# Supplementary Information

# Formate electrosynthesis from aqueous carbon dioxide over Pb-Zn catalysts

with core-shell structure

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#### **Experimental Section**

#### **Chemicals and Materials**

Lead nitrate (Pb(NO<sub>3</sub>)<sub>2</sub>), Potassium bicarbonate (KHCO<sub>3</sub>), Potassium hydroxide (KOH), Sodium borohydride (NaBH<sub>4</sub>), and Nafion solutions (5 wt%) were purchased from Sinopharm Chemical Reagent (Shanghai, China). Zinc nitrate hexahydrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) and Isopropanol alcohol (C<sub>3</sub>H<sub>8</sub>O) were obtained from Aladdin (Shanghai, China). Each analytical reagent was directly used without further purification and all aqueous solutions were prepared in deionized water.

### **Preparation of Catalysts and Electrodes**

Catalysts were prepared as follows. 0.3 mmol of  $Pb(NO_3)_2$  and 0.1 mmol of  $Zn(NO_3)_2$ ·6H<sub>2</sub>O were added to 15 ml of deionized water, and then the solution was added to 20 ml aqueous solution containing 0.057 g NaBH<sub>4</sub>. After stirring for 10 mins, the product is centrifuged at 9000 rpm min<sup>-1</sup> for 2 mins, and finally dried at 60 °C overnight. The resulting product is named Pb<sub>3</sub>Zn<sub>1</sub> catalyst. Pb<sub>1</sub>Zn<sub>1</sub> catalyst and Pb<sub>5</sub>Zn<sub>1</sub> catalyst were prepared by changing the feed ratio of Pb(NO<sub>3</sub>)<sub>2</sub> and Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O without changing the total cation concentration. Electrodes were prepared as follows. Disperse 8 mg of ground catalyst in 1 ml of C<sub>3</sub>H<sub>8</sub>O and 40  $\mu$  L Nafion solutions mixed solution until it is ink like, and then evenly drip it onto carbon paper (2 × 2 cm<sup>-2</sup>). After drying, the electrodes materials in the flow-cell are 2 mg of ground catalyst, 20  $\mu$  L Nafion solutions and carbon paper (2 × 0.5 cm<sup>-2</sup>).

#### **Physical and Chemical Characterization**

The crystal structures of Pb-Zn catalysts were characterized by XRD using an X-ray diffractometer (RIGAKU 3 KW D/MAX-2200V PC, Japan) equipped with a Cu-Ka radiation source operated at a scan rate of 8° min<sup>-1</sup>. X-ray photoelectron spectroscope (XPS) was performed using a Thermo Scientific KAlpha apparatus (U.S.A) equipped with a monochromatic Al Ka X-ray source to analyze the surface chemical composition and element valence state of the catalysts. The surface morphology and micro-structures were observed using a scanning electron microscope (SEM, ZEISS Gemini 300) and a transmission electron microscope (TEM, FEI Tecnai G2 F20) equipped with an energy-dispersive X-ray spectrometer (EDS). The ratio of Pb to Zn was determined by an inductively coupled plasma optical emission

spectroscopy (ICP-OES, Agilent 5110). Nitrogen adsorption and desorption measurements were carried out by a Quanta chrome ASAP 2020 M nitrogen adsorption instrument (U.S.A) to obtain the Brunauer-Emmett-Teller (BET) specific surface area.

# **Electrochemical Measurements**

All electrochemical experiments to study the electrochemical performance of the Pb-Zn series catalysts were performed on an H-cell connected to an electrochemical workstation (Shanghai Chenhua Instruments Co., Ltd., China). In the conventional three-electrode system, the working electrode (WE) was the as-prepared Pb-Zn catalyst, and the Pt wire and Ag/AgCl (saturated KCl) electrodes were used as the counter electrode (CE) and reference electrode (RE), respectively. The electrolyte was KHCO<sub>3</sub> (0.5 M, 50 mL) and Nafion® 117 film (Dupont, USA) was used to separate the cathodic and anodic compartments. Before measurement, Ar (99.999%) was bubbled into the electrolyte in the cathode chamber for at least 20 min and then  $CO_2$  (99.999%) was continuously introduced until the electrolyte was saturated. The ECR performance of the catalysts were investigated by various electrochemical experiments, such as cyclic voltammetry (CV), linear sweep voltammetry (LSV), double-layer capacitance (Cdl), and electrochemical impedance spectroscopy (EIS). The calculation formula of electrochemically active surface area (ECSA) is given as follows:

