Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary Information

Synthesis of Hierarchical Mesoporous Prussian Blue Analogues in Ionic Liquid/Water/$MgCl_2$ and Application in Electrochemical Reduction of CO_2

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Content

Experimental Section

Materials: 1-butyl-3-methylimidazolium tetrafluoroborate ($BmimBF_4$, purity>99%) and 1-butyl-3-methylimidazolium hexafluorophosphate ($BmimPF_6$, purity>99%) were purchased from the Centre of Green Chemistry and Catalysis, LICP, CAS. $Cu(NO_3)_2 \cdot 3H_2O$ (A. R. grade), $Co(NO_3)_2 \cdot 6H_2O$ (A. R. grade), $Ni(NO_3)_2 \cdot 6H_2O$ (A. R. grade), acetonitrile (A. R. grade), ethanol (A. R. grade), acetone (A. R. grade), $K_3Fe(CN)_6$ (A. R. grade), ethanol (A. R. grade), Cu foil (purity>99.99%) were provided by Sinopharm Chemical Reagent Co., Ltd. $MgCl_2$ (purity>98%) and $K_3Co(CN)_6$ (purity>98%) were obtained from J&K Scientific Ltd. Toray Carbon Paper (CP, TGP-H-60, 19×19 cm) and Nafion N-117 membrane (0.180 mm thick, ≥0.90 meg/g exchange capacity) were purchased from Alfa Aesar China Co., Ltd. Polytetrafluoroethylene (PTFE, 60 wt% aqueous solution) was purchased from Sigma-Aldrich Co. LLC. The CO_2 (99.99%) and N_2 (99.99%) were provided by Beijing Analytical Instrument Company.

Conductivity measurements: The conductivities of all the mixtures were measured using a conductivity meter (FE30) and a LE703 conductivity electrode, produced by Mettler-Toledo Instruments Co., Ltd. (Shanghai, China). The electrode was calibrated by standard NaCl solution with a conductivity of 12.88 $ms \cdot cm^{-1}$. In a typical experiment, the solution was added into a glass tube and the head of the electrode was immersed in the solution. The tube was sealed and immersed in a water bath of 25°C±0.1°C controlled by a YKKY A2 temperature controller (Beijing Changliu Scientific Instruments Co., Ltd.).

Dynamic light scattering (DLS) study: The experiments were performed on a Zetasizer Nano ZS ZEN3600 (Malvern, U.K.).[S1] The sample was placed in a four-way quartz colorimetric utensil. The experiment was carried out at 25 ^oC and at 90° scattering angle with the light of 633 nm. The signal was recorded and was repeated for at least three times.

SAXS study: SAXS experiments were carried out at Beamline 1W2A at the Beijing Synchrotron Radiation Facility.[S2] The data were collected using a CCD detector (MAR) with maximum resolution of 3450×3450 pixels. The wavelength of the X-ray was 1.54 Å, and the distance of the sample to detector was 1.45 m. In a typical experiment, the sample was added into the sample cell controlled at 25 ^oC, and the X-ray scattering data were recorded. The 2-D SAXS images were obtained from the detector and then transformed into the profiles of intensity (I) *vs* wavevector (q) by the software SAXS Data Pre-process V2.0.0.

Materials synthesis: We describe mainly the procedures to synthesize mesoporous Cu-PBAs (Fig. S1) because those to synthesize Co-PBA and Ni-PBA were similar. In a typical experiment, 0.15 mmol $Cu(NO_3)_2 \cdot 3H_2O$ was dissolved into 10 g solution containing 70 wt% IL and 30 wt% water with known amount of $MgCl_2$, and 0.1 mmol $K_3Co(CN)_6$ was dissolved into 20 g solution with the same composition. Then the solution containing $Cu(NO_3)_2$ were added into the mixture containing $K_3Co(CN)_6$ very slowly using a syringe. The whole reaction process was kept at 25 ^{o}C with stirring. After completely adding, the mixture was stirred for extra 24 hrs and was then aged without stirring for 48 hrs.[S3] The obtained mixture containing the materials was centrifuged with a centrifugal speed of 5000 rpm. The obtained Cu-PBAs were washed with water for 5 times (5×50 mL) and ethanol for 5 times (5×50 mL), and then dried in a vacuum oven at 40 ^{o}C for 24 h. To synthesize Co-PBA or Ni-PBA, the procedures were the similar, the main difference was that $Co(NO_3)_2 \cdot 6H_2O$ or $Ni(NO_3)_2 \cdot 6H_2O$ were used instead of $Cu(NO_3)_2 \cdot 3H_2O$. For bulk Cu-PBA synthesis, 0.15 mmol $Cu(NO_3)_2 \cdot 3H_2O$ was dissolved in 10 g water, and 0.1 mmol $K_3Co(CN)_6$ was dissolved in 20 g water, and the other procedures are similar to that described above.

