

Supporting Information

Detection of $\text{CO}_2^{\cdot-}$ in the Electrochemical Reduction of Carbon Dioxide in DMF by Scanning Electrochemical Microscopy

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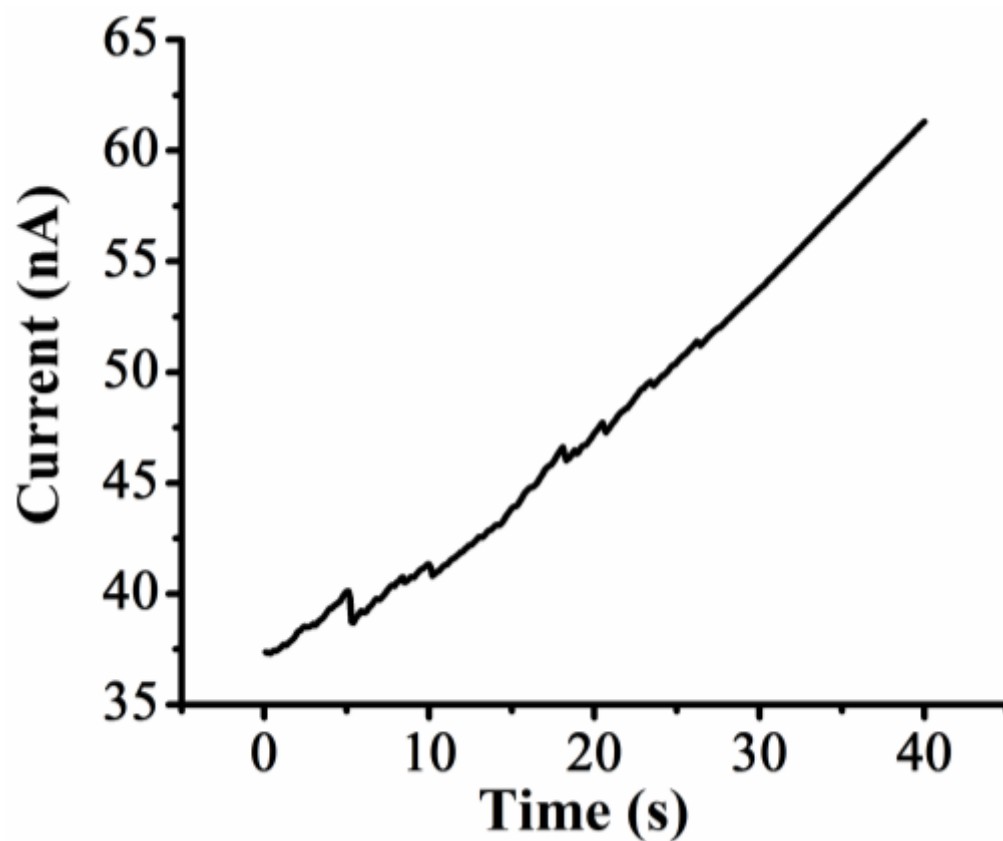


Figure S1. Chronoamperogram of 10 mM $\text{Hg}_2(\text{NO}_3)_2$ at a Pt UME of 5 μm radius (*a*) in an aqueous solution containing 0.1 M KNO_3 and 0.5% HNO_3 . The potential was held at -0.1 V vs Ag/AgCl.