$$ECSA = \frac{C_{dl}}{C_s}$$

For the estimation of surface area, we used general specific capacitances of  $C_s = 0.029$  mF on the basis of typical reported value <sup>1, 2</sup>.

During the measurement, the flow rate of CO<sub>2</sub> pumping into the cathode chamber was maintained at 120 mL min<sup>-1</sup> to ensure that the electrolyte remained CO<sub>2</sub>-saturated at ambient pressure and temperature. In particular, additional electrochemical tests were conducted on Pb<sub>3</sub>Zn<sub>1</sub> catalyst in the flow-cell (1 M, 100 mL), the flow rate of CO<sub>2</sub> was maintained at 40 mL min<sup>-1</sup>, with other conditions remaining unchanged. The concentrations of formate and gas products in cathode cell were quantitatively measured by an ion chromatograph (IC1820, Shanghai Sunny Hengping Scientific Instrument Co. Ltd., China) and gas chromatograph (GC-2014C, Shimadzu analytical technology research and a development (Shanghai) Co. Ltd., China), respectively. The calculation formula of FE is given as follows:

$$FE_{Product} = \frac{E \, n \, F}{Q_{total}} \times 100\%$$

Where  $Q_{\text{total}}$  is the total of electric during electrolysis; *E* represents the number of electrons required, 2 represents the number of transferred electrons; n is the mol amount of product (formate), mol; *F* denotes the Faraday constant (96485 C mol<sup>-1</sup>).



Fig. S1 XRD patterns of Pb,  $Pb_5Zn_1$ , and  $Pb_1Zn_1$ .



Fig. S2 SEM images of (a) Pb, (b)  $Pb_5Zn_1$ , and (c)  $Pb_1Zn_1$ .



Fig. S3 The SEM elemental mappings of Pb<sub>5</sub>Zn<sub>1</sub> (a, b, c, d), Pb<sub>3</sub>Zn<sub>1</sub> (e, f, g, h) and Pb<sub>1</sub>Zn<sub>1</sub> (i, j, k, l).



Fig. S4 (a) TEM image, FFT and IFFT pattern. (b) Integrated pixel intensity of ZnO (red curve).



Fig. S5 Nitrogen adsorption-desorption isotherms and the pore size distributions (appended figures) for (a) Pb, (b)  $Pb_5Zn_1$ , (c)  $Pb_3Zn_1$ , (d)  $Pb_1Zn_1$  and (e) BET surface area of the four catalysts.



Fig. S6 CV curves of (a) Pb, (b)  $Pb_5Zn_1$ , (c)  $Pb_3Zn_1$ , and (d)  $Pb_1Zn_1$  catalysts in 0.5 M KHCO<sub>3</sub> solution under Ar- and CO<sub>2</sub>-saturated atmosphere. (e) CV curves in Ar-saturated 0.5 M KHCO<sub>3</sub> solution. (The potential is scanned from 0.64  $V_{RHE}$  to  $-1.46 V_{RHE}$ ; Scan rate is 50 mV s<sup>-1</sup>)



Fig. S7 CV curves of (a) Pb, (b) Pb<sub>5</sub>Zn<sub>1</sub>, (c) Pb<sub>3</sub>Zn<sub>1</sub>, and (d) Pb<sub>1</sub>Zn<sub>1</sub> catalysts, respectively.



Fig. S8 The current density in H-cell (a) and Flow-cell (b) and  $FE_{formate}$  (c) of  $Pb_3Zn_1$  catalyst.



