pore in Figure S6) will be replaced by the CO₂ outside of the pores. Therefore, an accurate calculation of CO₂ concentrations will require consideration of CO₂ mass transport in both *X* and *R* (radial) directions, which is complicated. Same complexity is also present in the calculation of the concentration of HCO₃⁻ or H₂PO₄⁻ consumed during the CO₂RR. To simplify the calculation of the substrate effect, the CO₂RR was also assumed to occur on the surface of M with an apparent flux density (FD). The trend, but not the exact concentrations are therefore predicted.

On the basis of the above assumptions, the flux density (*FD*) associated with acid (HA represents either HCO_3^- or $H_2PO_4^-$) can be estimated using Eqn S5 since both HER and CO_2RR consume HA,

$$FD_{HA} = D_{HA} \frac{([HA]_{bulk} - [HA]_{surf})}{L} = -\left(\frac{j_{HER}}{F} + \frac{j_{CO_2RR}}{2F}\right)$$
(S5)

while the flux density associated with CO₂ can be estimated using Eq S6,

$$FD_{CO_2} = D_{CO_2} \frac{([CO_2]_{bulk} - [CO_2]_{surf})}{L} = -\frac{j_{CO_2RR}}{2F}$$
(S6)

where D is the diffusion coefficient, j is partial current density and F is the Faraday constant. Since the surface concentration of HA or CO₂ is the only unknown parameter in these equations, their values can be calculated using the partial current density values given in Table S2 and the values for other parameters given in Table S4. The surface pH can be calculated using the following equation once the surface concentration of HA is known,

$$pH^{surf} = pK_a + log \frac{[A^-]_{surf}}{[HA]_{surf}}$$
(S9)

Since the assumption (6) is superior, but even then only approximately correct when the rate of the CO_2RR is moderate, only the current density values obtained at -0.75 V were used in the calculation and the results obtained are given in Table 1.

Table S1. Summary of bulk electrolysis data obtained for CO_2 reduction using dendritic Sn/Pt, Sn/In, Sn/Sn and Sn/Cu electrodes. The electrolysis was undertaken in a CO_2 saturated 0.5 M NaHCO₃ aqueous electrolyte solution.

Applied Potential [E / V vs. RHE]		-0.75	-0.95	-1.15
Sn/Pt	FE (formate) [%]	36.2	16.3	11.5
511/1 (FE (CO) [%]	5 2	19	1
	FE (H ₂) [%]	48.1	64.3	81.2
	Current density	-29.8	-40.5	-56.5
	Partial current density (formate)	-10.8	-6.6	-6.5
	Partial current density (CO)	-1.5	-0.8	-0.6
	Partial current density (H ₂)	-14.4	-26.2	-45.8
Sn/In	FE (formate) [%]	39.8	42.5	41.4
	FE (CO) [%]	3.6	1.3	0.7
	FE (H ₂) [%]	54.8	48.9	57.2
	Current density	-12.0	-25.9	-46.6
	Partial current density (formate)	-4.8	-11	-19.3
	Partial current density (CO)	-0.4	-0.3	-0.3
	Partial current density (H ₂)	-6.6	-12.7	-26.6
Sn/Sn	FE (formate) [%]	43.8	45.8	37.6
	FE (CO) [%]	5.6	2.3	1.5
	FE (H ₂) [%]	50.9	48.9	56.4
	Current density	-11.4	-26.9	-44.4
	Partial current density (formate)	-5	-12.3	-16.7
	Partial current density (CO)	-0.6	-0.6	-0.7
	Partial current density (H ₂)	-5.8	-13.1	-25
Sn/Cu	FE (formate) [%]	51.1	61.1	50.9
	FE (CO) [%]	7.6	2.9	1.2
	FE (H ₂) [%]	39.2	37.2	43.1
	Current density	-15.7	-28.2	-44.8
	Partial current density (formate)	-8	-17.2	-22.8
	Partial current density (CO)	-1.2	-0.8	-0.5
	Partial current density (H ₂)	-6.1	-10.5	-19.3

Table S2. Summary of bulk electrolysis data obtained for CO_2 reduction using In, Sn and Cu foils. The electrolyses were undertaken in a CO_2 saturated 0.5 M NaHCO₃ aqueous electrolyte solution.