Material Characterization: X-Ray diffraction (XRD) analysis of the samples was performed on the X-ray diffractometer (Model D/MAX2500, Rigaka) with Cu-Kα radiation, and the scan speed was 5^{o}/min. The morphologies of the products were characterized by JEOL-1011 TEM operated at 100 kV. The porosity properties of the materials were obtained from nitrogen adsorption-desorption isotherms determined using a Micromeritics ASAP 2020M system. Barrett-Joyner-Halenda method was used for mesopores and Horvath-Kawazoe method for micropores. The adsorption isotherms of CO_2 of the degassed Cu-PBAs were determined at 273 K in the pressure range of 0-1 atm on a TriStar II 3020 device. The composition of the Cu-PBAs was determined by ICP-AES (VISTA-MPX).

Fabrication of Cu-PBA electrodes: The working electrodes were prepared by loading sample suspension onto the carbon papers (CPs).[S4] Briefly, as-prepared Cu-PBAs containing 0.5 wt% PTFE were dispersed in 95 wt% acetone aqueous solution and ultrasonicated for 30 min to form uniform suspension, and the concentration of the Cu-PBA was 1 $mg \cdot mL^{-1}$. 0.1 mL of the Cu-PBA suspension was loaded on the 1 cm × 1 cm CP. The electrode was dried at room temperature overnight before the electrochemical experiment.

Linear sweep voltammetric (LSV) study: An electrochemical workstation (CHI 6081E, Shanghai CH Instruments Co., China) was used for all CO_2 reduction experiments. LSV scans were carried out in a single compartment cell with a three-electrode configuration, which consisted of working electrode, a platinum gauze auxiliary electrode, and Ag/Ag^+ (0.01 M $AgNO_3$ in 0.1 M TBAP-MeCN) reference electrode. Before each set of experiment, the electrolyte (acetonitrile containing 0.5 M $BmimBF_4$) was bubbled with CO_2 (or N_2) for 30 min until CO_2-saturated solution (or N_2-saturated solution) was formed, which was confirmed by the fact that the LSV trace was not changed with gas bubbling time. LSV measurements in gas-saturated electrolyte were carried out between -1.3 V and -2.3 V vs. Ag/Ag^+ at a sweep rate of

20 mV/s. For better mixing, slight magnetic stirring was applied in the process. When Cu foil was used as the electrode, Cu foil was polished with fine sand paper and then were sonicated in acetone for 10 min prior to the experiment, followed by washing with water and ethanol, and finally dried in N_2 atmosphere.

Electrochemical surface area measurement: The electrochemical surface areas of the Cu-PBA/carbon paper electrodes were determined by steady-state cyclic voltammetry (CV) in a solution of 0.01 M $[Fe(CN)_6]^{3-/4-}$ with 1 M KCl at a scan rate of 50 $mV\cdot s^{-1}$.[S5] The electrochemical surface area was estimated according to the Randles-Sevcik equation.[S6]

CO_2 reduction and product analysis: The electrolysis was performed under room temperature in an H-type cell with an Ag/Ag^+ (0.01 M $AgNO_3$ in 0.1 M TBAP-MeCN) reference electrode. The apparatus was similar to that reported by other authors,[S7] and is shown schematically in Fig. S4. The cathode and anode compartments were separated by a proton exchange membrane (Nafion 117). MeCN containing 0.5 M $BmimPF_6$ and 0.5 M H_2SO_4 aqueous solution were used as cathodic and anodic electrolytes, respectively. Before electrolysis, CO_2 was bubbled through the catholyte (2 mL per min) for 30 min with stirring. Potentiostatic electrochemical reduction of CO_2 was carried out with CO_2 bubbling (5 mL per min), and the gaseous product was collected in a gas bag. After 5 hrs, the gaseous product in the gas bag was collected and analyzed by gas chromatography (GC, HP 4890D), which was equipped with TCD and FID detectors using helium as the internal standard, and the liquid mixture was analyzed by ^1H-NMR method, which recorded on a Bruker Avance III 400 HD spectrometer in DMSO-d_6 with TMS as an internal standard. The Faradaic efficiency the products was calculated.[S8]

