Supporting information for

A Covalent Organic Framework for High-rate Aqueous Calcium-ion Batteries

Linyuan Li,[a] Guobin Zhang,[a,] *Xianming Deng,[a] Jing Hao,[a] Xu Zhao,[a] Hongfei Li,[b] Cuiping Han,[c, d,] *

and Baohua Li[a,] *

[a.]Shenzhen Key Laboratory on Power Battery Safety and Shenzhen Geim Graphene Center, Tsinghua Shenzhen International Graduate School, Tsinghua University, Shenzhen 518055, China. Email: libh@mail.sz.tsinghua.edu.cn (B. Li)

[b.]School of System Design and Intelligent Manufacturing, Southern University of Science and Technology, Shenzhen, Guangdong, 518055, China.

[c.]Faculty of Materials Science and Engineering/ Low Dimensional Energy Materials Research Center, Shenzhen Institutes of Advanced Technology, Chinese Academy of Sciences, 518060, Shenzhen, China. Email: cp.han@siat.ac.cn (C. Han)

[d.]College of Materials Science and Engineering, Shenzhen Key Laboratory of Special Functional Materials, Shenzhen University, Shenzhen, 518060, China.

Calculation of theoretical specific capacity

Theoretical capacity can be calculated by the following equation[1].

$$Q = \frac{nF}{3.6M_W} \text{.....(Equation S1)}$$

Where Q (mAh g^{-1}) is theoretical capacity, F (C mol^{-1}) is Faraday constant, n is the electron transfer number per unit, and M_w is the corresponding molecular weight (g mol^{-1}).

For each unit, there were 6/3=2Tp (with three C=O groups)and 6/2=3Hq (with two C=O groups). For the convenience of calculation, it is considered that C-OH were all converted to C=O. M_w=3×159+2×136=726 g mol^{-1}, During the reaction, one C=O group corresponded to the transfer of one electron, then n=3×2+2×3=12.

$$Q = \frac{12 \times 96485}{3.6 \times 726} = 442\ mAh\ g^{-1}$$

Calculation based on Nernst Equation

According to a previously reported method[2], the electrochemical reaction of HqTp with H+ in 1M HCl can be expressed as below:

$$HqTp\ +\ nH^+\ + ne^- \rightleftharpoons H_nHqTp \text{.....(Equation S2)}$$

Nernst Equation：

$$\varphi = \varphi^\theta + \frac{2.303RT}{nF}\log\frac{[HqTp][H^+]_n}{[H_nHqTp]} = \varphi^\theta + \frac{0.0592}{n}\log\frac{[HqTp][H^+]_n}{[H_nHqTp]} \text{.....(Equation S3)}$$

Where φ is electrode potential; $\varphi\theta$ is the standard potential; R is the universal gas constant(8.314 J K^{-1} mol^{-1}); T is the temperature 298.15 K; n is the electron transfer numbers; F is the Faraday constant(96500 C mol^{-1}). We consider the activity of HqTp and H_nHqTp as 1, then simplified the equation:

$$\varphi = \varphi^\theta + \frac{0.0592}{n}\log[H^+]^n = \varphi^\theta + \frac{0.0592}{n}\log[H^+] \text{.....(Equation S4)}$$

For 1M HCl aqueous solution (pH=1) and 1 M $CaCl_2$ aqueous solution (pH≈7.8), Δφ can be calculated as:

$$\Delta\varphi = 0.0592\log\frac{[H^+]_{HCl}}{[H^+]_{CaCl_2}} = 0.0592\log\frac{1}{10^{-7.8}} = 0.462\ V$$

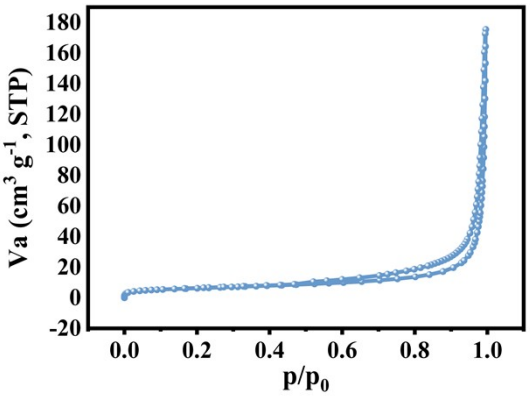

Figure S1. N_2 gas adsorption analysis of HqTp, the area of the HqTp is 22.9 m^2 g^{-1}.

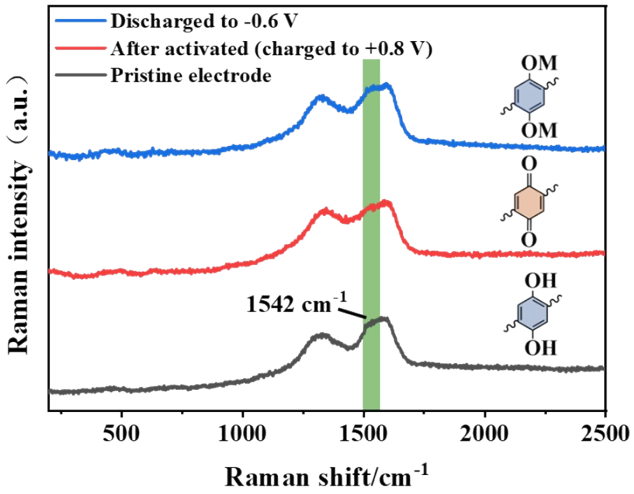

Figure S2. The Raman spectra of the electrodes in different states (M= proton / calcium).