Applied Potential [E / V vs. RHE]		-0.75	-0.95	-1.15
In foil	FE (formate) [%]	30.9	49.5	28.3
_	FE (CO) [%]	6.5	1.3	0.6
	FE (H ₂) [%]	65.1	56.4	74.7
	Current density	-0.3	-3.4	-6.5
	Partial current density (formate)	-0.09	-1.7	-1.8
	Partial current density (CO)	-0.02	-0.04	-0.04
	Partial current density (H ₂)	-0.2	-1.9	-4.9
Sn foil	FE (formate) [%]	5.4	17.9	25.5
	FE (CO) [%]	2.8	1.3	0.8
	FE (H ₂) [%]	87.8	75.6	72
	Current density	-0.9	-3.2	-9.3
	Partial current density (formate)	-0.05	-0.6	-2.4
	Partial current density (CO)	-0.03	-0.04	-0.07
	Partial current density (H ₂)	-0.8	-2.4	-6.7
Cu foil	FE (formate) [%]	-	-	-
	FE (CO) [%]	-	-	-
	FE (H ₂) [%]	87.2	98.7	102.6
	Current density	-0.7	-2.2	-5.1
	Partial current density (formate)	-	-	-
	Partial current density (CO)	-	-	-
	Partial current density (H ₂)	-0.6	-2.2	-5.2

Table S3. Summary of electrocatalytic performance for CO ₂ reduction using Sn catalysts in	
aqueous solutions.	

Electrode	Electrolyte	Applied	Total Current	FE of formate	Ref.
		potential (v vs.	density (mA am^{-2})	(%0)	
		KIIL)	cm)		
Sn/SnO _x	0.5 M NaHCO ₃	-0.7	\sim -2	~38	1
SnO ₂ on carbon cloth	0.5 M NaHCO ₃	-0.88	-45	87	2
Reduced nano- SnO ₂ on graphene	0.1 M NaHCO ₃	-1.16	-10.2	93.6	3
Annealed Sn dendritic	0.1 M KHCO3	-1.36	-17.1	71.6	4
Sn foam	0.1 M NaHCO ₃	-1.31	-23.5	90	5
SnO _x /CNT	0.1 M KHCO3	-0.76	~ -8	64	6
$ \begin{array}{c} SnO_{x(100-8)} nano-\\ catalyst \end{array} $	0.5 M KHCO ₃	-0.92	~ -10	87.1	7
Electrodeposited Sn	0.1 M KHCO ₃	-0.76	-15	91	8
Dendritic Sn on Cu	0.5 M NaHCO ₃	-0.95	-14	67.3	This work

Table S4. Parameters^{*} employed for calculation of the concentration of CO_2 and pH on the

Initial equilibrium values for CO ₂ in 0.5 M NaHCO ₃ electrolyte solution	34.2 mol/m ³
Initial equilibrium values for HCO ₃ ⁻ in 0.5 M NaHCO ₃ electrolyte solution	500 mol/m ³
Diffusion coefficient for CO ₂	1.79×10 ⁻⁹ m ² /s
Diffusion coefficient for HCO ₃ -	8.65×10 ⁻¹⁰ m ² /s
Thickness (L)	70 µm
pK_a for HCO ₃ ⁻ (step 2)	10.33
Diffusion coefficient for H ₂ PO ₄ -	8.03×10 ⁻¹⁰ m ² /s
pK_a for H ₂ PO ₄ - (step 2)	7.21

surface of Sn/M electrodes.

* All values were taken from literature^{9,10,11} and were measured at 298 K. All the diffusion coefficient values were further corrected for the electrolyte concentration dependent viscosity using the Stokes–Einstein equation $(D\eta/T = \text{constant} \text{ at } T = 298 \text{ K}, \eta \text{ is viscosity})$. A small systematic error may be present in the estimated values for the concentration of CO₂ and pH since our measurements were undertaken at 295 K.

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