Supplementary Figures

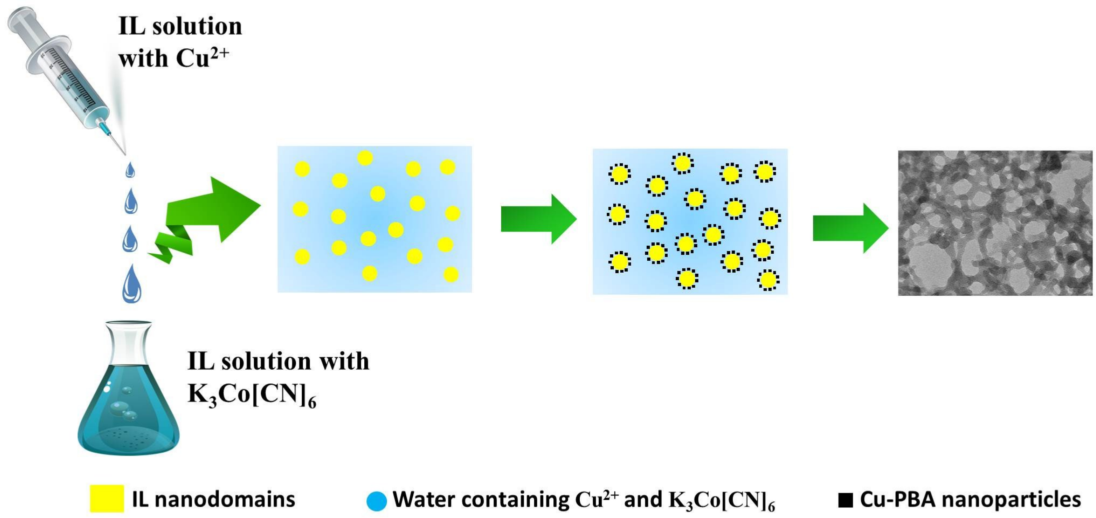

Fig. S1 The route for the synthesis of Cu-PBAs.

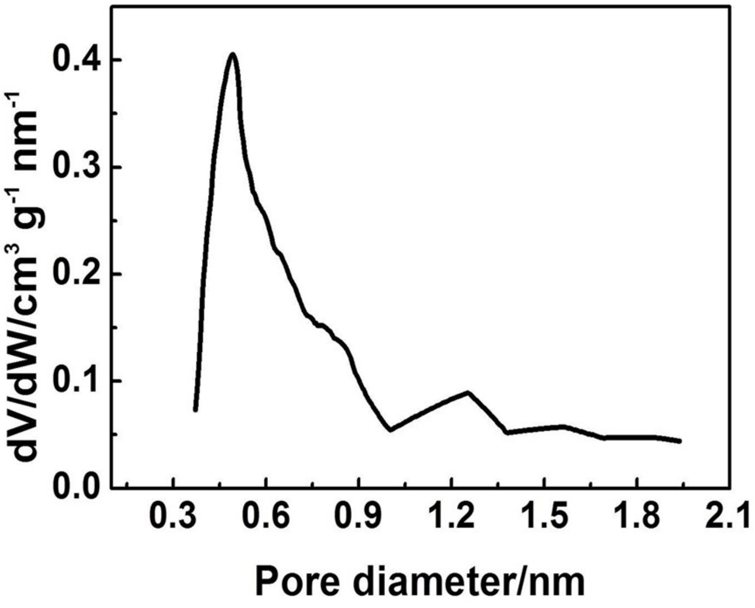

Fig. S2 Micropore size distribution of the Cu-PBA-2.2.

