

Electronic Supplementary Information (ESI)

Highly Selective and Efficient Reduction of CO₂ to CO on Cadmium Electrode Derived from Cadmium Hydroxide

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Experimental Procedures

Materials

1-Butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF₆, purity > 99 %) was purchased from Centre of Green Chemistry and catalysis, LICP, CAS. Cd(NO₃)₂·4H₂O (purity > 98.5%), Toray Carbon Paper (CP, TGP-H-60, 19×19 cm²) and Nafion N-117 membrane (0.180 mm thick, ≥ 0.90 meq g⁻¹ exchange capacity), ferrocene (99.5%) and silver nitrate (purity > 99%) were purchased from Alfa Aesar China Co., Ltd. Tetrabutylammonium Perchlorate (TBAP) (purity > 98.0%) was purchased from TCI. CO₂ (Purity ≥ 99.999%, V/V) and N₂ (Purity ≥ 99.999%, V/V) were provided by Beijing huanyu jinghui city gas technology Co., Ltd. and Beijing Tai Long Electronic Technology Co., Ltd., respectively. Acetonitrile (MeCN) (HPLC) was obtained from Xilong Scientific Co., Ltd. sulfuric acid, ethanol and acetone (A. R. Grade) were produced by Beijing Chemical Works.

All chemicals were used directly without additional purification.

Electrode Synthesis and Structural Characterization

An electrochemical workstation (CHI 660e, Shanghai CH Instruments Co., China) was used for all the electrodeposition and CO₂ reduction experiments. The Cd(OH)₂/CP cathode was prepared by electrodeposition method. The electrodeposition was performed in a single compartment cell containing 25 mL 10 mM Cd(NO₃)₂ solution with a three-electrode cell system (the platinum mesh (1×1 cm²) as counter electrode, carbon paper (1×0.5 cm²) as working electrode and Ag/AgCl (saturated KCl) reference electrode). Prior to experiment, the carbon paper substrate was sonicated in acetone for 10 min, followed by washing with water and ethanol, and finally dried in N₂ atmosphere. The electrodeposition was carried out at different constant potentials (−0.8 V, −0.9 V, −1.0V, −1.1 V and −1.2 V) vs. Ag/AgCl (saturated KCl) with the same charge consumption 0.1 C, respectively. Slight magnetic stirring was applied in the process.

The morphologies of the cathodes were characterized by HITACHI SU8020 SEM and JEOL-2100F TEM. X-ray diffraction (XRD) was performed using a Rigaku D/max-2500 200 mA.

Electrochemical Study

Electrochemical measurements were carried out in a two-compartment and three-electrode electrochemical H-type cell, which consists of working electrode, a platinum gauze auxiliary electrode, and Ag/Ag⁺ (0.01 M AgNO₃ in 0.1 M TBAP-MeCN) reference electrode, as is shown schematically in Fig. S3. In the experiment, the cathode and anode compartments were separated by a Nafion 117 proton exchange membrane. Cathode compartment contained 25 mL [BMIM]PF₆/MeCN (0.5M) electrolyte and anode compartment contained 25 mL H₂SO₄ aqueous solution (0.5 M). H⁺ can be transferred from anode compartment to cathode compartment through Nafion 117 proton exchange membrane as the proton source. The electrolyte was bubbled with N₂ or CO₂ for at least 30 minutes to form N₂ or CO₂ saturated solution before experiment.

The LSV measurement in gas-saturated electrolyte was carried out in the potential range of −0.45 V to −1.95 V vs. reversible hydrogen electrode (RHE) at a sweep rate of 20 mV s⁻¹. Slight magnetic stirring was applied in the process.