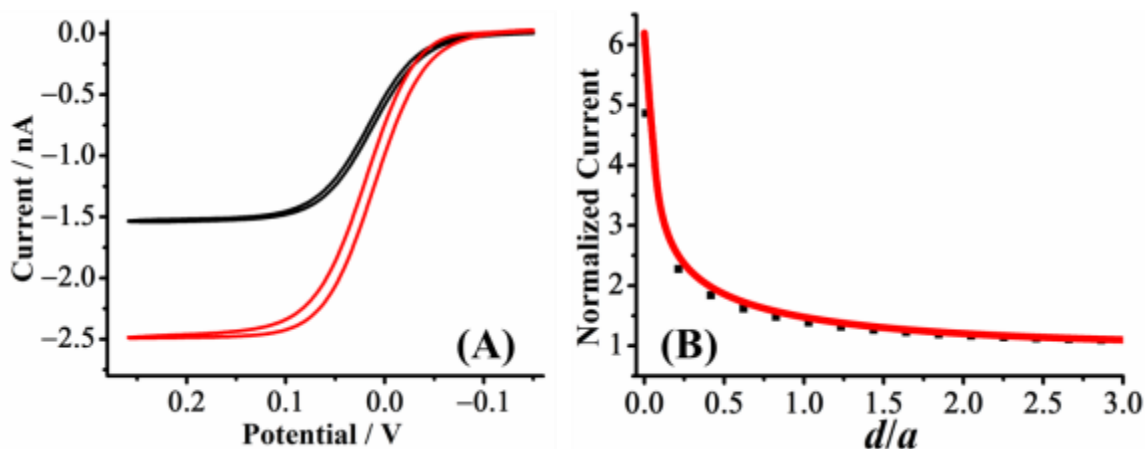


Figure S2. (A) CVs of 1 mM decamethylferrocene (DMFc) in DMF containing 0.1M TBAPF₆ at a $a = 5$ μm hemisphere-shaped Hg/Pt UME (Black curve) and a $a = 12.5$ μm Au disk UME (Red curve), respectively. The scan rate was $20 \text{ mV}\cdot\text{s}^{-1}$. (B) Positive feedback approach curve (Red curve) for 1 mM DMFc in DMF containing 0.1 M TBAPF₆ obtained with a $a = 5$ μm hemisphere-shaped Hg/Pt UME (SECM tip, RG = 5) and a $a = 12.5$ μm Au disk UME (SECM Substrate). The tip and substrate potentials were held at 0.25 V and -0.15 V, respectively. A theoretical approach curve (Black dotted curve) was obtained from COMSOL simulation.

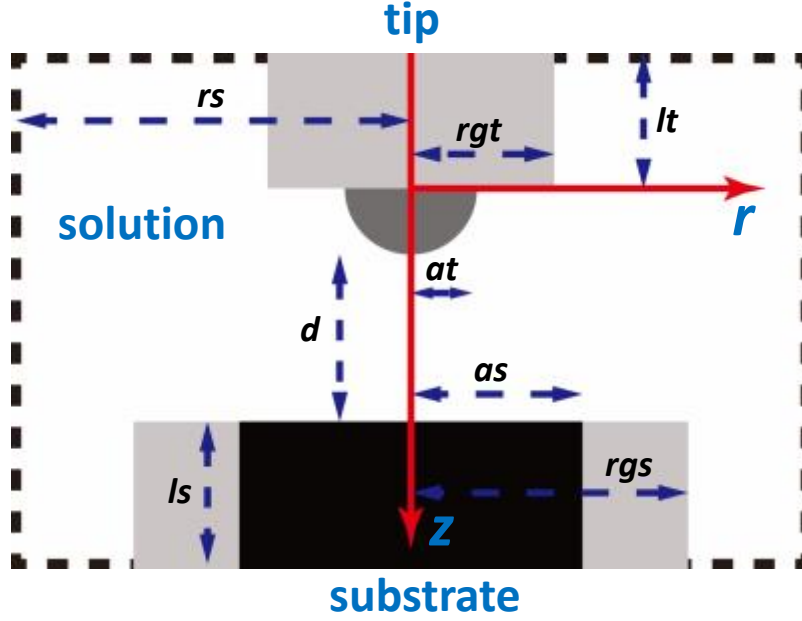


Figure S3. Geometry and related parameters for the diffusion simulation in the operation of SECM, where a hemisphere-shaped tip approaches an inlaid disk substrate.

The steady-state diffusion problem for tip generation/substrate collection (TG/SC) mode of SECM is formulated for the diffusion-controlled reduction of CO_2 (species 1) at the hemisphere-shaped tip and oxidation of $\text{CO}_2^{\cdot -}$ (species 2) at the inlaid disk substrate (Figure S3). $\text{CO}_2^{\cdot -}$ take a homogenous second-order dimerization in the solution with a rate constant of k_c , as shown in



Here, the as-described diffusion problem can write in cylindrical coordinates as:

$$\frac{\partial^2 c_1}{\partial r^2} + \frac{1}{r} \frac{\partial c_1}{\partial r} + \frac{\partial^2 c_1}{\partial z^2} = 0; \quad 0 \leq r < rs, \quad -lt < z < at + d + ls \quad (1.2)$$

$$\frac{\partial^2 c_2}{\partial r^2} + \frac{1}{r} \frac{\partial c_2}{\partial r} + \frac{\partial^2 c_2}{\partial z^2} = \frac{kc_2^2}{D_2}; \quad 0 \leq r < rs, \quad -lt < z < at + d + ls \quad (1.3)$$

where r and z are the spatial coordinates and $c_i(r, z)$ is the concentration of the solution species.

