Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Electrochemical reduction of CO_2 on metastable Bi derived from Bi_2S_3 with enhanced formate selectivity

Ying Zhang,[a,b] Fengwang Li,[a,b] Xiaolong Zhang,[a] Tim Williams,[c] Christopher D. Easton,[d] Alan. M. Bond*[a,b] and Jie Zhang*[a,b]

[a]School of Chemistry, Monash University, Wellington Road, Clayton 3800, VIC, Australia

[b]ARC Centre of Excellence for Electromaterials Science, Monash University, Wellington Road, Clayton 3800, VIC, Australia

[c]Monash Centre for Electron Microscopy, Monash University, Clayton 3800, Victoria, Australia

[d]CSIRO Manufacturing, Bayview Ave, Clayton 3168, Victoria, Australia

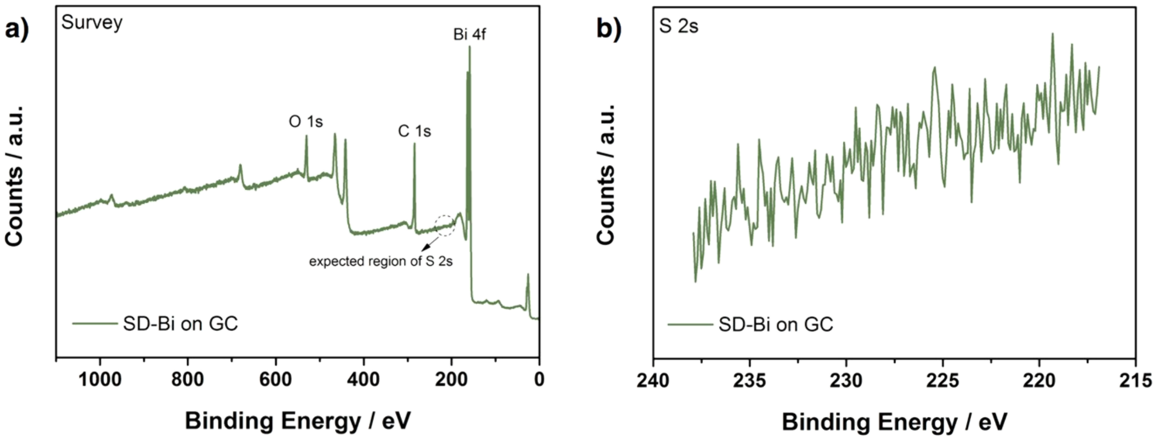

Figure S1. The XPS survey spectrum of (a) SD-Bi on GC and (b) the high-resolution scan of S 2s.

