Supporting information for:

Highly efficient electrochemical reduction of CO_2 to formic acid over lead dioxide in an ionic liquid catholyte mixture

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Experimental Section

Materials: Ionic liquids, including 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF_4, purity >99%), 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim]BF_4, purity >99%), 1-hexyl-3-methylimidazolium tetrafluoroborate ([Hmim]BF_4, purity >99%), 1-octyl-3-methylimidazolium tetrafluoroborate ([Omim]BF_4, purity >99%), 1-decyl-3-methylimidazolium tetrafluoroborate ([Dmim]BF_4, purity >99%), 1-benzyl-3-methylimidazolium tetrafluoroborate ([Bzmim]BF_4, purity >99%), and 1-benzyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Bzmim]NTf_2, purity >99%), were purchased from the Centre of Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences. Molybdenum trioxide (>99%), copper oxide (>97%), zinc oxide (>99%) and lead dioxide (purity > 99%) were supplied by J&K Scientific Co., Ltd. Titanium dioxide (P25) was supplied by Acros Organics. Bismuth oxide (>99%), Nafion N-117 membrane (0.180 mm thick, ≥ 0.90 meg/g exchange capacity), Nafion D-521 dispersion (5 % w/w in water and 1-propanol, ≥ 0.92 meg/g exchange capacity) and Toray Carbon Paper (CP, TGP-H-60, 19×19 cm) were obtained from Alfa Aesar.

Preparation of electrode*:* 10 mg PbO_2 was suspended in 1 mL ethanol with 20 μL Nafion D-521 dispersion (5 wt%) to form a homogeneous emulsion assisted by ultrasound. Then, the ink was spread onto the carbon paper surface by a micropipette and then dried under room temperature.

Cyclic voltammetry (CV) measurement: An electrochemical workstation (CHI 6081E, Shanghai CH

Instruments Co., China) was used in all the experiments. Cyclic voltammetry (CV) measurements were carried out in a H-type cell, which was separated by Nafion membrane with three-electrode configuration consisting of working electrode (PbO_2), a platinum gauze auxiliary electrode, and an Ag/Ag^+ (0.01 M $AgNO_3$ in 0.1 M TBAP-MeCN) reference electrode. Prior to experiment, electrolyte was bubbled with N_2 or CO_2 for 30 min to form N_2 or CO_2 saturated solution. The CV measurement in gas-saturated electrolyte was conducted in the potential range of -1.0 to -2.5 V *vs.* Ag/Ag^+ at a sweep rate of 20 $mV \cdot s^{-1}$. Slight magnetic stirring was applied in the process.

CO_2 reduction electrolysis and product analysis: Electrolysis was carried out at room temperature in a typical H-type cell, which was separated by a Nafion membrane. In a typical experiment, IL containing solution and H_2SO_4 aqueous solution (0.5 M) were used as cathodic and anodic electrolytes, respectively. The amount of electrolyte used was 20 mL in all the experiments. Before electrolysis experiment, CO_2 was bubbled through the catholyte for 30 min with stirring and electrolysis was conducted under a steady follow of CO_2 (2 $mL \cdot min^{-1}$). The gaseous product of electrochemical experiments was analyzed by gas chromatography (GC, HP 4890D) equipped with FID and TCD detectors using helium as the internal standard. The liquid product was analyzed by ^1H NMR (Bruker Avance III 400 HD spectrometer) in DMSO-d_6 with TMS as an internal standard. The total current density and Faradaic efficiency of the products were calculated on the basis of GC and NMR analysis.

