Electronic Supplemental Information for:

A coordination polymer based on dinuclear (pyrazinyl tetrazolate) copper(II) cations and Wells-Dawson anions for high-performance supercapacitor electrodes

Guangning Wang,[ab] Tingting Chen,[ab] Shaobin Li,[ac] Haijun Pang*[a] and Huiyuan Ma*[a]

[a]*Key Laboratory of Green Chemical Engineering and Technology, College of Heilongjiang Province, College of Chemical and Environmental Engineering, Harbin, University of Science and Technology, Harbin 150040, China.*

[b]*Key Laboratory for Photonic and Electronic Bandgap Materials, Ministry of Education, School of Physics and Electronic Engineering, Harbin Normal University, Harbin 150025, China.*

[c]*College of Materials Science and Engineering, Qiqihar University, Qiqihar 161006, China.*

CONTENTS

Section 1 Experimental Section

I. Materials and General Methods

All reagents were purchased commercially and used as received. Fourier transforms infrared spectroscopy (FTIR) spectra on KBr pellets were recorded on a Nicolet AVATAR FT-IR 360 spectrophotometer in the range 400-4000 cm^{-1}. The morphology of the samples is analyzed by scanning electron microscopy (SEM, Hitachi SU-70).

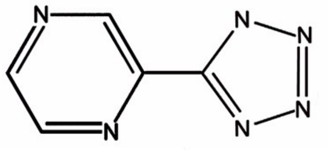
The electrochemical properties had been evaluated on a Lab-logic electrochemical workstation (VMP3, France) by a three-electrode configuration in 1 M H_2SO_4, in which **1**-based and α-$K_6P_2W_{18}O_{62}\cdot 15H_2O$ modified glassy carbon electrode were working electrode, a platinum plate was the counter and the saturated calomel electrode is reference electrodes. Cyclic voltammetry (CV) measurement was filed in the range of -0.72 to 0.6 V at scan rates of 50, 75, 100, 125, 150, 175, and 200 mV s^{-1} under room temperature. The galvanostatic charge/discharge (GCD) performances were experimented at current densities of 5, 10, 20, 50, and 70 A g^{-1} with the potential ranging from -0.66 to 0.6 V. Electrochemical impedance spectroscopy (EIS) tests were conducted on this apparatus at the frequency from 100 kHz to 10 mHz. The specific capacitance (Cs) was computed with the equation below:

$$C_s = \frac{I\Delta t}{m\Delta V} \qquad (1)$$

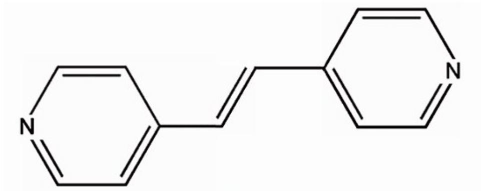
Where I (A) refer to the current in the course of the discharge, Δt (s) means the time of discharge, m (g) is the mass of the electrode materials, and ΔV (V) is the voltage difference between the upper and lower potential limits.

II. Synthesis of 1

A mixture of α-$K_6P_2W_{18}O_{62}\cdot 15H_2O$ (0.3602 g, 0.08 mmol), $Cu(NO_3)_2$ (0.1801 g, 0.75 mmol), pzta (0.0300 g, 0.20 mmol), bpe (0.0400 g, 0.22 mmol), NH_4VO_3 (0.0601 g, 0.51 mmol), and H_2O (17 mL) was stirred for 1 h at room temperature. The pH value was adjusted to 3.5 with 0.1 mol L^{-1} H_2SO_4. The resulting solution was transferred to a 23 mL Teflon-lined autoclave and heated at 160 °C for 5 days with 8 °C/min. After cooling to room temperature at a rate of 10 °C/h, green crystals were filtered and washed with deionized (DI) water (45% yield based on W). The reproducibility of compound **1** is good. Anal. calcd for $C_{41}H_{49}N_{12}CuP_2W_{18}O_{68}$: C 9.41; H 0.94; N 3.21; P 1.18; Cu 1.21; W 63.24 (%). Found: C 9.48; H 0.86; N 3.25; P 1.15; Cu 1.10; W 63.88 (%).



pzta



bpe

Scheme 1. The pzta and bpe ligands.