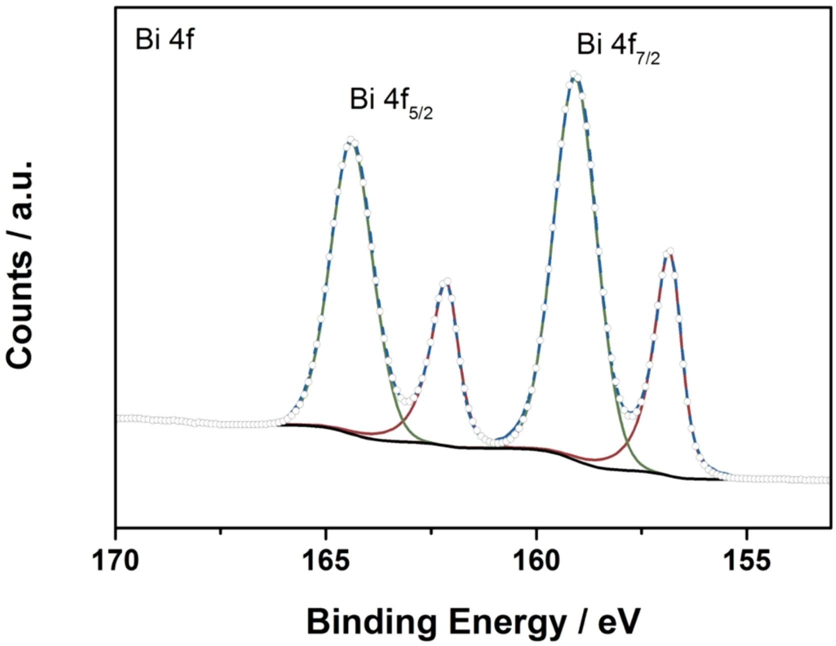

Figure S2. High-resolution Bi 4f XPS spectra of SD-Bi on GC. The blue dashed line represents the experimental data and the open circles represent the fitted data. The two red components represent the Bi 4f doublet for Bi(0) with an Lorentzian asymmetric line shape while the two green components represent the Bi 4f doublet for BiO_x with a Gaussian Lorentzian line shape. The black line represents the Shirley background. The ratio of Bi(0):BiO_x is roughly 3:7 on the surface of the SD-Bi sample.

Based on the elemental quantification (atomic%) from survey data and fitting of the high resolution Bi 4f spectra, approximately 8.9% of the total 12.7% of Bi is associated with BiO_x. If the oxide was in the form of Bi_2O_3 that would result in approximately 13.4% of the total 19.6% of O associated with Bi. The peak shape of the high resolution C 1s spectra is consistent with adventitious carbon including C-O and COOR groups, in addition to a minor contribution from CO_3 groups; fitting this peak indicates that approximately 14.5% of O is associated with C. Accounting for only two contributions to O, Bi_2O_3 and carbon-oxygen groups, there is insufficient oxygen detected on the surface for the oxide to be in the form Bi_2O_3 (i.e. 13.4%

$O_{(Bi2O3)}$ + 14.5% $O_{(carbon\text{-}oxygen\ groups)}$ > 19.6% $O_{(total\ measured)}$). The origin of oxygen has been discussed below.

When reducing Bi_2S_3 to metallic Bi in a CO_2 saturated 0.5 M aqueous $NaHCO_3$ solutions, the following equilibria are established.

$$CO_2(aq) + H_2O(l) \overset{K_1^C}{\leftrightarrow} H^+(aq) + HCO_3{}^-(aq) \overset{K_2^C}{\leftrightarrow} 2H^+(aq) + CO_3{}^{2-}(aq) \tag{S1}$$

$$H_2S(aq) + H_2O(l) \overset{K_1^S}{\leftrightarrow} H^+(aq) + HS^-(aq) \overset{K_2^S}{\leftrightarrow} 2H^+(aq) + S^{2-}(aq) \tag{S2}$$

Where $K_1{}^C$, $K_2{}^C$, $K_1{}^S$ and $K_2{}^S$ are the equilibrium constants and given as

$$K_1^C = \frac{[H^+][HCO_3{}^-]}{[CO_2(aq)]} \approx \frac{[H^+][HCO_3{}^-]}{\left[H_2CO_3{}^*\right]} \tag{S3}$$

$$K_2^C = \frac{[H^+][CO_3{}^{2-}]}{[HCO_3{}^-]} \tag{S4}$$

$$K_1^S = \frac{[H^+][HS^-]}{[H_2S(aq)]} \tag{S5}$$

$$K_2^S = \frac{[H^+][S^{2-}]}{[HS^-]} \tag{S6}$$

where $pK_1{}^C = 6.35$, $pK_2{}^C = 10.33$, $pK_1{}^S = 7.05$ and $pK_2{}^S = 19$ at 25 °C; $H_2CO_3{}^*$ represents H_2CO_3 and dissolved CO_2 in the solution. The total concentrations of dissolved carbon and sulphur species are

$$c_{total}^C = \left[H_2CO_3{}^*\right] + \left[HCO_3{}^-\right] + [CO_3{}^{2-}] \tag{S7}$$

$$c_{total}^S = [H_2S(aq)] + [HS^-] + [S^{2-}] \tag{S8}$$

Then the concentrations of each species can be derived from the following equations:

$$\left[CO_3{}^{2-}\right] = \frac{K_1^C K_2^C c_{total}^C}{[H^+]^2 + K_1^C[H^+] + K_1^C K_2^C} \tag{S9}$$