Under continuous magnetic stirring, the controlled potential electrolysis (CPE) experiment was performed with CO₂ bubbling through the catholyte all the time, and the gaseous product was collected in a gas bag. The gaseous products were analyzed by gas chromatography (GC, HP 4890D), which was equipped with TCD and FID detectors using helium as the internal standard. The liquid mixture was analyzed by ¹H NMR method, which conducted on a Bruker Avance III 400 HD spectrometer in DMSO-d₆ with TMS as an internal standard.

Reference Electrode Calibration

The calibration of Ag/Ag⁺ reference electrode was based on the reported literatures.^{S1,S2} It was carried out in a three-electrode electrochemical cell, where two glassy carbon electrodes (0.5 mm diameter) served as anode and cathode, Ag/Ag⁺ (0.01 M AgNO₃ in 0.1 M TBAP-MeCN) connected to the electrolyte with a Luggin capillary served as reference electrode. The potentials of ferrocene/ferrocenium couple (2.5 mM) in 25 mL acetonitrile and 0.5 M [BMIM]PF₆/MeCN (each electrolyte contains 0.1 M TBAP) were measured with a scan rate of 10 mV/s, respectively.

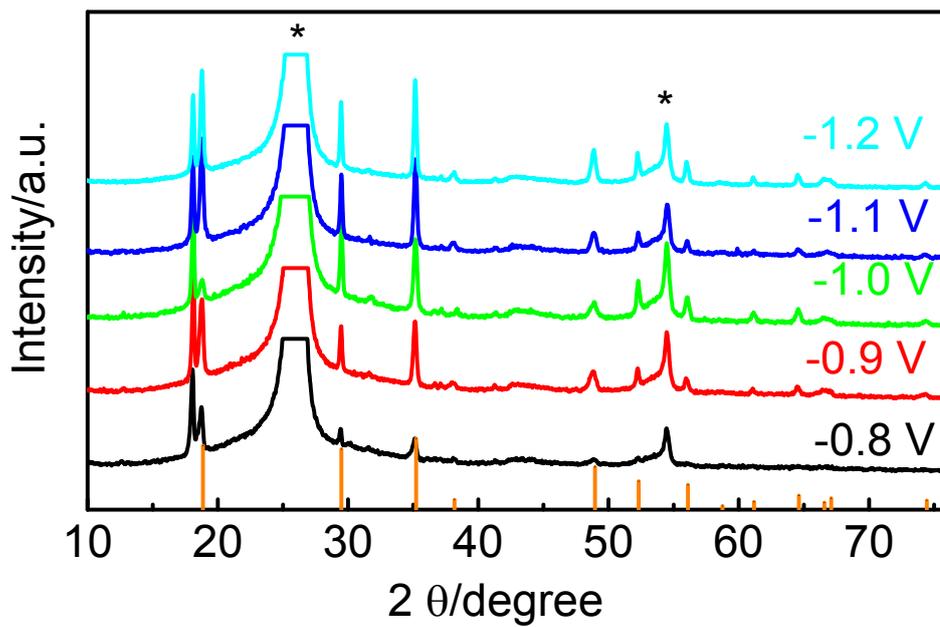


Fig. S1. XRD patterns of $\text{Cd}(\text{OH})_2$ electrodeposited on CP at different voltages (vs. Ag/AgCl). The vertical lines at bottom are the standard diffractions of $\text{Cd}(\text{OH})_2$ (JCPDS 31-0228). The mark of * represents diffraction from CP.

