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Electronic Supplementary Information

Sandwich-type catalytic composite reassembled with birnessite layer and metalloporphyrin as a water oxidation catalyst

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1. Preparation of 5,10,15,20-tetrakis(4-aminophenyl)manganese porphyrin (MnTAPP)

1.1. Preparation of 5,10,15,20-tetrakis(4-nitrophenyl)porphyrin (TNPP)

25 mmol of p-nitrobenzaldehyde, 7 mL of lactic acid, and 25 mL of nitrobenzene were added into a 100 mL three-neck flask equipped with a condenser and a constant pressure dropping funnel, and the mixture was heated to 130 °C with stirring. 5 mL of a nitrobenzene solution containing 25 mmol of pyrrole was added dropwise at a constant rate over 1 h, and the reflux reaction was continued for 1 h. The reaction solution gradually changed from light yellow to dark black, and the wall of the three-necked flask was covered with a purple solid. After the reaction was completed, the reaction mixture was cooled to 60 °C, followed by adding 20 mL of methanol and stirring for another 30 minutes. Then the reaction product was placed in a refrigerator overnight to fully precipitate the product. The mixture was filtered by suction to give a purple-black solid. The purple-black solid was recrystallized in 80 ml pyridine and left in the refrigerator overnight. Finally, the mixture was suction filtered and the solid was washed with acetone until the filtrate was colorless, and 0.7947 g purple TNPP product was obtained by vacuum drying at 50 °C.

MS: m/z ($C_{44}H_{26}N_8O_8$) calcd: 794.73, found: 794.21;

FT/IR (KBr, cm^{-1}): 1595, 1517, 1343, 965;

UV-Vis (λ,nm, DMF): 416, 514, 548, 592, 648.

1.2. Synthesis of 5,10,15,20-tetrakis(4-aminophenyl)porphyrin (TAPP)

2 mmol of TNPP and 80 mL of HCl (12 mol/L) were added to a 250 mL three-necked flask equipped with a condenser and a constant pressure dropping funnel under a nitrogen atmosphere, and the porphyrin was fully dispersed evenly when stirred at room temperature for 30 min. Then, 20 mL of a concentrated hydrochloric acid solution containing 30 mmol of stannous chloride dissolved therein was added dropwise and reacted at room temperature for 2 h and then heated to 70 °C for 1 h. The green solid was then collected by filtration and dissolved in 200 mL of deionized water. Then, concentrated ammonia was added to adjust the pH to 10. The blue solid was collected by filtration and dried under vacuum at 50 °C. A mixed solution of chloroform and methanol in a volume ratio of 5:1 was used as a developing solvent, and column chromatography was performed using 100 to 200 mesh neutral alumina to collect the first red ribbon. After rotating evaporation and vacuum drying, 1.134 g blue crystalline TAPP was obtained. The yield is about 84%.

MS: m/z ($C_{44}H_{34}N_8$) calcd: 674.79, found: 674.69;

FT/IR (KBr, cm^{-1}): 3380, 1614, 1345;

UV-Vis (λ, nm, DMF): 444, 520, 562, 600, 654.

1.3. Preparation of 5,10,15,20-tetrakis(4-aminophenyl)manganese porphyrin (MnTAPP)

0.25 mmol of TAPP, 1.25 mmol of $MnCl_2$ and 100 mL of DMF were placed in a 250 mL three-necked flask, and the above reaction product was reacted at 140 °C for 3 h under nitrogen-protected conditions. During the course of the reaction, the solution slowly changed from purple-black to red-black. The reaction solution was evaporated to 20 mL by rotary evaporation under reduced pressure. After cooling to room temperature, a large amount of distilled water was added thereto, after which

MnTAPP precipitated. After filtering, washing and drying, the blue crystalline product MnTAPP was obtained.

MS: m/z ($C_{44}H_{32}N_8MnCl$) calcd: 763.22, found: 763.32;

FT/IR (KBr, cm^{-1}): 1614, 1348, 1008;

UV-Vis (λ, nm, DMF): 484, 590, 648.

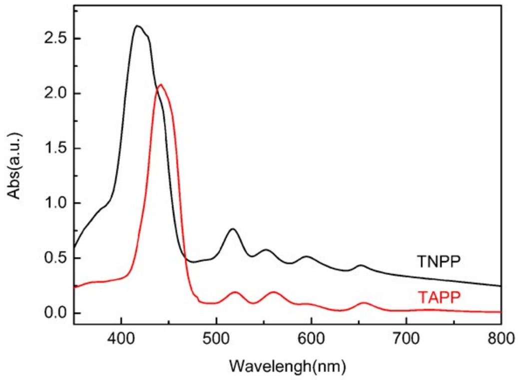

Fig. S1 UV-Vis spectrum of TNPP and TAPP.

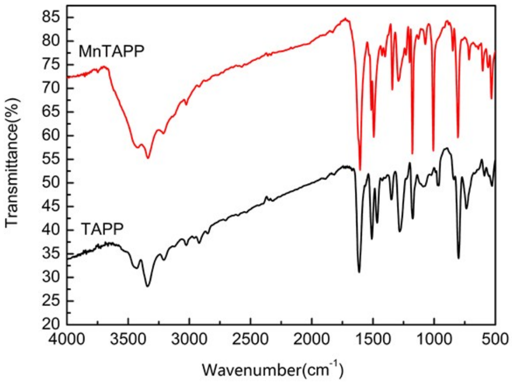

Fig. S2 FTIR spectrum of TAPP and MnTAPP.

2. Synthesis of high purity birnessite

In this paper, high purity birnessite was prepared by air oxidation method reported by our research group.[1, 2] 1.352 g $MnSO_4•H_2O$ and 2.992 g EDTA-2Na were dissolved in deionized water and stirred for 30 min to obtain a white suspension solution, known as S_a. 1.2 g NaOH was dissolved in 50 mL of deionized water until complete dissolution, known as S_b. S_b was slowly added dropwise to S_a under rapidly stirring. After the addition is complete, the mixture was stirred for another 2 h. The precipitate was filtered and washed several times with deionized water. Then the precipitate was dried under vacuum at 50 °C for 12 h, the product is birnessite powder. The products were characterized by XRD, IR and SEM/TEM, which were proved to be nano flower-like birnessite (δ-MnO_2).

Reference

1. M. Qin, H. Zhao, W. Yang, Y. Zhou and F. Li, *RSC Adv.*, 2016, **6**, 23905.
2. L. Wang, M. Qin, W. Yang, Y. Gao and Y. Li, *ChemistrySelect*, 2017, **2**, 5587.