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Lead—Porphyrin Metal—Organic Framework: Gas Adsorption Properties and Electrocatalytic Activity for Water Oxidation

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A 3D non-interpenetrating porous metal-organic framework [Pb₂(H₂TCPP)]·4DMF·H₂O (Pb-TCPP) (H₆TCPP = 5,10,15,20-tetra(carboxyphenyl)porphyrin) was synthesized by employment of a robust porphyrin ligand. Pb-TCPP exhibits a one-dimensional channel possessing fairly good capability of gas sorption for N₂, H₂, Ar, CO₂ gases, and also features selectivity for CO₂ over CH₄ at 298 K. Furthermore, Pb-TCPP shows electrocatalytic activity for water oxidation in alkaline solution. It is the first 3D porous Pb-MOF that exhibits both gas adsorption property and electrocatalytic activity for oxygen evolution reaction (OER).

INTRODUCTION

Porous metal-organic frameworks (MOFs) have attracted great attention as an emerging class of porous materials, which are of fascinating structures and important applications in gas storage and separation, chemical absorption, luminescence, electronics, catalysis, and so on.[1-2] The utilities of MOFs are mostly attributed to their large internal surface areas and permanent porosities. The past decade has seen significant progress in design and synthesis of MOFs by reasonable selection of proper organic linkers and metal ions in the assembly process.[3-4] Multi-topic organic linkers with multi-functional groups have gained huge interest due to the diversity for constructing 3D porous materials.[5] Lots of MOFs with high surface areas and large pore sizes were constructed by employment of multi-topic ligands. For example, 2,2'-bipyridyl-derived ligands containing nitrogen donor groups and carboxyl groups have been used to construct MOFs for efficient catalytic organic transformations.[6] In recent years, a number of MOFs comprising porphyrin as a ligand has been

repoted,[7] for example, a reversible crystallinity-preserving phase transition in metal–porphyrin frameworks has been reported by Zhou's group[8], and using the pre-assembled [Fe₃O(OOCCH₃)₆] as the building block to assemble with metalloporphyrin ligands, they have constructed a series of highly stable mesoporous metalloporphyrin Fe-MOFs.[9] Wu et al have reported a series of tetra-carboxylate porphyrin ligands and Pb(II) cations to construct five MOFs and they have studied their structures carefully.[10]

Most of reported MOFs were focused on the structures, stability, luminescence, and so on, the electrochemical reactivity of MOFs systems, especially for oxygen evolution reaction (OER) was seldom studied.[11] As developing highly efficient electrocatalysts for OER has emerged as one of the most research hot spots in clean energy generation and storage.[12] It is of great importance to explore new family of materials to substitute traditional cost-effective oxygen evolution catalysts. However, the well-established catalysts for water oxidation up to now are mainly recorded in some precious metal or traditional metal material,[13] the MOFs used for OER are nearly unexplored.[14] Actually, porous structure of MOFs would help to increase the active surface area, which can further ensure efficient contact between the electrolyte and active catalysts. As porphyrin ligands always keep excellent electrical conductive property, hence, porphyrinic MOFs may act as an excellent electrocatalyst for OER. Herein, we report a porous lead-porphyrin MOF, [Pb₂(H₂TCPP)]·4DMF·H₂O (**Pb-TCPP**), based on 5,10,15,20-tetra(carboxyphenyl)porphyrin (H₆TCPP) ligand. Although **Pb-TCPP** has been reported by Wu and co-workers, only structure was focused in their work.[10] In the present work, we pay much attention on its gas adsorption and electrocatalytic activity for OER.

Materials and General Methods

The H₆TCPP ligand was synthesized according to the previous literatures.[15] All the starting materials and solvents were purchased from commercial vendors and used without further purification. The powder XRD diffractograms were obtained on a PANanalytical X-Pert pro diffractometer with Cu-Kα

Dalton Transactions Accepted Manuscript

COMMUNICATION

Journal Name

radiation. Gas sorption experiments were carried out on the surface area analyzer ASAP-2020. Crystallographic data deposited at the Cambridge Crystallographic Data Center (CCDC: 871466) can be obtained from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB21EZ, U.K.