$$\left[HCO_3{}^-\right] = \frac{K_1^C[H^+]c_{total}^C}{[H^+]^2 + K_1^C[H^+] + K_1^C K_2^C} \tag{S10}$$

$$\left[H_2CO_3{}^*\right] = c_{total}^C - \left[CO_3{}^{2-}\right] - \left[HCO_3{}^-\right] \tag{S11}$$

$$\left[S^{2-}\right] = \frac{K_1^S K_2^S c_{total}^S}{[H^+]^2 + K_1^S[H^+] + K_1^S K_2^S} \tag{S12}$$

$$\left[HS^-\right] = \frac{K_1^S[H^+]c_{total}^S}{[H^+]^2 + K_1^S[H^+] + K_1^S K_2^S} \tag{S13}$$

$$[H_2S] = c_{total}^S - \left[S^{2-}\right] - \left[HS^-\right] \tag{S14}$$

The concentration of S species is ~0.5 mM if all the Bi_2S_3 on the working electrode is released into the solution. Thus, the concentration of S^{2-} and OH^- in an electrolyte are calculated to be 4.6×10^{-16} mol L^{-1} and 1.6×10^{-7} mol L^{-1} (pH = 7.2), respectively. Therefore, Bi_2S_3 is thermodynamically more stable upon reduction to metallic Bi than $Bi(OH)_3$ under our experimental conditions taking into account the difference in their K_{sp} values (4.0×10^{-31} for $Bi(OH)_3$ vs. 1.8×10^{-99} for Bi_2S_3). Since Bi_2S_3 is absent under our experimental conditions with an applied potential of -1.4 V, the presence of BiO_x is less likely. Therefore, the BiO_x observed under XPS is most likely from the partial oxidation of Bi by air during sample transfer.

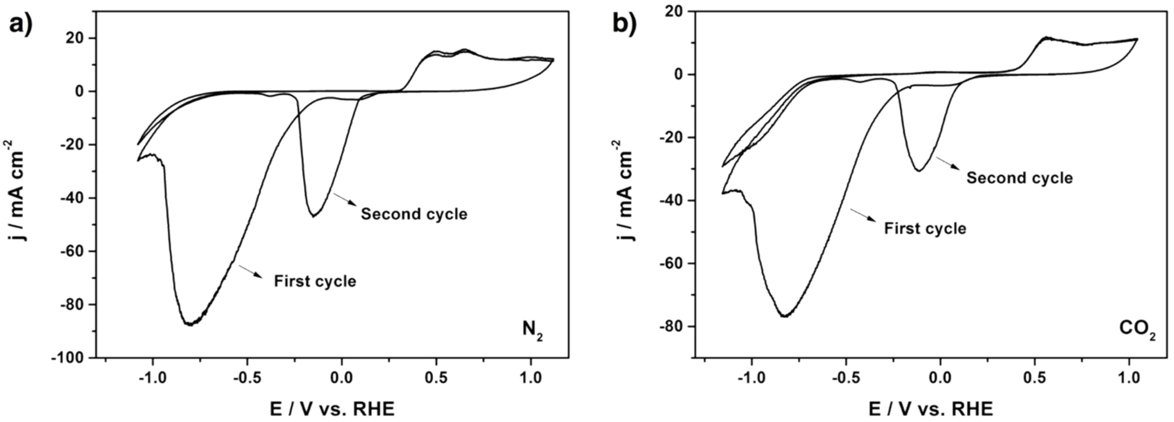

Figure S3. The first and second cycle in cyclic voltammograms obtained with Bi_2S_3 modified electrode in (a) N_2 and (b) CO_2 saturated 0.5 M $NaHCO_3$ aqueous electrolyte solution at a scan rate of 50 mV/s under stirring.