III. X-ray Crystallography

Single crystal X-ray diffraction data collection of compound **1** was performed using a Bruker Smart Apex CCD diffractometer with Mo-*Ka* radiation (λ = 0.71073 Å) at 296 K. Multi-scan absorption corrections were applied. The structure of **1** was solved by Direct Methods and refined on F^2 with full-matrix least-squares methods, using the SHELXTL package,[1] and all of the non-hydrogen atoms were refined anisotropically. The organic hydrogen atoms were generated geometrically. The hydrogen atoms on the lattice water molecules in **1** were not located in the refinement but were included in the structure factor calculations. Further details of the crystallographic data and structural determination for compound **1** are listed in Table 1. Crystallographic data and structure refinement, bond lengths and angles, and anisotropic displacement parameters have been deposited in the Cambridge Crystallographic Data Center (CCDC No.1554016).

IV. Preparation of the Modified Electrodes

The glassy carbon (GCE) working electrode was polished before each experiment with 1, 0.3, and 0.05 mm alumina power on chamois leather, respectively, rinsed thoroughly with DI water between each polishing step. To prepare the working electrode, a mixture of the **1** or parent α-$K_6P_2W_{18}O_{62}\cdot15H_2O$, and acetylene black in a weight ratio of 1:1 was ground in a mortar with 1 mL of ethyl alcohol, and 3 mL of DI water and was as the solvent to make slurry. 5 μL of well dispersed slurry was dropped onto the glassy carbon surface and dried for 2 hours at room temperature, in order to form a uniform thin film. Then, 5 μL of Nafion solution (Aldrich) was dropped onto the GCE surface and the electrode was then dried at room temperature.

Section 2 Supplementary Physical Characterizations

I. Additional Figures of SEM and EDS

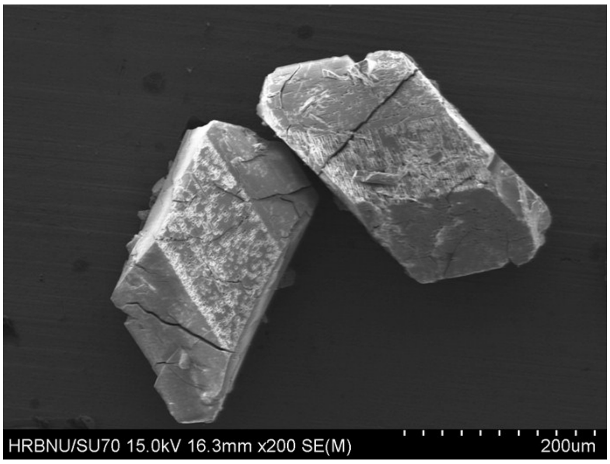


Fig. S1 The SEM images of the as-synthesized compound **1**.

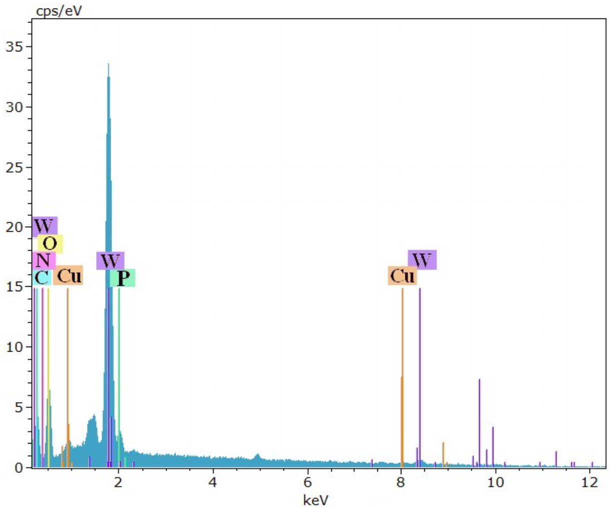


Fig. S2 The EDS microanalysis of the as-synthesized **1**.

II. Analyses of BVS, PXRD, and IR measurements

BVS: Compound **1** was synthesized under hydrothermal conditions. All copper atoms in **1** are in the +II oxidation state, confirmed by their octahedral coordination environments, green crystal color and BVS calculations.[2]

PXRD: The PXRD patterns for compound **1** are presented in Fig. S3. The diffraction peaks of both simulated and experimental patterns match well, indicating that the phase purities of **1** are good. The difference in reflection intensities between the simulated and the experimental patterns is due to the different orientation of the crystals in the powder samples.