RESULTS AND DISCUSSION

The Synthesis method are shown in Supporting Information (SI). There is 1D rod-shaped polymeric chain of carboxyl oxygen bridging Pb^{2+} ions in **Pb-TCPP**. The porphyrin ligand connect the 1D polymeric chain to form the 3D porous framework structure with pore dimensions of 11.34×8.63 Å^2 viewed along the *b*-axis (Figures 1a-1d). PLATON calculations indicate that **Pb-TCPP** contains 39.5% (1120.2 Å^3 per unit cell) void space that is accessible to the solvent molecules. The measured PXRD patterns of the complex closely match the simulated patterns generated from the results of single-crystal diffraction data by the mercury program, which indicated the complex were pure products (Figure 1e).
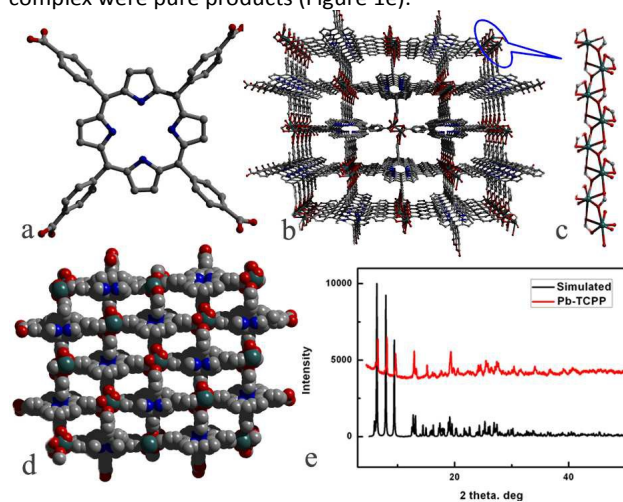

Figure 1. (a) the porphyrin ligand in **Pb-TCPP**. (b) and (d) the 3D porous framework of **Pb-TCPP** along the *b*-axis, showing the 1D opening channels. (c) the 1D polymeric chain of carboxyl oxygen bridging Pb^{2+} ions. (e) XRD pattens of **Pb-TCPP**.

Gas sorption properties. For most of the Pb-MOFs, there is no delightful report on their gas adsorption properties, and most of the gas adsorption abilities of Pb-MOFs are restricted, for example, Xie et al reported a Pb-DDQ (H_2DDQ = N,N'-dibenzoic acid-2,3-diaminoquinoxaline) MOF with low N_2 uptake (about 10 cm^3/g at 77 K).[16] Wang et al reported three 3D Pb-MOFs, and one of them displayed adsorbing N_2 and CO_2 of 136.8, and 127.5 cm^3 g^{-1} at 1 atm, and H_2 of 79.1 cm^3 g^{-1} at 760 torr, respectively.[17]

To investigate the permanent porosity of **Pb-TCPP**, the gas adsorption isotherms were measured. The as-synthesized **Pb-TCPP** was guest-exchanged with dry methanol and dichloromethane, respectively, followed by activation at 333 K under high vacuum for 3 h to get the activated **Pb-TCPP**. As shown in Figure 2a, the N_2 adsorption isotherm shows a typical

Type-I adsorption isotherm for N_2, which suggests the retention of the microporous structure after removal of guest molecules. The uptake of N_2 is 180.0 cm^3·g at 77 K and 1 bar with the langmuir surface area of 713.36 cm^2·g^{-1}. The measured pore volume based on N_2 sorption isotherm is 0.10285 cm^3·g^{-1}, similar result for Ar adsorption was observed for **Pb-TCPP**. The uptake of Ar for **Pb-TCPP** is 220 cm^3·g^{-1}, which is even higher than that for some Zn-MOF compounds (~160 cm^3·g^{-1}).[18] The infinite 1D rod-shaped chain in **Pb-TCPP** is responsible for the stability of the framework (Figure SI1) and the gas uptakes.