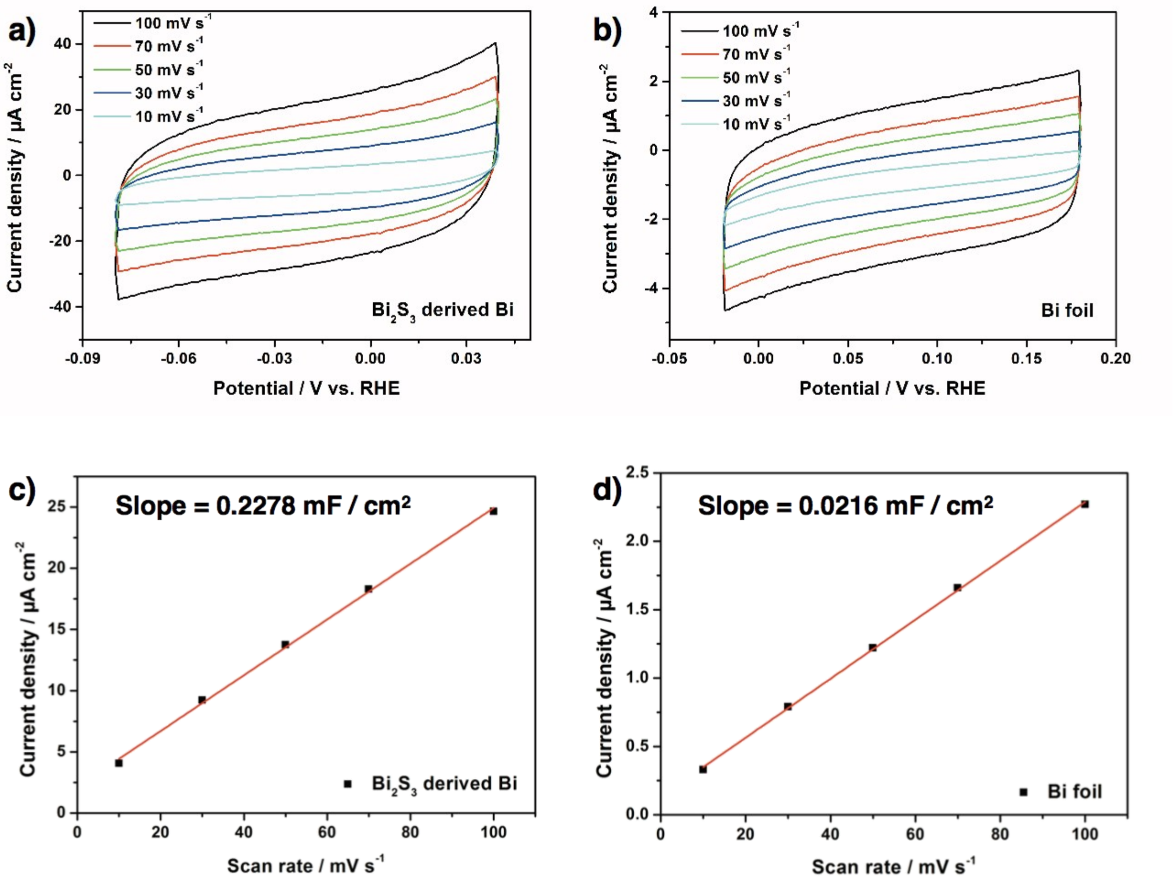

Figure S4. Cyclic voltammetric curves of the (a) SD-Bi and (b) Bi foil obtained within a potential range where double-layer charging and discharging are occurring using N_2 saturated 0.5 M $NaHCO_3$ aqueous solution. The double-layer capacitances of the (c) SD-Bi and (d) Bi foil.