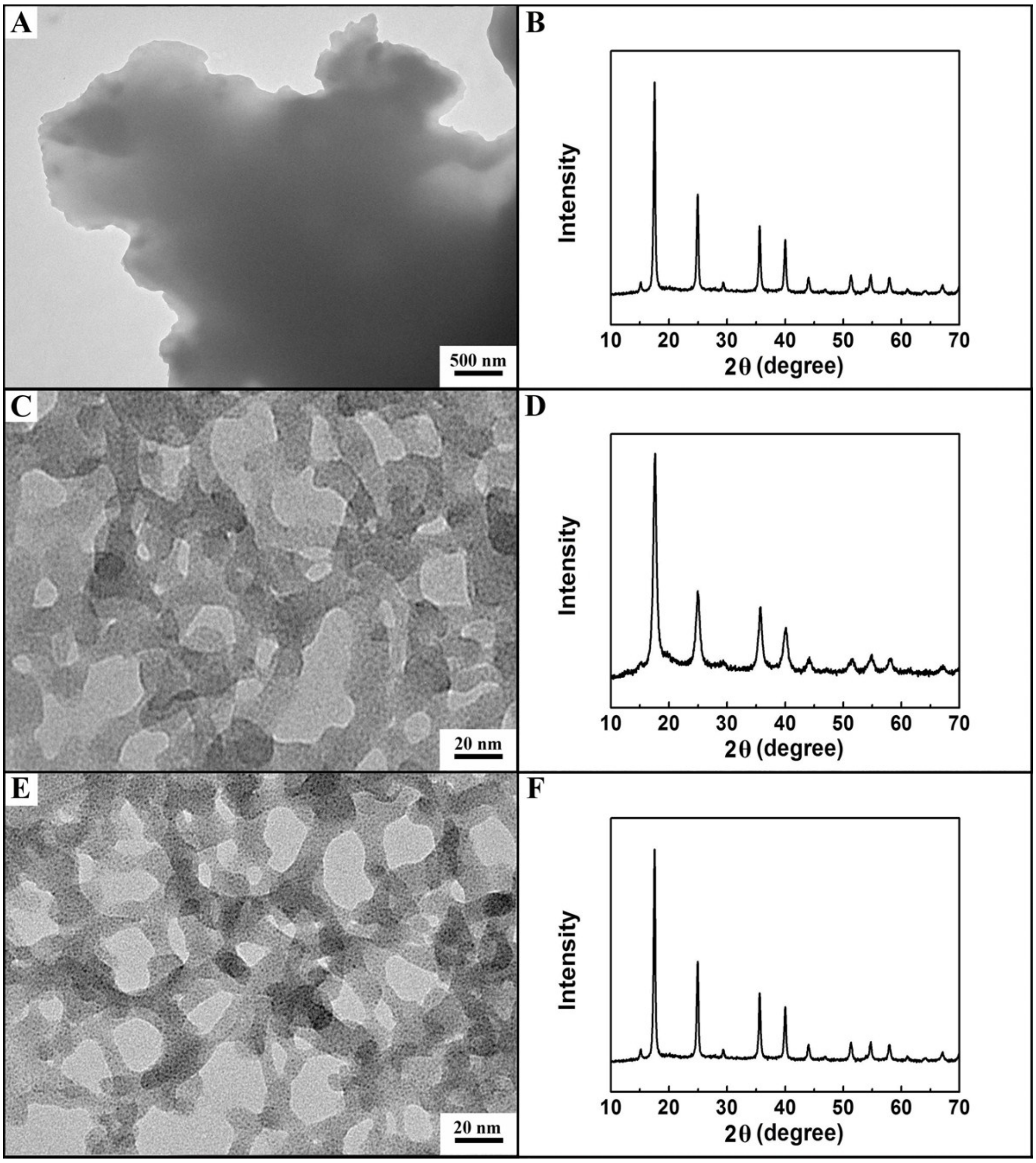

Fig. S3 TEM images and XRD patterns of Cu-PBA-w (A-B), Co-PBA-2.2 (C-D) and Ni-PBA-2.2 (E-F).