Under the conditions of 1 bar and 77K, desolvated **Pb-TCPP** exhibits the H_2 uptake capacity of 112.3 cm^3·g^{-1} (1.02 wt %, Figure 2b). The value surpasses that of the favorable zeolite ZSM-5 (0.7 wt %) and some other reported Pb-MOFs at the same condition.[19] The gas isosteric heat of adsorption (Q_{st}) can be calculated by fitting the gas adsorption isotherms at different temperature to a virial-type expression.[20] By the method, the Q_{st} for H_2 was obtained by fitting the H_2 adsorption isotherms at 77 K and 87 K and showed the estimated value of 8.1 kJ·mol^{-1} (Figure 2c), which also compares well with other MOFs.[21] In addition, this is the first Pb-MOF with high gas adsorption capacities, suggesting that **Pb-TCPP** has potential application in gas storage.
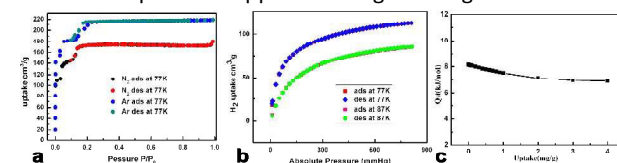

Figure 2. (a) N_2 and Ar isotherms of **Pb-TCPP** at 77 K; (b) H_2 isotherm of **Pb-TCPP** at 77 K and 87 K; (c) Q_{st} of H_2 for **Pb-TCPP**.
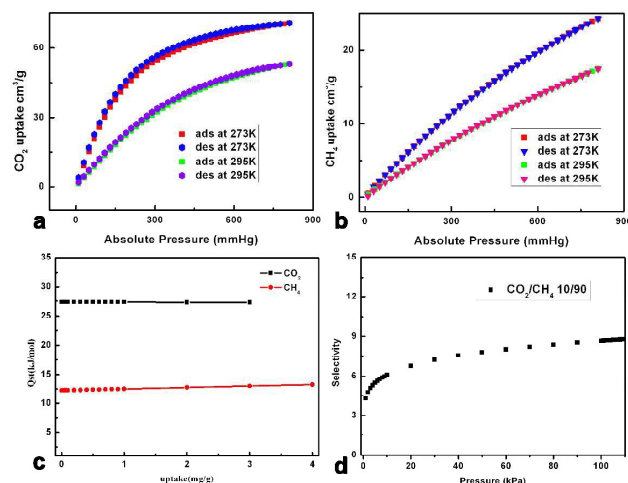
Figure 3. (a) and (b) CO_2 and CH_4 isotherm of **Pb-TCPP** at 273 K and 295 K; (c) Q_{st} of CO_2, CH_4 for **Pb-TCPP**; and (d) IAST selectivity of CO_2/CH_4 with 10/90 molar ratio.

In addition, low-pressure CO_2 and CH_4 sorption experiments for **Pb-TCPP** were measured at a variety of temperatures. Their sorption isotherms are displayed in Figures 3a-3b. The sorption isotherms for CO_2 reveal that **Pb-TCPP** can adsorb CO_2 up to