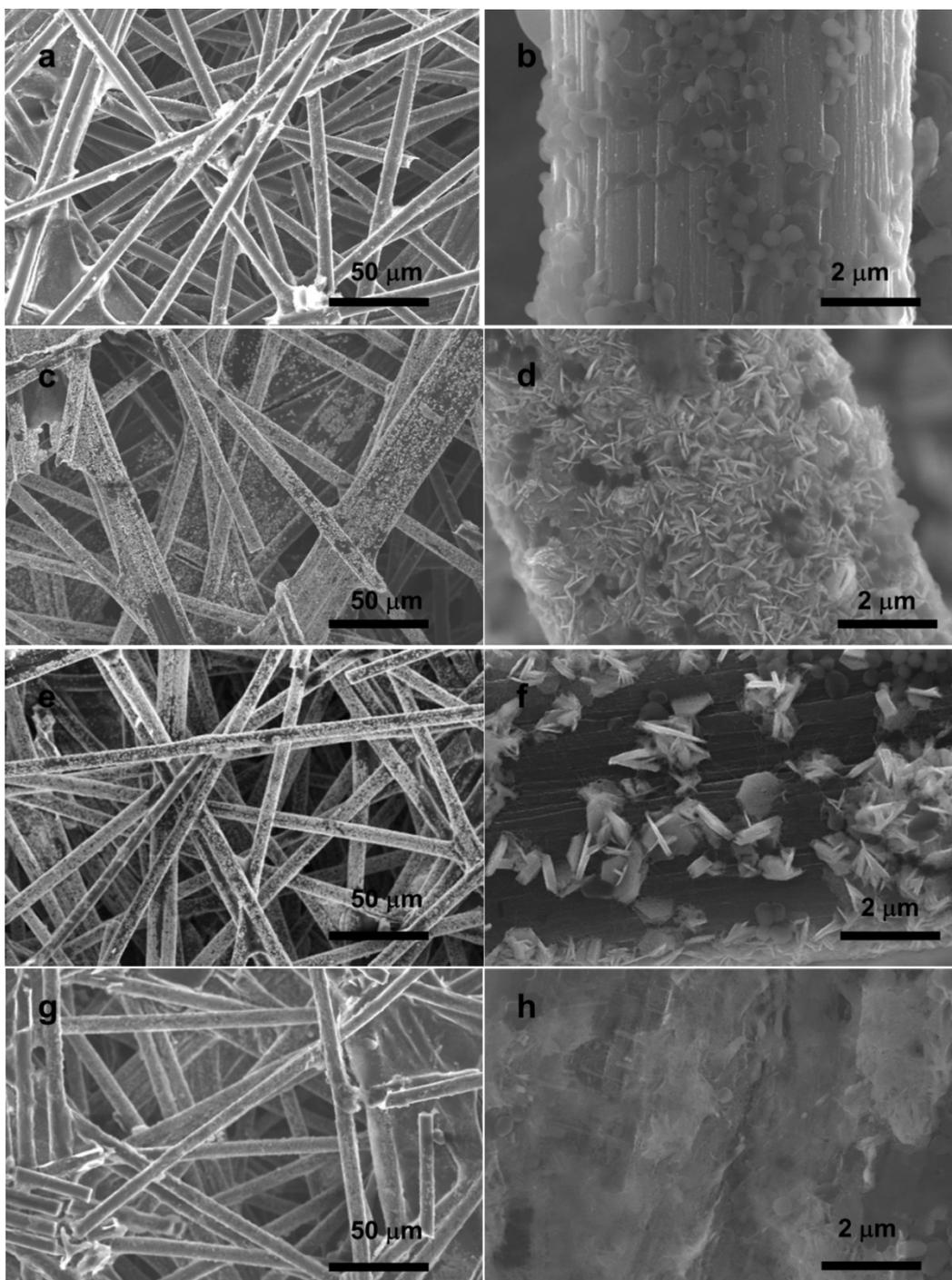


Fig. S2. SEM images of Cd(OH)₂ electrodeposited on carbon papers at -0.8 V (a, b), -0.9 V (c, d), -1.1 V (e, f) and -1.2 V (g, h) (vs. Ag/AgCl).