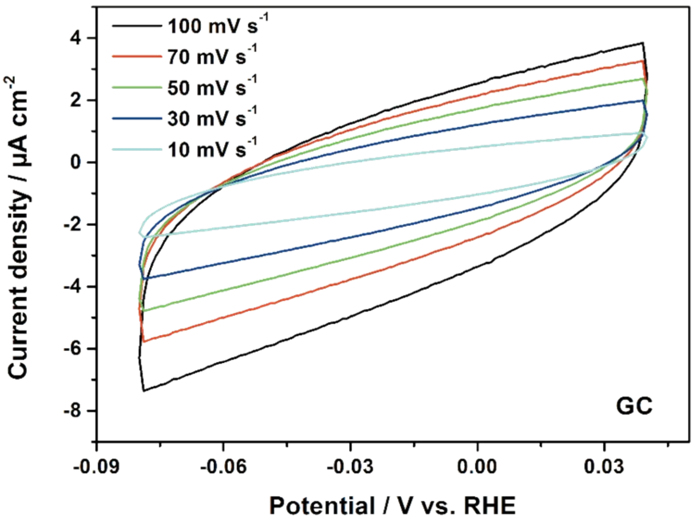

Figure S5. Cyclic voltammograms obtained at a GC electrode in N_2 saturated 0.5 M $NaHCO_3$ over a potential range where faradaic current is absent. The double layer capacitance of this GC electrode was determined to be 0.0252 mF cm^{-2}.

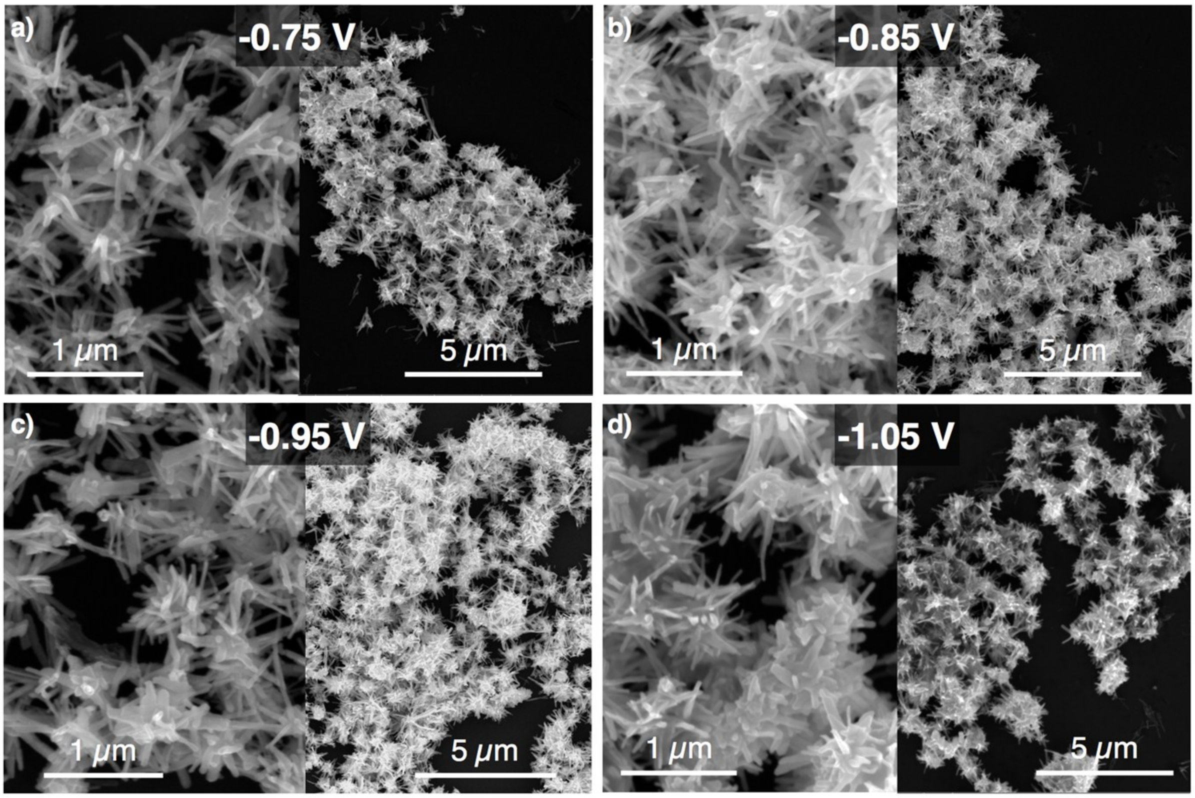

Figure S6. SEM images of SD-Bi after 30 min of bulk electrolysis at potentials of -0.75 V, -0.85 V, -0.95 V and -1.05 V with low (right) and high (left) magnification.