Journal Name COMMUNICATION

70.5 cm^3·g^{-1} (13.8 wt%) at 273 K and 1.0 atm, and 52.9 cm^3·g^{-1} (10.3 wt%) at 295 K and 1 atm. However, **Pb-TCPP** can adsorb 24.3 cm^3·g^{-1} of CH$_4$ at 273 K and 1 atm, and 17.4 cm^3·g^{-1} of CH$_4$ at 295 K and 1.0 atm. The Q_{st} for CO$_2$ and CH$_4$ at low coverage are calculated by fitting the gas adsorption isotherms at 273 K and 295 K. The values are 27.3 kJ·mol^{-1} and 12.2 kJ·mol^{-1} for CO$_2$ and CH$_4$, respectively (Figure 3c). The Q_{st} for CO$_2$ is higher than the enthalpy of liquefaction of CO$_2$ (17 kJ·mol^{-1}) and lower than that observed for adsorption values on MOFs containing amine functionality (35-41 kJ·mol^{-1}).[22] At the same condition, the adsorption capacity for CO$_2$ is much higher than that of CH$_4$. To predict the selectivity of CO$_2$ versus CH$_4$, we used the ideal adsorbed solution theory (IAST) to calculate the multi-component adsorption behavior from the experimental pure-gas isotherms.[23] The adsorption selectivity for CO$_2$-CH$_4$ mixtures (10/90 molar ratio) as a function of pressure is presented in Figure 3d. The selectivity of CO$_2$ over CH$_4$ reaches a maximum of 8.8 at a pressure of 1.0 bar, indicating Pb-TCPP exhibits selectivity to CO$_2$ over CH$_4$, although the selectivity is somewhat low.

Electrocatalytic activity. Electrocatalytic properties for a myriad of electrochemical reactions such as OER have gained great research attention.[24] As slightly MOFs structures have been researched for it, we therefore investigate the electrocatalytic activity of the **Pb-TCPP**, experiment for electrochemical measurements and the calculation method of the turnover frequency (TOF)[25] are listed in SI.
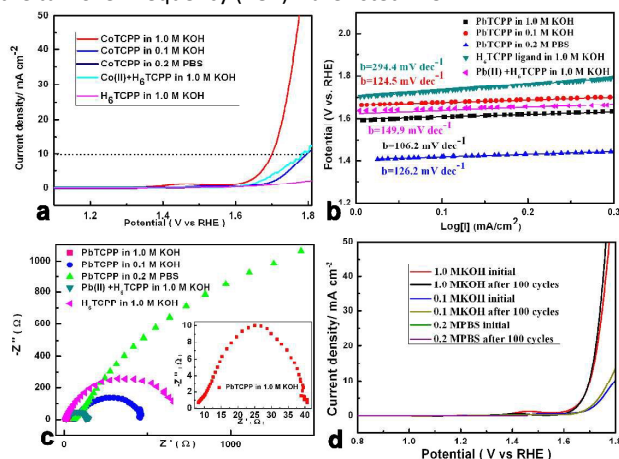

Figure 4. Electrocatalytic activity of **Pb-TCPP** for OER. (a) Polarization curves and (b) Tafel plots in 1.0 M, 0.1M KOH and 0.2M PBS solution (5 mV/s). (c). Nyquist plots examined at at 0.5 V (vs SCE). (d) OER linear sweeps before and after potential sweeps for 100 cycles in different solutions**.**

Figure 4a shows the polarization curves of **Pb-TCPP**. The potential required for a current density of 10 mA·cm^{-2}, which is a metric associated with solar fuel synthesis. The **Pb-TCPP** deliver a current density of 10 mA·cm^{-2} at a potential of 1.70 V in 1.0 M KOH, whereas in 0.1 M KOH solution the **Pb-TCPP catalyst** exhibited overpotential of 1.79V, and it even can not reach 10 mA·cm^{-2} in PBS solutions, which is due to the lower concentration of OH$^-$ in 0.2 M PBS solution.[26] Enhanced OER activity in alkaline solutions is important due to the benign

nature of the electrolyte, causing more active sites to the electrode surface. The OER kinetics of the electrodes is estimated by their corresponding Tafel plots. As shown in Figure 4b, the Tafel slope of the **Pb-TCPP** is 106.20, 124.50, and 126.20 mV·dec^{-1} in 1M KOH, 0.1M KOH and 0.2M PBS respectively.