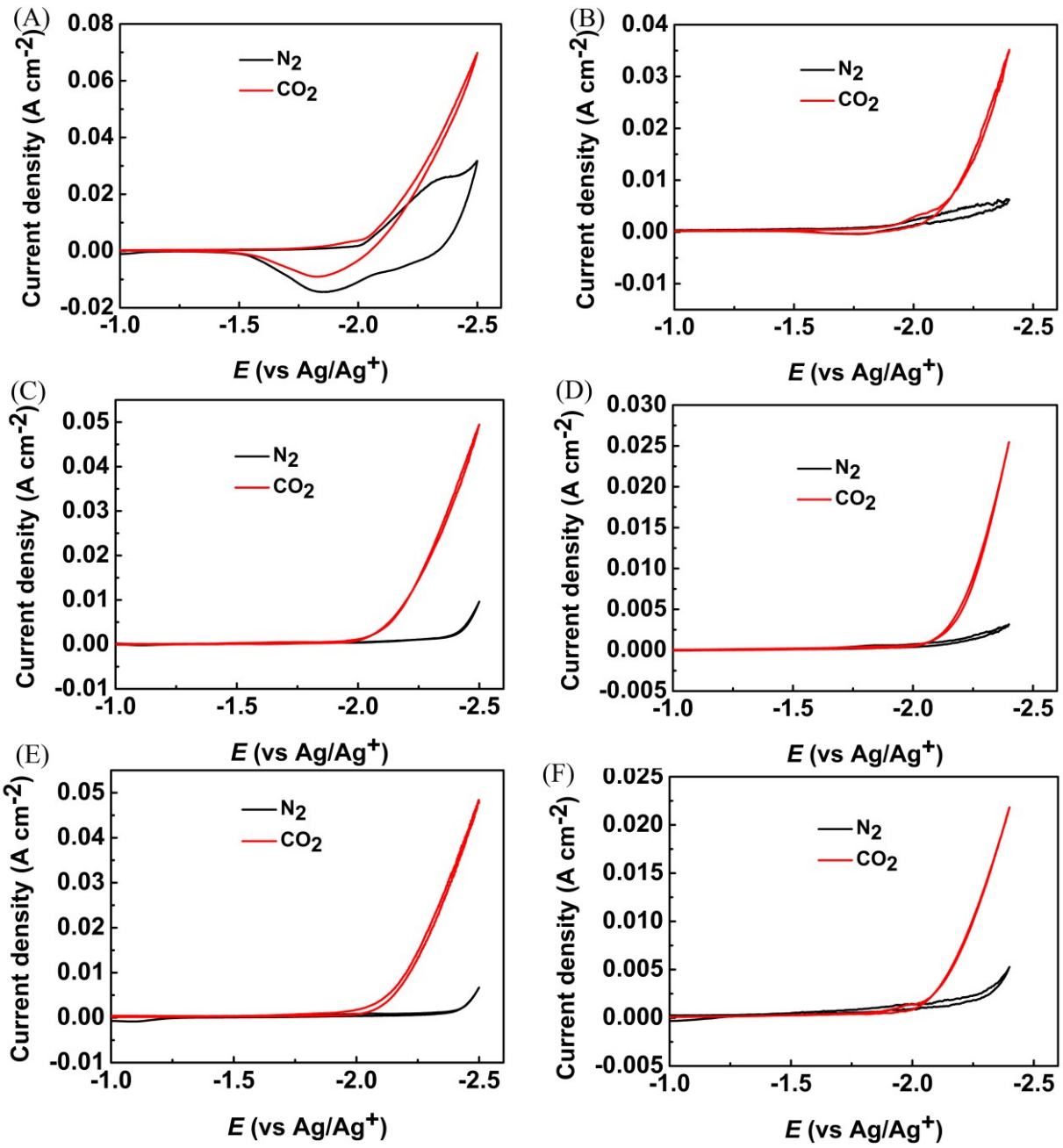

Fig. S1. CV measurements using PbO_2 electrode in CO_2 or N_2 saturated electrolyte of IL (14.6 wt%)-acetonitrile-H_2O (11.7 wt%) at room temperature. (A) [Emim]BF_4, (B) [Bmim]BF_4, (C) [Hmim]BF_4, (D) [Omim]BF_4, (E) [Dmim]BF_4, and (F) [Bzmim]NTf_2.

Table S1. Faradaic efficiency (FE) of HCOOH and current density (CD) in CO_2 reduction using various electrodes and electrolytes.

Electrode	Potential (V)	Electrolyte	FE (%)	CD (mA cm^{-2})	Reference
PbO_2 on carbon paper	-2.3 V vs Ag/Ag^+	[Bzmim]BF_4 (14.7wt%)-CH_3CN-H_2O (11.7%)	95.5	40.8	This work
Co_3O_4 on glassy carbon	-0.88 V vs. SCE	0.1M $KHCO_3$	60	0.68	S1
$Pd_{70}Pt_{30}$/C	-0.4 V vs RHE	0.1M KH_2PO_4/0.1M K_2HPO_4	88	5.0	S2
SnO_2@N-PC	-2.2 V vs Ag/Ag^+	0.5 M [Bmim]PF_6-CH_3CN	94.1	28.4	S3
Sn sheets in graphene	-1.8 V vs. SCE	0.1M $NaHCO_3$	85	21.1	S4
SnO_2 on carbon cloth	-1.6 V vs. Ag/AgCl	0.5 M $NaHCO_3$	89.0	45.0	S5
SnO_2 on carbon black	-1.15 V vs RHE	0.1 M $KHCO_3$	75	10.8	S6
Nano-Bi on carbon paper	-1.8 V vs. SHE	0.5 M $NaHCO_3$	96.4	15.2	S7
Pb	-2.2 V vs Ag/Ag^+	[Bmim]PF_6 (30 wt%)/AcN-H_2O (5 wt%)	91.6	41.0	S8
$BiOCl_{0.5}Br_{0.5}$/GCE	-1.6 V vs SCE	0.5 M $KHCO_3$	98.4	9.7	S9
Sn/SnS_2	-1.4 V vs. Ag/AgCl	0.5 M $NaHCO_3$	84.5	13.9	S10
MoO_2	-2.45 V vs Fe/Fc^+	0.1 M $TBAPF_6$/MeCN	40	4.0	S11
Cu_2O	-0.5 V vs RHE	0.1M $KHCO_3$	35	2.0	S12

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