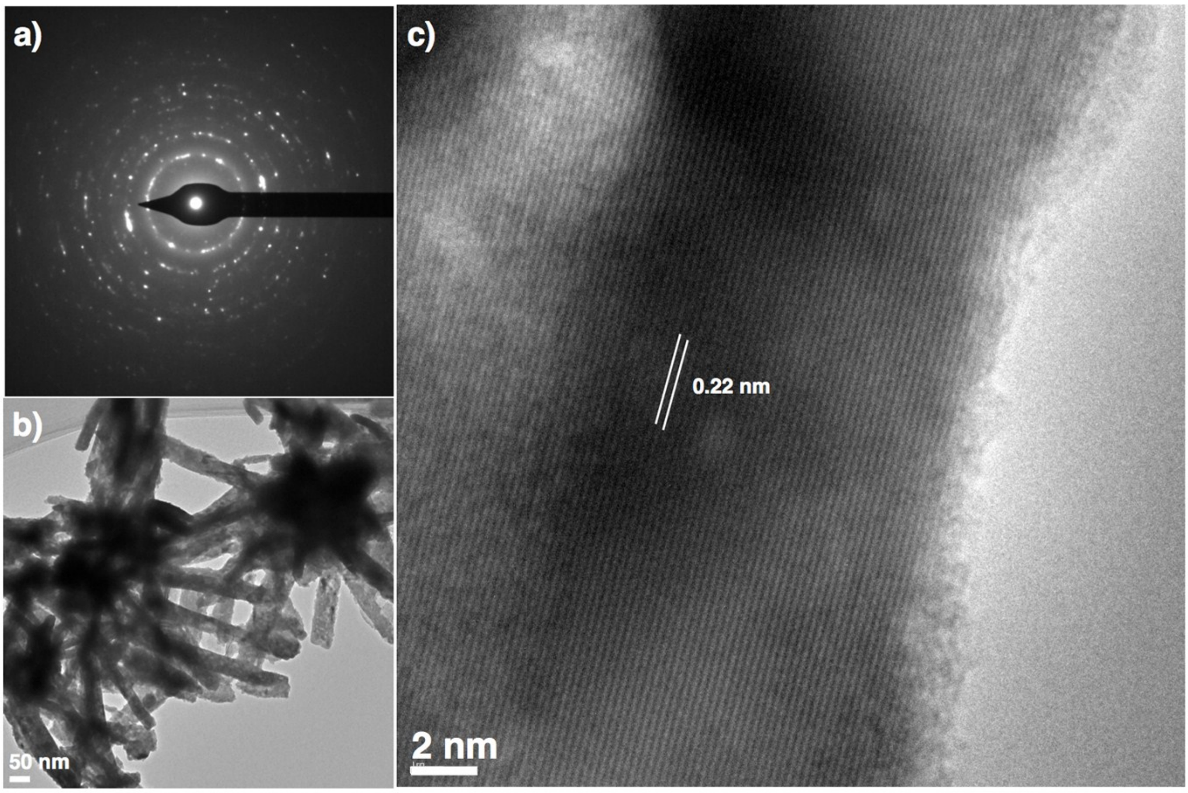

Figure S7. (a) SAED pattern, (b) TEM and (c) HRTEM images of SD-Bi post annealing at 150 ℃ for 30 min. The lattice fringe of 0.22 nm shown in (c) corresponds to the (110) plane of Bi.

