Electronic Supporting Information to the manuscript

Negative electrodes for supercapacitors with good performance using conductive bismuth-catecholate metal–organic frameworks

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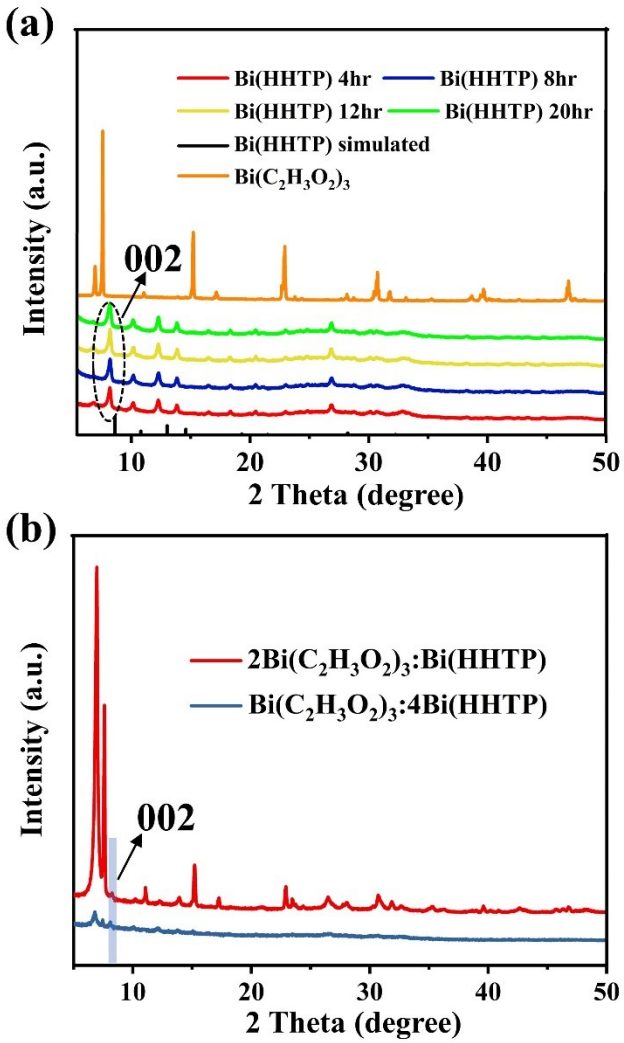

Figure S1 (a) XRD patterns of Bi(HHTP) 4hr, Bi(HHTP) 8hr, Bi(HHTP) 12hr, Bi(HHTP) 20hr, $Bi(C_2H_3O_2)_3$, and Bi(HHTP) simulated. (b) XRD patterns of $2Bi(C_2H_3O_2)_3$:Bi(HHTP) 12hr and $Bi(C_2H_3O_2)_3$:4Bi(HHTP) 12hr.

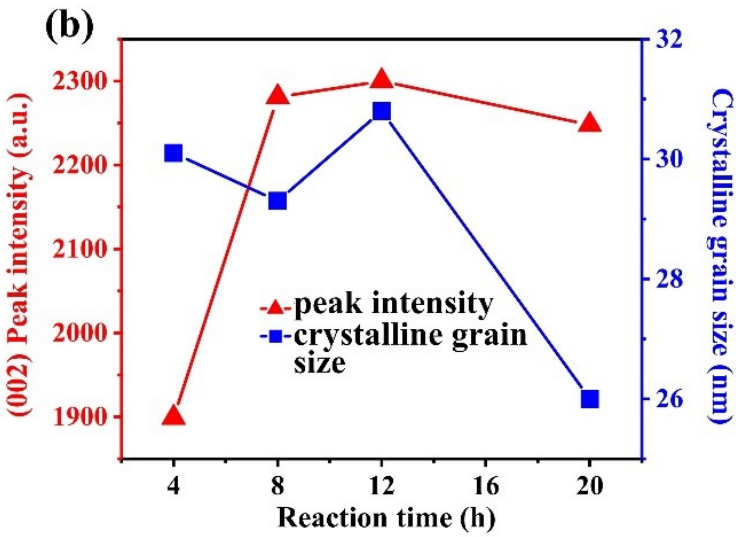

Figure S2. (002) peak intensity and crystalline grain size of Bi(HHTP) 4hr, Bi(HHTP) 8hr, Bi(HHTP) 12hr, and Bi(HHTP) 20hr samples.