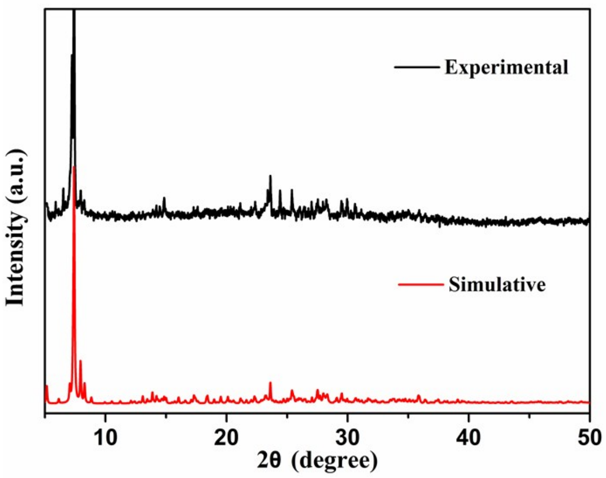


Fig. S3 The simulative (red) and experimental (black) PXRD patterns for **1.**

FTIR: The FTIR spectrum is presented in Fig. S4 Characteristic peaks at 1087, 955, 913, and 788 cm^{-1} for compound **1** are attributed to ν(P-O$_a$), ν(W-O$_d$), ν_{as}(W-O$_b$-W), and ν_{as}(W-O$_c$-W) vibrations of P_2W_{18}, respectively.[3] Furthermore, the characteristic absorption bands in the regions of 1636-1197 cm^{-1} for **1** are assigned to characteristic peaks of pzta and bpe components.

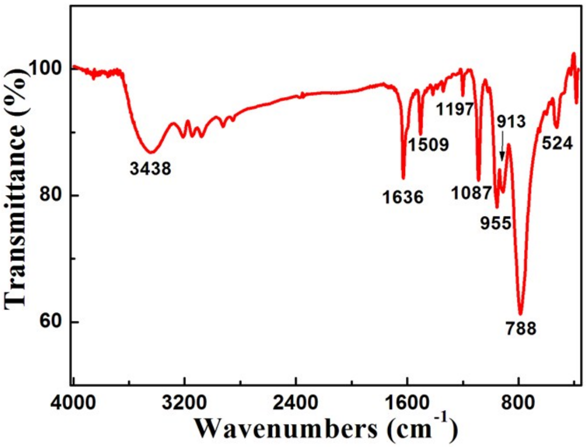


Fig. S4 The fourier transform infrared spectroscopy spectrum of **1.**

III. Catalytic Efficiency (CAT) of 1-CPE

The CAT of both CPEs can be calculated by using the CAT formula.[4]

$$\mathrm{CAT} = 100\% \times \frac{[I_{\mathrm{P}}(\mathrm{POM, substrate}) - I_{\mathrm{P}}(\mathrm{POM})]}{I_{\mathrm{P}}(\mathrm{POM})} \tag{2}$$

Where *I*p (POM) and *I*p (POM, substrate) are the catalytic currents of the POM in the absence and presence of the substrate, respectively.

Reference

1 G. M. Sheldrick, shelxtl (version 6.10), Bruker Analytical Instrumentation: Madison, WI, 2000.

2 I. D. Brown and D. Altermatt, *Acta Crystallogr. Sect. B: Struct. Sci.*, 1985, **41**, 244.

3 (a) Y. Yu, H.-Y. Ma, H.-J. Pang, L. Zhang, S.-B. Li, C.-Y. Zhao and Z.-F. Zhang, *RSC Adv.*, 2014, **4**, 61210–61218; (b) X.-L. Wang, N. Li, A.-X. Tian, J. Ying, G.-C. Liu, H.-Y. Lin, J.-W. Zhang and Y. Yang, *Dalton Trans.*, 2013, **42**, 14856-14865.

4 B. Keita, A. Bel houari, L. Nadjo and R. Contant, *J. Electroanal. Chem.*, 1995, **381**, 243-250.