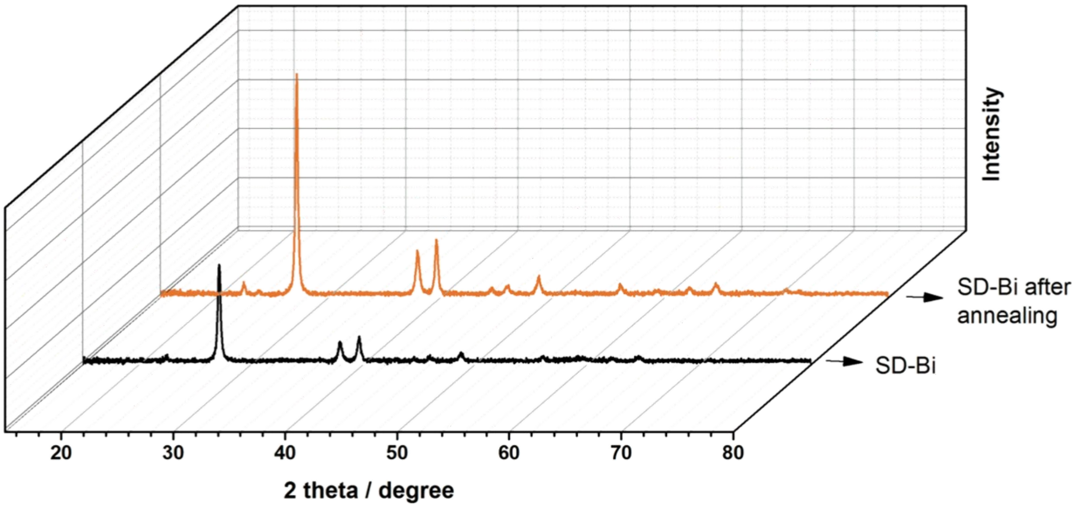

Figure S8. XRD patterns of SD-Bi electrode before and post annealing for 30 min at 150 °C.

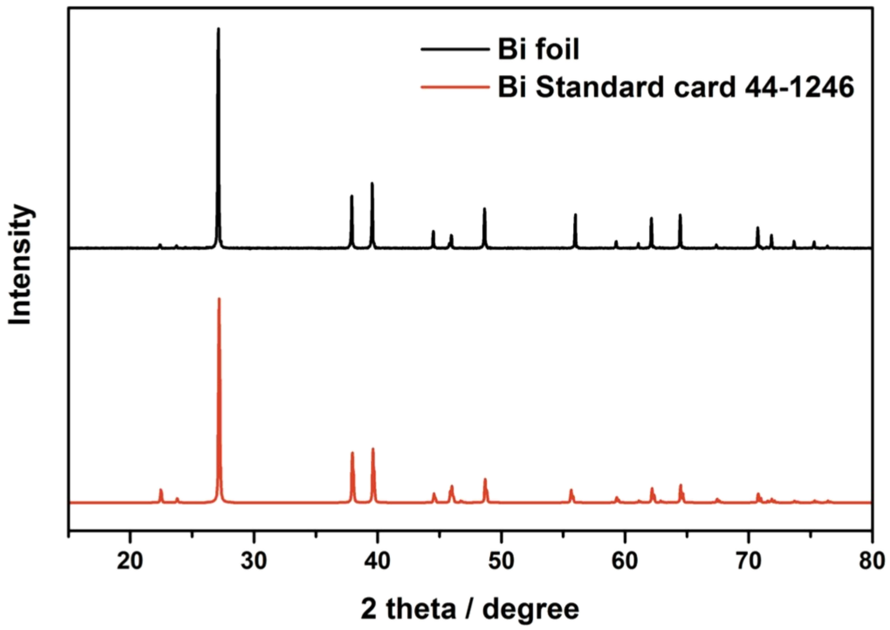

Figure S9. XRD patterns of Bi foil and the Bi standard card 44-1246.