It is necessary to understand the origination of the OER activity of the as-prepared **Pb-TCPP**. We have mixed Pb(II) and H$_6$TCPP ligand thoroughly in dmf solution. The results show the Pb(II) + H$_6$TCPP mixture deliver a current density of 10 mA·cm^{-2} at a potential of 1.78 V in 1.0 M KOH, and OER study fo pure H$_6$TCPP ligand has also been tested, which fails to reach 10 mA·cm^{-2} in 1.0 M KOH. The Tafel slopes for Pb(II) + H$_6$TCPP mixture is 149.9 mV·dec^{-1} and for H$_6$TCPP ligand is 294.4 mV·dec^{-1}, respectively. All the results show their proprieties are inferior to complex of **PbTCPP**. Several possibilities should be considered: First, it is known that electrocatalytic reaction is primarily a surface phenomenon,[27] **Pb-TCPP** own high specific surface area and offer sufficient active sites for OER, which could be verified by the above gas-sorption measurements and its structure; Second, TCPP is supposed to promote electron transport at heterogeneous surface due to its excellent electrical conductive property, and it act as an ideal platform for loading Pb^{2+}; Third, as carbon- and nitrogen-based organic frameworks have showed their promising electrocatalytic properties, such as in the hydrogen evolution reaction (HER), oxygen reduction reaction (ORR), and OER,[28] porphyrin's central ring could also show catalyst activity in some conditions, it is supposed that the H atoms could be deprotonated in alkaline solution, leave the porphyrin's central ring as the active catalysis center, and the crystals of **PbTCPP** are long-range ordered, so it showed higher activity than the Pb(II) + H$_6$TCPP mixture and H$_6$TCPP ligand. To gain further insight into the activity of as-synthesized **Pb-TCPP** modified electrodes toward OER, electrochemical impedance spectroscopy (EIS) analysis was also performed. Figure 4c describe the obtained Nyquist plots of **Pb-TCPP**. The charge-transfer resistance (Rct) at the surface of the catalysts is determined from the diameter of a semicircle at high frequencies in the Nyquist plot. Generally, Rct value varies inversely with the electrocatalytic activity. That is, smaller diameter corresponds to faster OER kinetics. Compared with Pb(II) + H$_6$TCPP mixture and H$_6$TCPP ligand in 1.0 M KOH, the Rct values of **Pb-TCPP** in 1.0M KOH, 0.1M KOH and 0.2M PBS showing that it keeps the smallest Rct value in 1M KOH (40 Ω). Thus, such a low Rct value of **Pb-TCPP** indicates that its high electrocatalytic activity for OER in alkaline solution could be ascribed to the highly conductive Pb^{2+} hybrid TCPP ligands improving the charge transfer characteristics of **Pb-TCPP**. In alkaline solutions, catalysts showed good stability in overpotential after 100 cycles test (Figure 4d). The TOF have been calculated as 5.1×10^{-4} s^{-1}, 3.5×10^{-4} s^{-1}, and 1.8×10^{-4} s^{-1} in 1.0 M KOH, 0.1 M KOH and 0.2 M PBS, respectively (Table 1) based on the catalysts at an applied potential of 1.2 V.

Table 1. OER data for **Pb-TCPP** as catalyst in different solvent.

Solvent	Over potential at 10 mA·cm^{-2} [V vs RHE]	mass activity at η= 1.2 [V vs RHE] (A/g)	Tafel slope [mv/dec]	TOF at η= 1.2 [V vs RHE] (s^{-1})
1.0M KOH	1.70	18.26	106.20	5.1×10^{-4}
0.1M KOH	1.79	12.56	124.50	3.5×10^{-4}
0.2M PBS	Fails to reach 10 mA·cm^{-2}	6.33	126.20	1.8×10^{-4}

CONCLUSIONS

In summary, we have reported lead-porphyrin constructed MOFs that formed a porous material with high selective adsorption of CO_2 over CH_4. Compared with those non-noble-metal electrocatalytic materials reported recently, **Pb-TCPP** electrode presents a large exchange current density and a relatively small Tafel slope in 1.0 M KOH, suggesting **Pb-TCPP** is a promising low-cost and earth-abundant metallic electrocatalyst for OER. With **Pb-TCPP** being electron-deficient and having a defined large cavity, it may be used as a host or 'molecular reactor' for guest molecules. Investigations of the porous MOFs used as good gas separator and electrocatalysts for OER are currently underway in our lab.

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