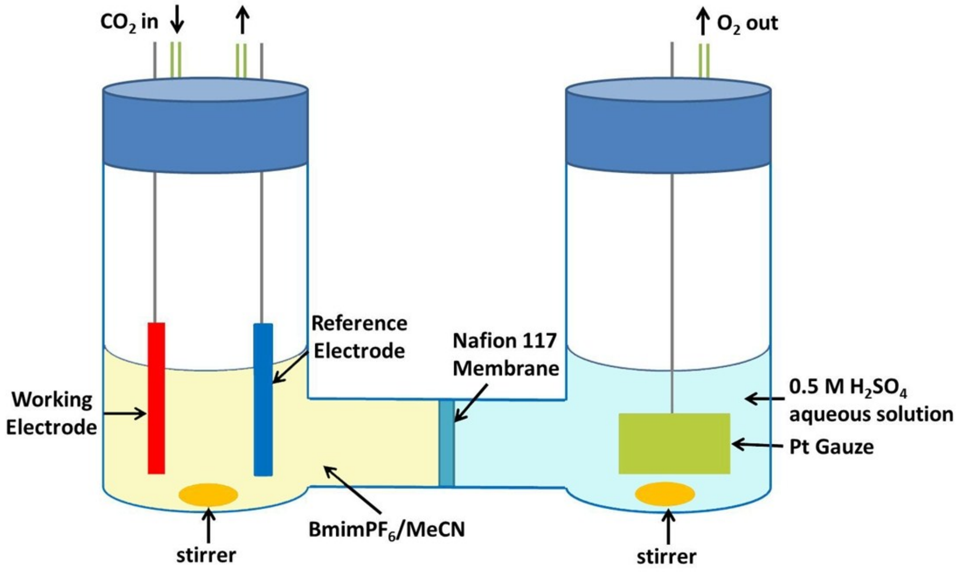

Fig. S4 The schematic diagram of the electrolysis device.

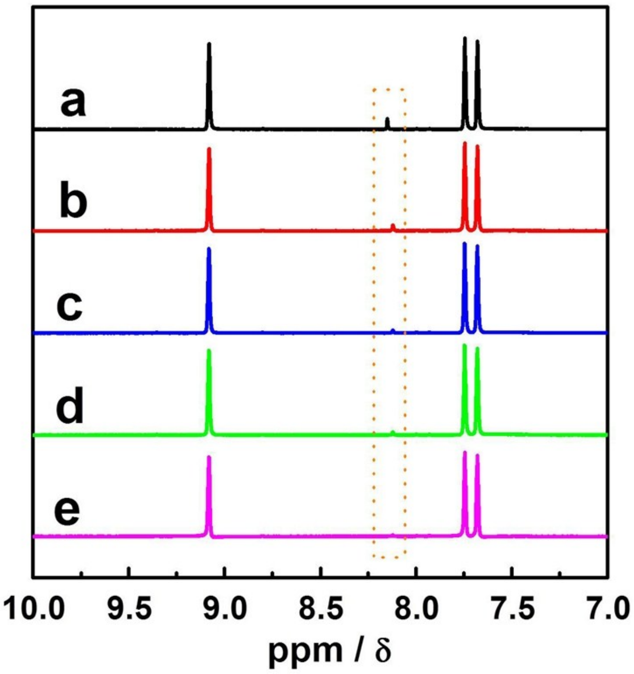

Fig. S5 ^{1}H-NMR spectra of the electrolyte after electrolysis for 5 hrs using different electrodes: (a) Cu-PBA-2.2; (b) Cu-PBA-1.0; (c) Cu-PBA-0; (d) Cu-PBA-w; (e) Cu-foil.

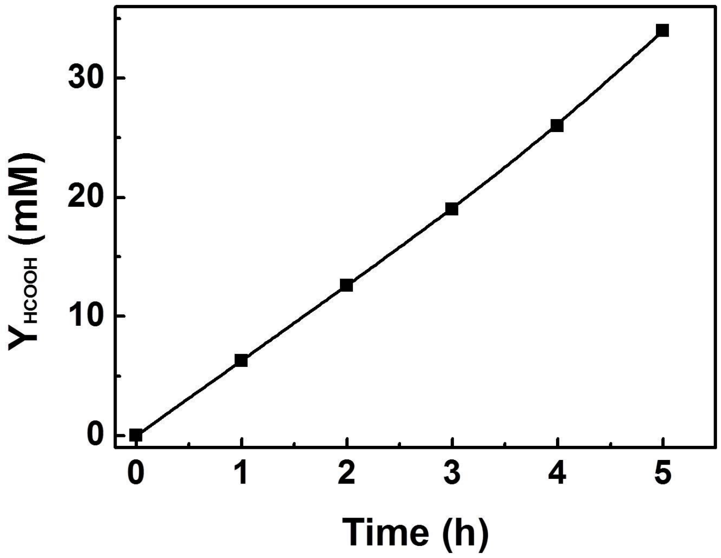

Fig. S6 The dependence of formic acid yield on electrolysis time using Cu-PBA-2.2 electrode at -2.0 V vs. Ag/Ag^+ in MeCN containing 0.5 M $BmimPF_6$.