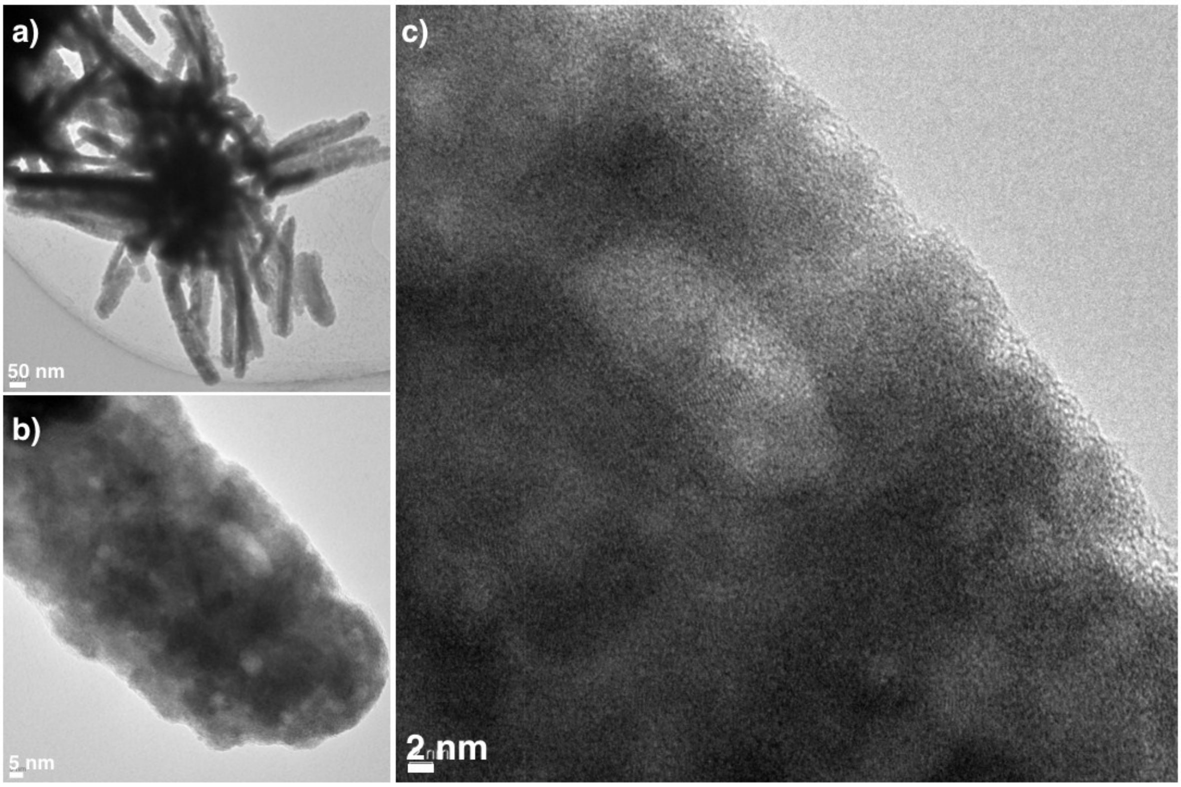

Figure S10. (a, b) TEM and (c) HRTEM images of SD-Bi after 24 h bulk electrolysis.

Applied Potential [E / V vs. RHE]		**-0.65**	**-0.75**	**-0.85**	**-0.95**	**-1.05**
SD-Bi	FE (formate) [%]	75.0	84.0	82.6	74.5	73.5
	FE (CO) [%]	1.1	1.5	2.6	1.1	1.1
	FE (H_2) [%]	29.5	15.6	18.1	31.2	28.6
	Current density [mA cm^{-2}]	-2.40	-6.00	-15.7	-21.1	-27.4
	Partial current density (formate) [mA cm^{-2}]	-1.80	-5.04	-13.0	-15.7	-20.1
	Partial current density (CO) [mA cm^{-2}]	-0.264	-0.0900	-0.408	-0.232	-0.301
	Partial current density (H_2) [mA cm^{-2}]	-0.708	-0.936	-2.84	-6.58	-7.84
Bi foil	FE (formate) [%]	36.2	49.5	47.9	32.3	36.4
	FE (CO) [%]	1.4	1.1	1.7	0.8	1.1
	FE (H_2) [%]	42.8	56.3	60.2	66.6	50.2
	Current density [mA cm^{-2}]	-1.20	-3.80	-8.10	-13.2	-15.3
	Partial current density (formate) [mA cm^{-2}]	-0.434	-1.90	-3.9	-4.3	-5.6
	Partial current density (CO) [mA cm^{-2}]	-0.0168	-0.0418	-0.138	-0.106	-0.168
	Partial current density (H_2) [mA cm^{-2}]	-0.514	-2.14	-4.88	-8.79	-7.68

Table S1. Summary of bulk electrolysis data obtained at room temperature for CO_2 reduction with SD-Bi and Bi foil electrodes in a CO_2 saturated 0.5 M $NaHCO_3$ aqueous electrolyte solution.