**Supporting information for:** 

## Design of naturally derived lead phytate as an electrocatalyst for highly efficient CO<sub>2</sub>

## reduction to formic acid

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## **Experimental Section**

Materials. Ionic liquids, 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim]PF<sub>6</sub>, purity >99%), 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF<sub>4</sub>, purity >99%), 1ethyl-3-methylimidazolium tetrafluoroborate ([Emim]BF<sub>4</sub>, purity >99%), 1-benzyl-3methylimidazolium tetrafluoroborate  $([Bzmim]BF_4,$ purity >99%), 1-benzyl-3methylimidazolium bis(trifluoromethylsulfonyl)imide ([Bzmim]NTf<sub>2</sub>, purity >99%), 1dodecyl-3-methylimidazolium chloride ([Domim]Cl, purity >99%) and 1-benzyl-3methylimidazolium hexafluorophosphate ( $[Bzmim]PF_6$ , purity >99%) were purchased from the Centre of Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences. Phytic acid (70% aqueous solution), lead acetate trihydrate (purity >99%), disodium terephthalate (TPA, 99%) and SnCl<sub>4</sub>·5H<sub>2</sub>O (98%) were obtained from Sinophar Chemical Reagent Co., Ltd. Zr(NO<sub>3</sub>)<sub>4</sub>·5H<sub>2</sub>O (98%) was purchased from Beijing InnoChem Science & Technology Co., Ltd. Amino tri(methylene phosphonic acid (ATMP, 50 wt% in water) was obtained from Tokyo Chemical Industry Co., Ltd. Nafion N-117 membrane (0.180 mm thick,  $\geq 0.90$  meg/g exchange capacity) were supplied by Alfa Aesar China Co., Ltd. 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 purchased from Alfa Aesar China Co., Ltd.

*Preparation of materials.* The electrode materials in this work were prepared by simple coprecipitation method. Taking the preparation of Pb-PhyA as an example: Simply, lead acetate trihydrate (0.1 g) and 1-dodecyl-3-methylimidazolium chloride (0.2 g) were dissolved in H<sub>2</sub>O (17 mL). Then, phytic acid (30  $\mu$ L) was added into the mixture under stirring. Immediately, precipitate was formed. This precipitate was denoted as lead phytate (Pb-PhyA). After a reaction time of 12 h, the precipitate was separated and washed with H<sub>2</sub>O and ethanol, then was moved into the oven at 80 °C under vacuum for 24 h. Meanwhile, other materials with different metal ions or different ligands were synthesized using a similar route for Pb-PhyA. The difference was the amount of the used precursor: Zr(NO<sub>3</sub>)<sub>4</sub>·5H<sub>2</sub>O (0.1 g), SnCl<sub>4</sub>·5H<sub>2</sub>O (0.1 g), and disodium terephthalate (TPA, 0.05 g), and amino tri(methylene phosphonic acid (ATMP, 60  $\mu$ L), respectively. The characterization of these materials was presented in Figure S2-S5.

**Preparation of electrode**. The preparation process of different electrodes was similar. Taking Pb-PhyA/CP electrode as an example, 10 mg Pb-PhyA was suspended in 1 mL ethanol with 20  $\mu$ L Nafion D-521 dispersion (5 wt%) to form a homogeneous emulsion assisted by ultrasound. Then, the emulsion was spread onto the CP surface by a micropipette and then dried under room temperature.

*Linear sweep voltammetry (LSV) measurement.* An electrochemical workstation (CHI 660e, Shanghai CH Instruments Co., China) was used in all the experiments. Linear sweep voltammetry (LSV) measurement was carried out in a H-type cell, which was separated by Nafion membrane with three-electrode configuration consisting of working electrode (Pb-PhyA/CP), a platinum gauze auxiliary electrode, and an Ag/Ag<sup>+</sup> (0.01 M AgNO<sub>3</sub> in 0.1 M TBAP-MeCN) reference electrode. Prior to experiment, electrolyte was bubbled with N<sub>2</sub> or CO<sub>2</sub> for 30 min to obtain N<sub>2</sub> or CO<sub>2</sub> saturated solution. The LSV measurement in gassaturated electrolyte was conducted in the potential range of 0 to -2.4 V *vs.* Ag/Ag<sup>+</sup> at a sweep rate of 20 mV·s<sup>-1</sup>. Slight magnetic stirring was applied in the process.

*Electrolysis of CO*<sub>2</sub> *and product analysis.* Electrolysis of CO<sub>2</sub> was carried out at room temperature in a typical H-type cell. IL containing solution and H<sub>2</sub>SO<sub>4</sub> aqueous solution (0.5 M) were used as cathodic and anodic electrolytes, respectively. The amount of electrolyte was 20 mL in all the experiments. Prior to electrolysis, CO<sub>2</sub> was bubbled through the catholyte for 30 min with stirring and electrolysis was conducted under a steady follow of CO<sub>2</sub> (5.0 cm<sup>3</sup>·min<sup>-1</sup>). The gaseous product of electrochemical experiments was analyzed by gas chromatography (GC, HP 4890D) equipped with TCD detector using helium as the internal standard. The liquid product was analyzed by <sup>1</sup>H NMR (Bruker Avance III 400 HD spectrometer) in DMSO-*d6* 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.



Scheme S1. Chemical structure of phytic acid (PhyA).



Fig. S1. XPS of Pb 4f and P 2p in Pb-PhyA.



Fig. S2. XRD patterns. (A) Pb-TPA, (B) Pb-ATMP, (C) Sn-PhyA, and (D) Zr-PhyA.



Fig. S3. FT-IR spectra. (A) Pb-TPA, (B) Pb-ATMP, (C) Sn-PhyA, and (D) Zr-PhyA.



Fig. S4. TEM images. (A) Pb-TPA, (B) Pb-ATMP, (C) Sn-PhyA, and (D) Zr-PhyA



Fig. S5. SEM images. (A) Pb-TPA, (B) Pb-ATMP, (C) Sn-PhyA, and (D) Zr-PhyA.



Fig. S6. The measured and fitted EIS spectra of Pb-PhyA.



Fig. S7. The measured and fitted EIS spectra of Pb-ATMP.



Fig. S8. The measured and fitted EIS spectra of Pb-TPA.



**Fig. S9.** Electrical equivalent circuit for fitting the measured impedance data. Rs, Cdl, Rct, Cads, Rads, and Zw represent solution resistance, double layer capacitance, electron transfer resistance, surface adsorption capacitance, surface adsorption resistance and Warburg impedance, respectively.



Fig. S10. LSV measurements using Pb-PhyA electrode in CO<sub>2</sub> or N<sub>2</sub> saturated electrolyte of IL (12.8 wt%)-acetonitrile-H<sub>2</sub>O (9.9 wt%) at room temperature. (A) [Emim]BF<sub>4</sub>, (B) [Bmim]BF<sub>4</sub>, (C) [Bmim]PF<sub>6</sub>, (D) [Bzmim]NTf<sub>2</sub>, and (E) [Bzmim]PF<sub>6</sub>.