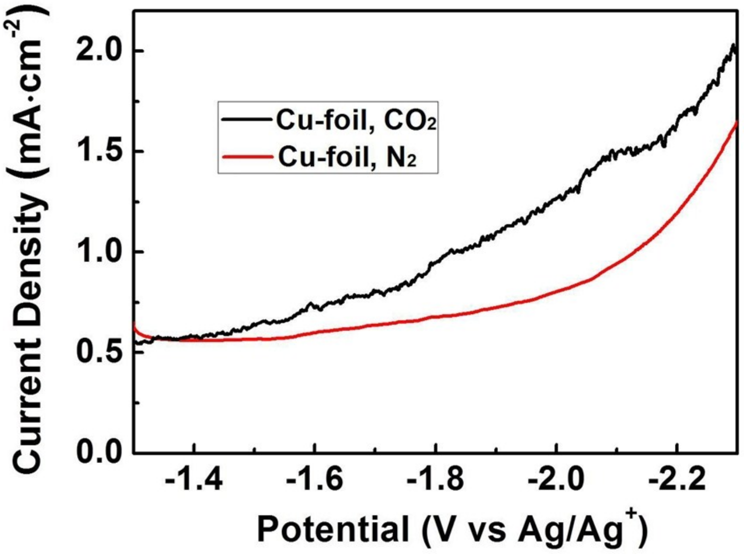

Fig. S7 LSV curves of Cu foil electrode in N_2-saturated and CO_2-saturated MeCN containing 0.5 M $BmimPF_6$.

Supplementary Tables

Table S1 The BET surface area (S), total mesopore volume (V) of different PBAs.

Entry	Sample	S [$m^2 \cdot g^{-1}$]	V [$cm^3 \cdot g^{-1}$]
1	Cu-PBA-0	379	0.11
2	Cu-PBA-1.0	417	0.34
3	Cu-PBA-2.2	487	0.71
4	Cu-PBA-w	366	-
5	Co-PBA-2.2	732	0.81
6	Ni-PBA-2.2	708	0.72

Table S2 j_{tot}, FE_{HCOOH}, FE_{H2} and Y_{HCOOH} at an applied potential of -2.0 V vs Ag/Ag^+ in MeCN containing 0.5 M $BmimPF_6$ with an electrolysis time of 5 hrs, the electrochemical surface areas (S), and CO_2 adsorption quantity under 1 atm at 273 K (A) of different Cu electrodes.

Entry	Electrodes	j_{tot} [$mA \cdot cm^{-2}$]	FE_{HCOOH} [%]	FE_{H2} [%]	Y_{HCOOH} [mM]	S [cm^2]	A [$cm^3 \cdot g^{-1}$]
1	Cu-PBA-0	3.0±0.4	73.5	26.1	22	0.77	54.5
2	Cu-PBA-1.0	4.2±0.6	89.9	9.2	28	1.05	71.2
3	Cu-PBA-2.2	4.8±0.8	93.1	6.0	34	1.1	91.3
4	Cu-PBA-w	2.3±0.2	50.7	46.0	12	0.42	41.9
5	Cu-foil	2.1±0.2	30.2	62.3	8.5	-	-

Table S3 j_{tot} and FE_{HCOOH} for CO_2 reduction using different electrodes.

Entry	Electrode	Electrolyte	Potential [V][a]	j_{tot} [mA·cm^{-2}]	FE_{HCOOH} [%]	Ref.
1	Cu-PBA	0.5 M $BmimPF_6$ in MeCN	-2.0 V vs Ag/Ag^+	4.8	93.1	This work
2	SnO_2	0.5M NaOH	-0.6 V vs RHE	3.5	67.6	S9
3	Cu_2O	0.1M $KHCO_3$	-0.5 V vs RHE	2.0	35	S10
4	Sn/GDE	0.1M $KHCO_3$	-1.2 V vs Ag/AgCl	3	64	S11
5	Pb	0.5M NaOH	-1.59 V	2.5	90	S12
6	Pb	0.1M K_2CO_3	-1.8 V vs SCE	0.51	12.5	S13
7	Pb	0.5M $KHCO_3$	-1.5 V vs SCE	0.79	30	S13
8	Sn	0.1M K_2CO_3	-1.7 V vs SCE	0.04	16.5	S13
9	Sn	0.5M $KHCO_3$	-1.7 V vs SCE	0.11	31.0	S13
10	Sn/SnO_x	0.5M $NaHCO_3$	-0.7 V vs RHE	2.0	38	S14

[a] NHE, RHE, and SCE stand for normal hydrogen electrode, reversible hydrogen electrode, and saturated calomel electrode, respectively.

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