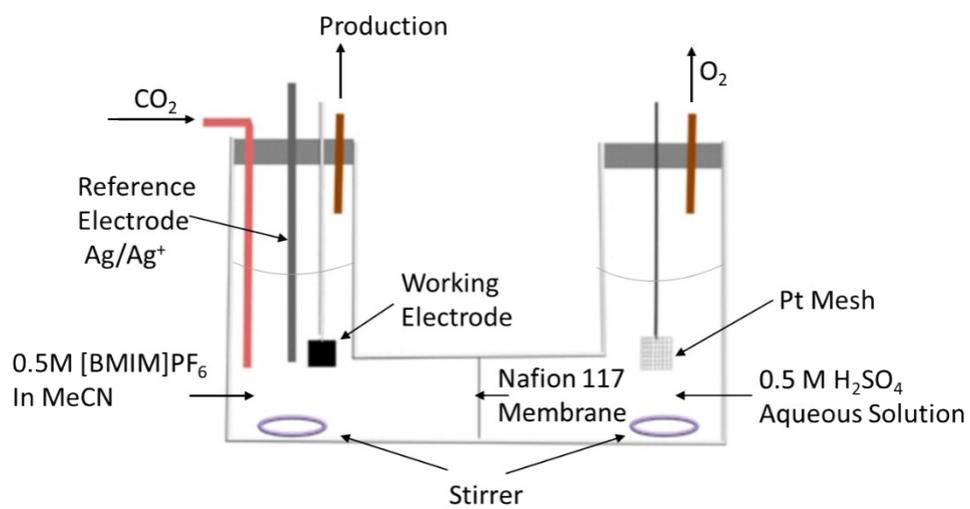


Fig. S3. Schematic diagram of the CO₂ electrochemical reduction system.

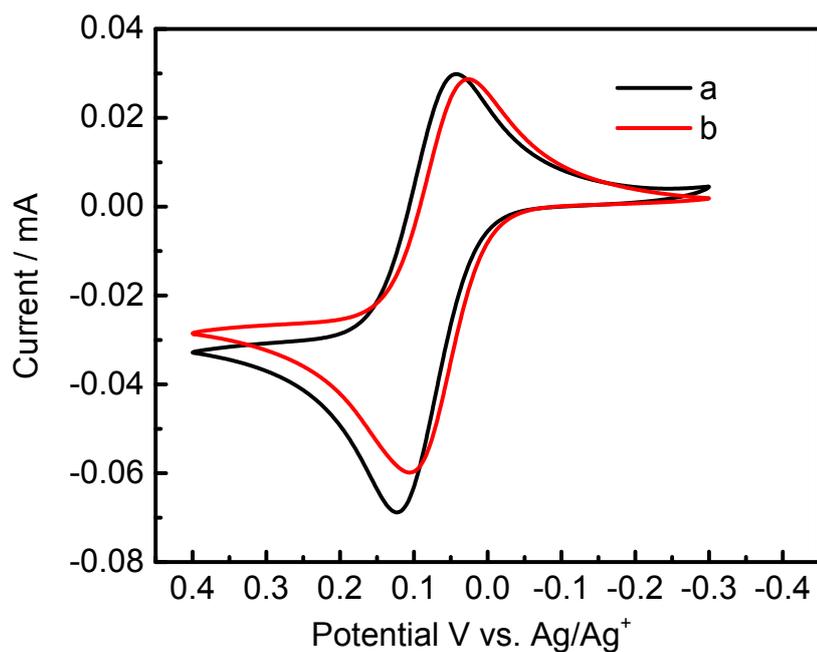


Fig. S4. Anodic and cathodic waves for ferrocene/ferrocenium (2.5 mM) redox couple in Acetonitrile (a) and [BMIM]PF₆/MeCN (b) using Ag/Ag⁺ reference. The averages of the peak potentials of the anodic and cathodic waves of the ferrocene/ferrocenium (2.5 mM) couple of two glassy carbon electrodes were measured to be +83 mV and +66 mV vs. Ag/Ag⁺ in acetonitrile and in [BMIM]PF₆/MeCN, respectively. There is 17 mV difference between the potentials of the ferrocene/ferrocenium standard in acetonitrile and in [BMIM]PF₆/MeCN. Therefore, it can be concluded that there is a 537+17=554 mV difference between the potentials of the Ag/Ag⁺ electrode in [BMIM]PF₆/MeCN and RHE at 25 °C.