The related boundary conditions are listed as follows:

$$c_1 = 0, \quad D_1 \frac{\partial c_1(r, z)}{\partial n} + D_2 \frac{\partial c_2(r, z)}{\partial n} = 0; \quad (\text{tip surface}) \quad (1.4)$$

$$0 \leq r \leq at, \quad z = \sqrt{at^2 - r^2}$$

$$c_2 = 0, D_1 \frac{\partial c_1(r, z)}{\partial n} + D_2 \frac{\partial c_2(r, z)}{\partial n} = 0; \quad (\text{Substrate surface}) \quad (1.5)$$

$$0 \leq r \leq as, z = at + d$$

where $\partial c_i(r, z) / \partial n$ is the normal derivative and D_i is the diffusion coefficient of the species.

$$\frac{\partial c_1(r, z)}{\partial n} = \frac{\partial c_2(r, z)}{\partial n} = 0;$$

$$at < r \leq rgt, z = 0;$$

$$-lt \leq z \leq 0, r = rgt; \quad (\text{Insulating surface}) \quad (1.6)$$

$$as < r \leq rgs, z = at + d;$$

$$at + d \leq z \leq at + d + ls, r = rgs;$$

$$c_1 = 1, c_2 = 0;$$

$$-lt \leq z \leq at + d + ls, r = rs; \quad (\text{Simulation space limit}) \quad (1.7)$$

$$rgt < r \leq rs, z = -lt;$$

$$rgs < r \leq rs, z = at + d + ls$$

$$\frac{\partial c_1(r, z)}{\partial n} = \frac{\partial c_2(r, z)}{\partial n} = 0; \quad r = 0, at \leq z \leq at + d \quad (\text{Axis of symmetry}) \quad (1.8)$$

The collection efficiency is defined as the ratio of the integrated diffusion flux of species 2 over the substrate surface to the integrated diffusion flux of species 1 over the tip surface.

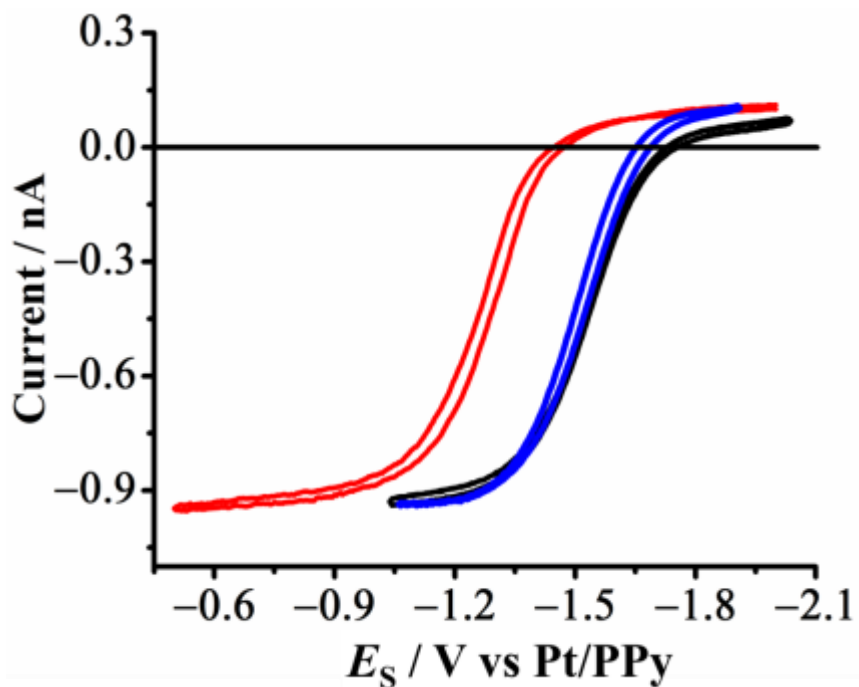


Figure S4. CVs of $\text{CO}_2^{\cdot-}$ obtained at $a = 12.5 \mu\text{m}$ Au (Black), Pt (Red) and Hg/Au (Blue curve) substrates in DMF containing 0.1 M TBAPF₆, respectively. SECM tip was a $a = 5 \mu\text{m}$ Hg/Pt UME and tip potential (E_T) was held at -2.8 V vs Pt/PPy ($d = 800 \text{ nm}$).