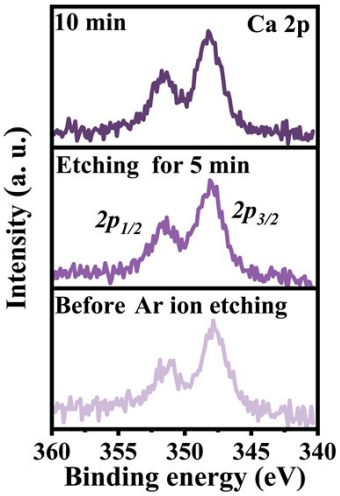

Figure S3. The XPS Ca 2p spectra of the HqTp electrode discharged to –0.6 V after different etching

time.

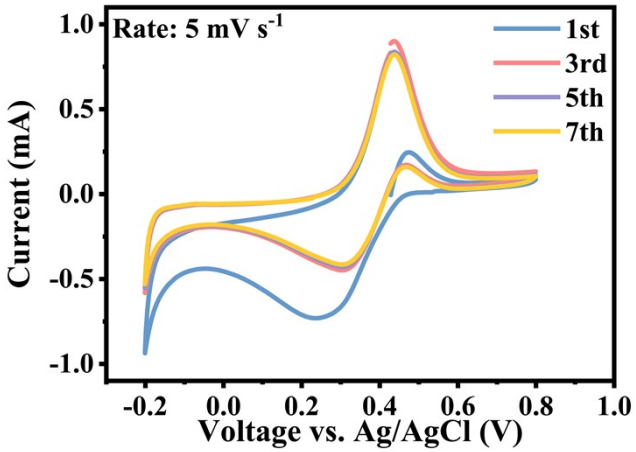

Figure S4. The CV curves in in HCl aqueous solution (pH=1) for 7 cycles.

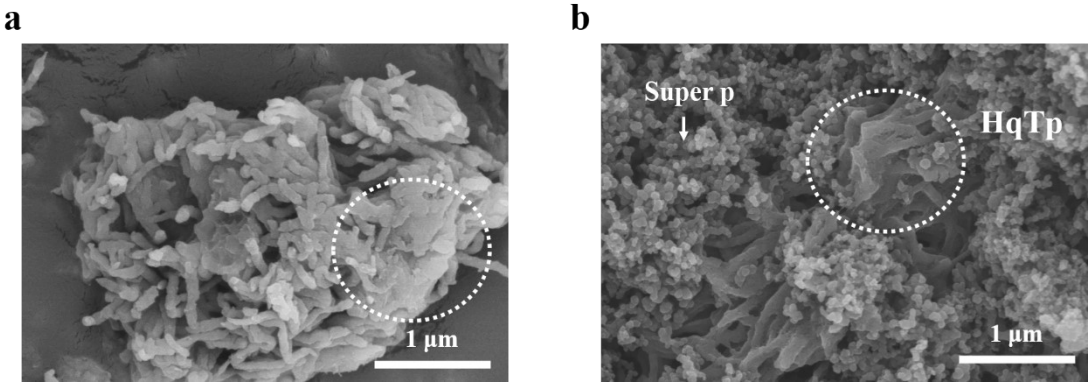

Figure S5. The SEM images of the (a) HqTp-COF powder and (b) the electrode discharged to -0.6 V.

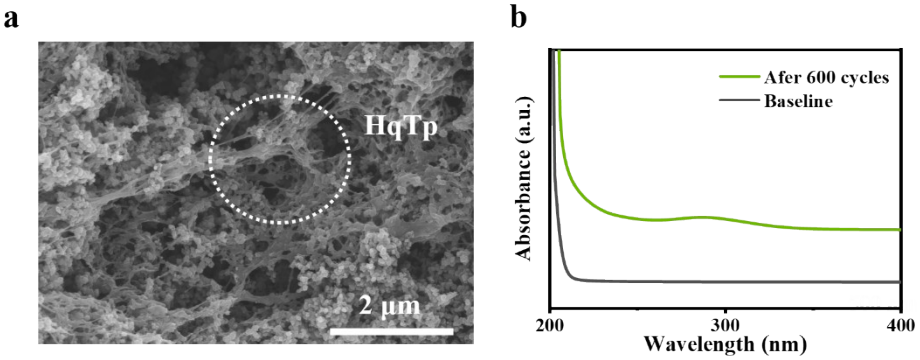

Figure S6. After 600 cycles, (a) the SEM image of the electrode and (b) the UV-vis spectra of the 1 M $CaCl_2$ electrolyte.

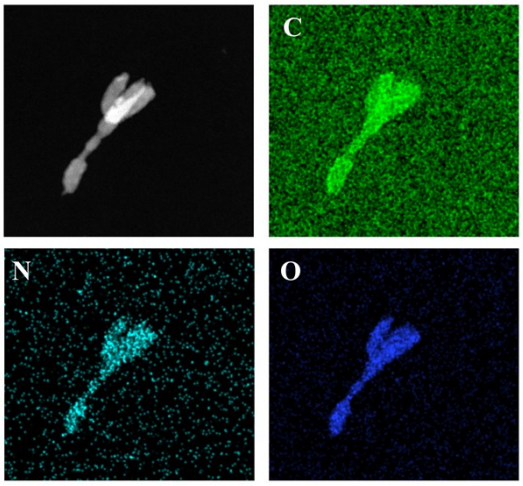

Figure S7. TEM images of the pristine HqTp and the EDS mapping.

1. M. Winter and R. J. Brodd, *Chemical Reviews*, 2004, **104**, 4245-4270.
2. Y. Wang, C. Wang, Z. Ni, Y. Gu, B. Wang, Z. Guo, Z. Wang, D. Bin, J. Ma and Y. Wang, *Advanced Materials*, 2020, **32**, 2000338.