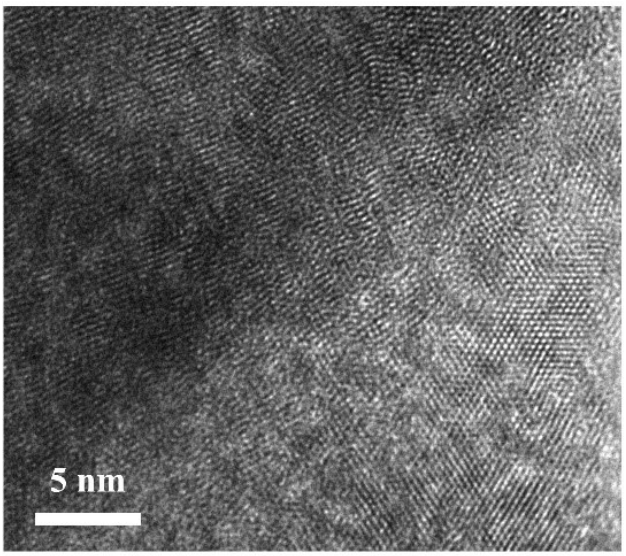

Figure S3. HRTEM image of Bi(HHTP) 12hr nanobelts

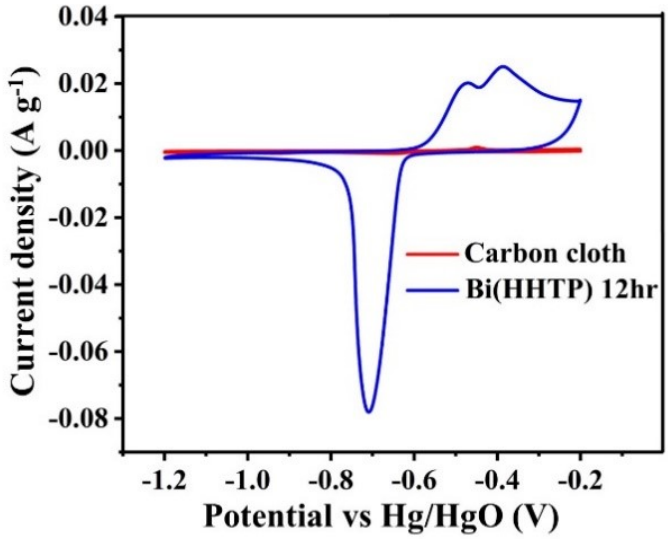

Figure S4. CV curves of Bi(HHTP) 12hr electrode and carbon cloth at 20 mV s^{-1}.

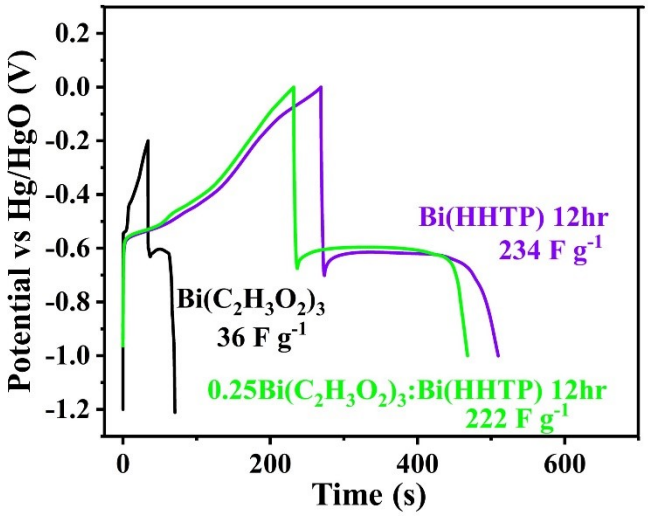

Figure S5 GCD curves of $Bi(C_2H_3O_2)_3$, Bi(HHTP) 12hr and $0.25Bi(C_2H_3O_2)_3$:Bi(HHTP) electrodes at 1 A g^{-1}.