Fig. S9 The FE for  $H_2$  on Pb and Pb-Zn catalysts at different potentials.



Fig. S10 (a) The stability test of  $Pb_3Zn_1$  catalyst in the H-cell (CO<sub>2</sub>-saturated 0.5 M KHCO<sub>3</sub>) at -1.26 V<sub>RHE</sub>, and current density and FE<sub>formate</sub> versus time curves. (b) XRD patterns of carbon paper (CP) and Pb<sub>3</sub>Zn<sub>1</sub>-CP after ECR test.



Fig. S11 Comparison of the maximum  $FE_{formate}$  and partial current density with reported Pbbased and Zn-based catalysts.



Fig. S12 Mechanistic scheme for  $CO_2$  electroreduction to HCOOH.

Catalysts	Nominal	ICP-OES	
	(mole ratio of Pb/Zn)	(mole ratio of Pb/Zn)	
$Pb_1Zn_1$	1.00	1.52	
$Pb_3Zn_1$	3.00	5.04	
$Pb_5Zn_1$	5.00	7.48	

Table S1. Metal molar ratio of Pb/Zn series materials according to ICP results

Electrocatalyst	Electrolyte	Electrolysis potential	FE <sub>formate</sub> (%)	Partial current density (mA cm <sup>-2</sup> )	Ref.
Pb(111)	a mixture of 0.1 mol·L <sup>-1</sup> HNO <sub>3</sub> and 0.01 mol L <sup>-1</sup> NaF in aqueous solution	-0.83 V (vs. RHE)	98.03	~2.4	3
PbPd bimetallic catalyst	0.5 M HCOOK	-1.5 V (vs. Ag/AgCl)	~85	5.6	4
Pb	0.5 M NaOH	-1.6 V (vs. SCE)	90	2.5	5
PbZn bimetallic catalyst	0.1 M KHCO <sub>3</sub>	-1.2 V (vs. RHE)	95	47	6
PbSn bimetallic catalyst	0.5 M KHCO <sub>3</sub>	-2.0 V (vs. Ag/AgCl)	79.8	45.7	7
Pd-doped Pb <sub>3</sub> (CO <sub>3</sub> ) <sub>2</sub> (OH) <sub>2</sub>	0.1 M KHCO <sub>3</sub>	-1.20 V (vs. RHE)	96.5	13	8
Sn <sub>1</sub> Pb <sub>3</sub> bimetallic catalyst	0.5 M KHCO <sub>3</sub>	-1.16 V (vs. SHE)	92	17.2	9
oxide-derived Sn-Pb- Sb alloy	0.1 M KHCO <sub>3</sub>	-1.4 V (vs. RHE)	91	8.3	10
BiPb bimetallic electrode	0.5 M KHCO <sub>3</sub>	-0.96 V (vs. RHE)	91.86	15.56	11
Bi-Modified Zn Catalyst	0.5 M NaHCO <sub>3</sub>	-0.8 V (vs. RHE)	94	3.8	12
Single-Atom Sn on ZnO Nanosheets	0.5 M KHCO <sub>3</sub>	-1.7 V (vs. RHE)	88	115	13
RAD-Zn	0.5 M NaHCO <sub>3</sub>	-1.9 V (vs. RHE)	87	12.8	14
CuZn-0.5	0.1 M KHCO <sub>3</sub>	-1.1 V (vs. RHE)	60	4.5	15

Table S2. Comparative study on the electrocatalytic performance of Pb-based and Zn-based catalysts.

$Zn_{0.95}In_{0.05}$	0.1 M KHCO <sub>3</sub>	-1.2 V (vs. RHE)	95	22	16
ZnCu@Cu	0.5 M NaHCO <sub>3</sub>	-1.25 V (vs. RHE)	48.6	22.5	17
Pb-Zn bimetallic catalyst	0.5 M KHCO <sub>3</sub>	-1.26 V (vs. RHE)	98.4	60	This work

# Notes and references

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