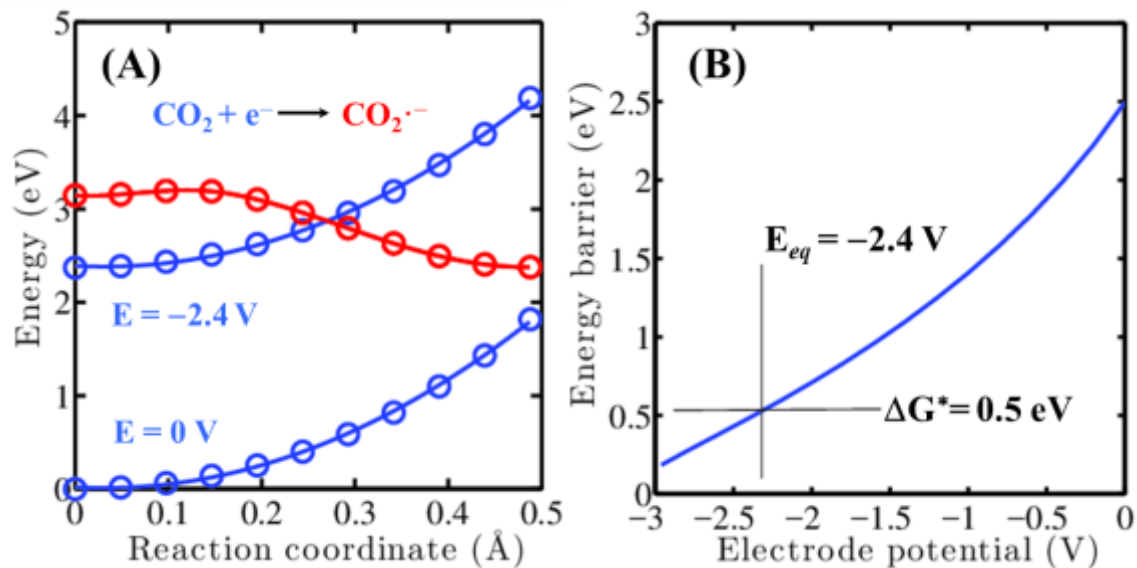


Figure S5. (A) Potential energy diagram of $\text{CO}_2 + e^-$ (Blue curves) and $\text{CO}_2 \cdot^-$ (Red curve) along the reaction coordinate of CO_2 bending. The potential energies of $\text{CO}_2 + e^-$ are evaluated at 0 V and -2.4 V , respectively. (B) The energy barrier required to cross from $\text{CO}_2 + e^-$ to $\text{CO}_2 \cdot^-$ as a function of applied electrode potentials.

Table S1: Electrolyte and double layer capacitance for 0.1 M different electrolyte solutions at the Hg/Pt-DMF interface

Supporting Electrolyte	Double layer capacitance C, $\mu\text{F cm}^{-2}$
0.1 M TEAPF ₆	10.0
0.1 M TPAPF ₆	7.7
0.1 M TBAPF ₆	7.0
0.1 M THeATPB	5.8
0.1 M TOABr	6.7

^aData were obtained by sweeping the potential within the double layer region from -1.5 V to -2.0 V vs Pt/PPy.

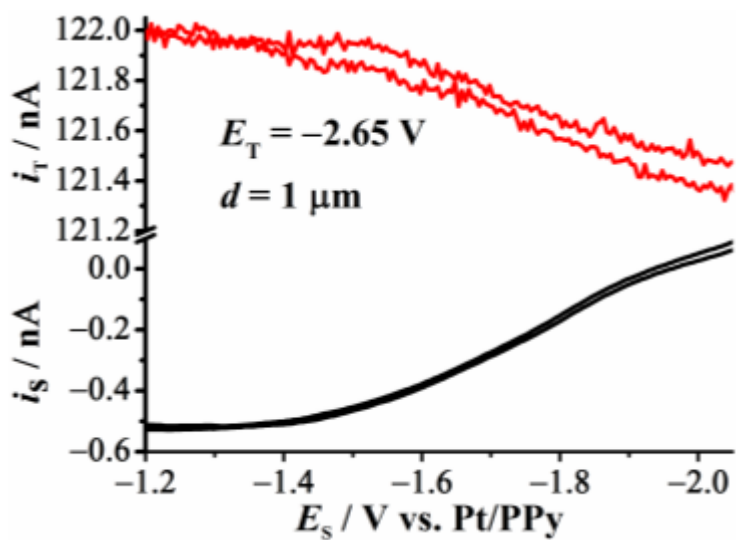


Figure S6. The collection of CO_2^- (Black curve) obtained with 0.1 M TEAPF_6 as the supporting electrolyte at the SECM substrate ($a = 12.5 \mu\text{m}$ Hg/Au UME). E_T was held at -2.65 V, while E_S was swept from -2.1 V to -1.2 V ($d = 1 \mu\text{m}$). i_T (Red curve) was obtained with a $a = 5 \mu\text{m}$ Hg/Pt UME, as shown on the top.