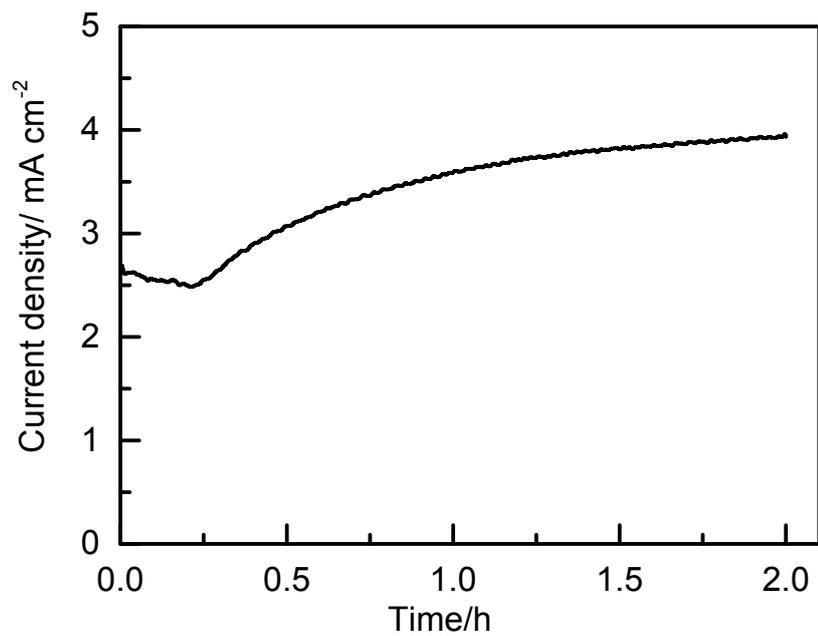


Fig. S5. Constant potential for CO₂ electroreduction at -1.35 V vs. RHE of the electrode prepared at -1.0 V (vs. Ag/AgCl).

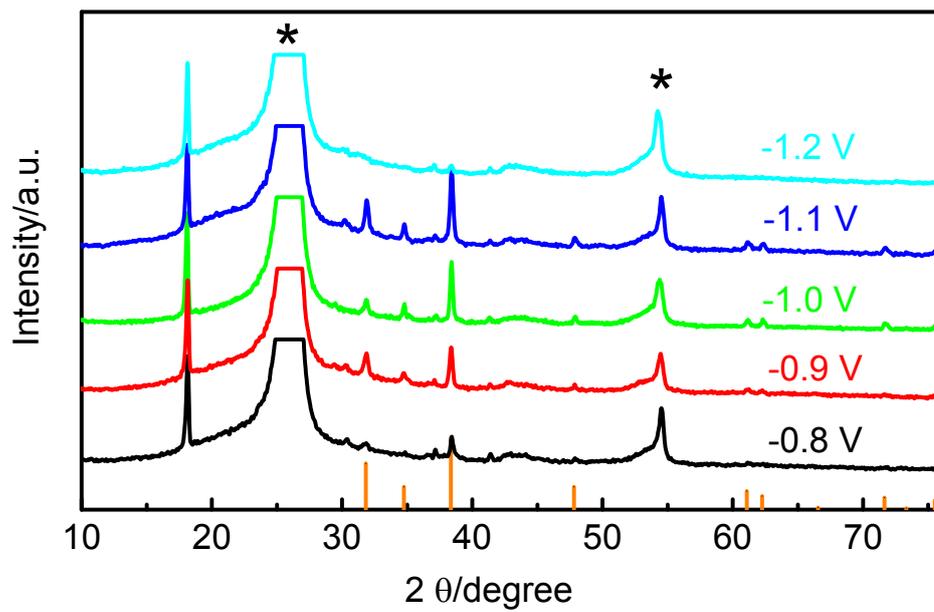


Fig. S6. XRD patterns of Cd electrodeposited on carbon papers at different voltages (vs. Ag/AgCl). The vertical lines are the standard diffractions of Cd (JCPDS 05-0674). The mark of * represents diffraction from CP.

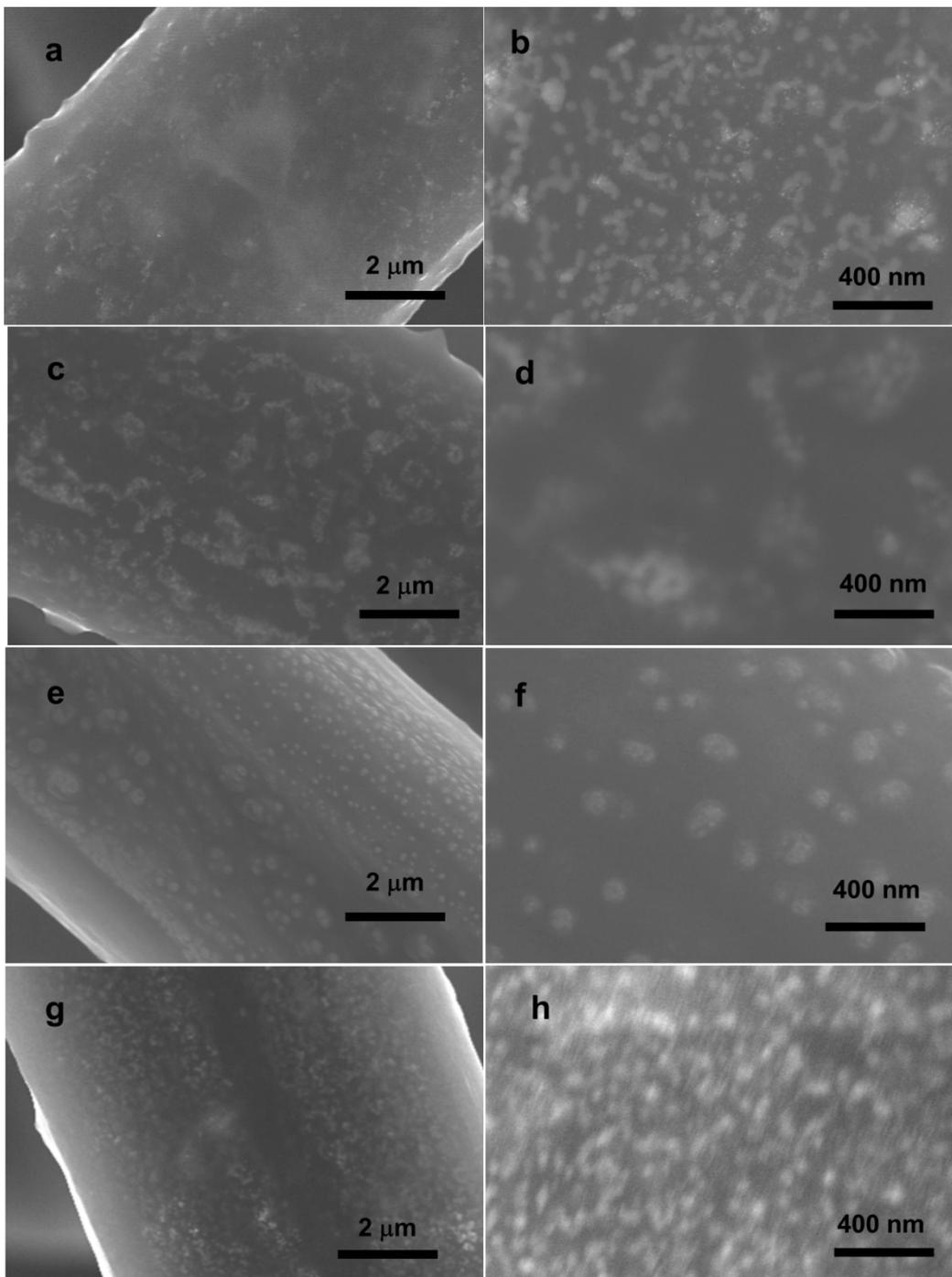


Fig. S7. SEM images of Cd electrodeposited on carbon papers at -0.8 V (a, b), -0.9 V (c, d), -1.1 V (e, f) and -1.2 V (g, h) (vs. Ag/AgCl) after 2 h electrolysis.

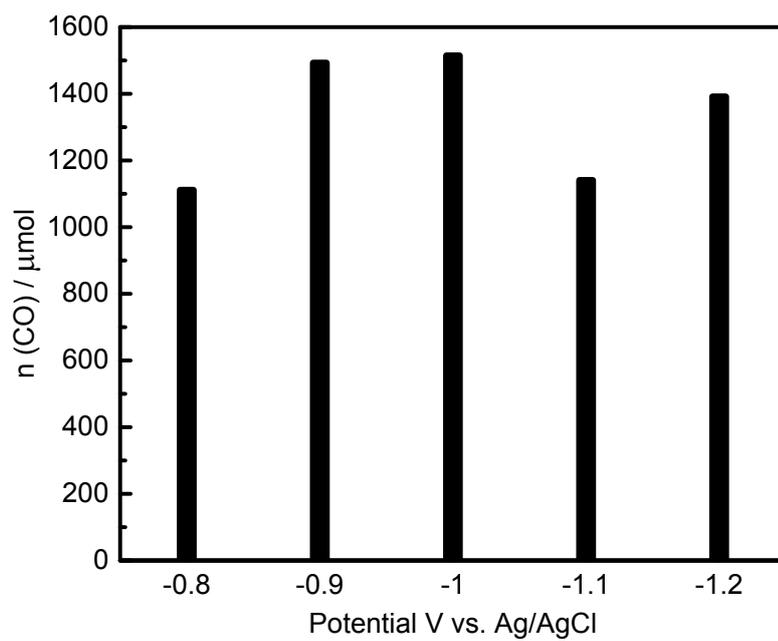


Fig. S8. Amounts of CO generated in 2 hours under -1.75 V (vs. RHE) for electrodes prepared at different potentials (vs. Ag/AgCl).

Table S1. Selectivities and current densities for CO₂ electroreduction to CO in this work and in literature.

Electrode	Electrolytes	Potential	Current density (mA cm ⁻²)	CO F.E. [%]	Ref.
Cd nanoparticles	[BMIM]PF ₆ /MeCN	-1.65 V vs. RHE	22.4	99	This work
Bi-based electrodes	[EMIM]BF ₄ / MeCN		4	93	
	[BMIM]BF ₄ / MeCN	-1.67 V vs. RHE	5.8	95	S3
	[BMIM]PF ₆ / MeCN		5.4	90	
Bi			10	78	
Sn	BMIM-OTf / MeCN	-1.67 V vs. RHE	7.2	77	S4
Sb			0.5	NA	
Pb			1.0	40	

References

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- S2 B. A. Rosen, A. Salehi-Khojin, M. R. Thorson, W. Zhu, D. T. Whipple, P. J. A. Kenis and R. I. Masel, *Science*, 2011, **334**, 643-644.
- S3 J. L. DiMeglio and J. Rosenthal, *J. Am. Chem. Soc.*, 2013, **135**, 8798-8801.
- S4 J. Medina-Ramos, R. C. Pupillo, T. P. Keane, J. L. DiMeglio and J. Rosenthal, *J. Am. Chem. Soc.*, 2015, **137**, 5021-5027.