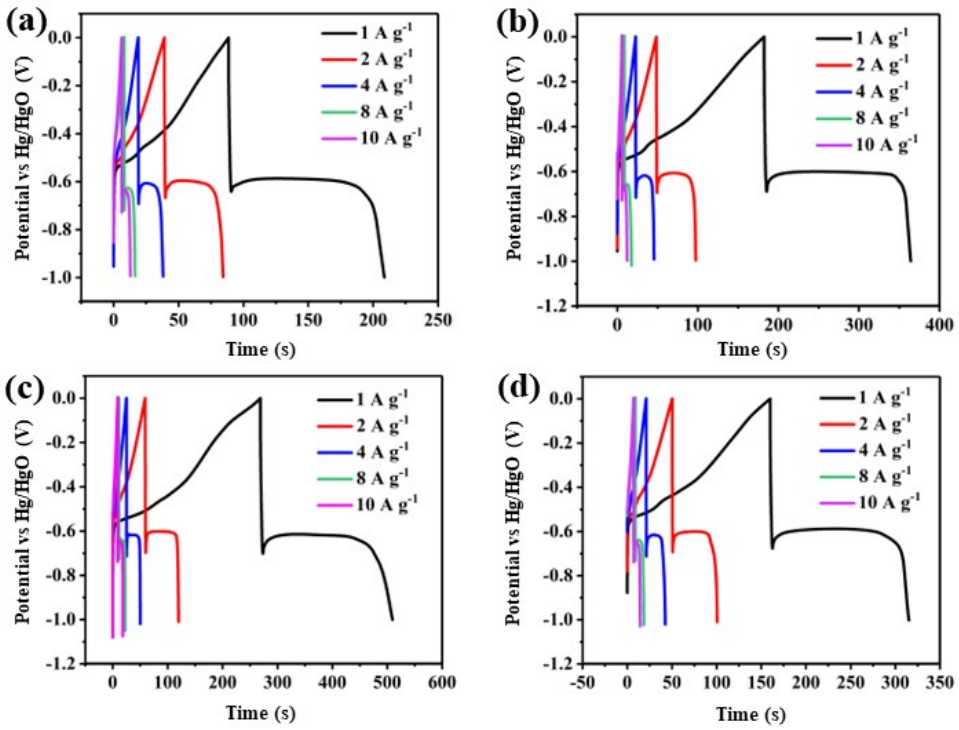

Figure S6. GCD curves of the (a) Bi(HHTP) 4hr, (b) Bi(HHTP) 8hr, (c) Bi(HHTP) 12hr, and (d) Bi(HHTP) 20hr electrodes at different current densities.

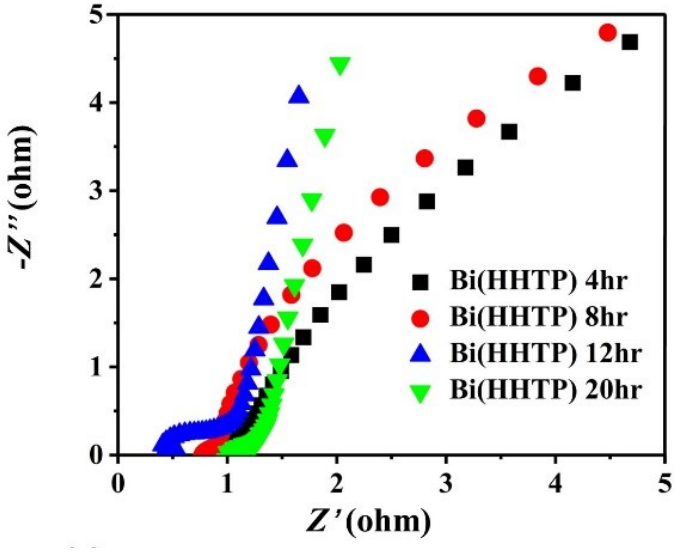

Figure S7. Enlarged nyquist plots of Bi(HHTP) 4hr, Bi(HHTP) 8hr, Bi(HHTP) 12hr, and Bi(HHTP) 20hr electrodes.

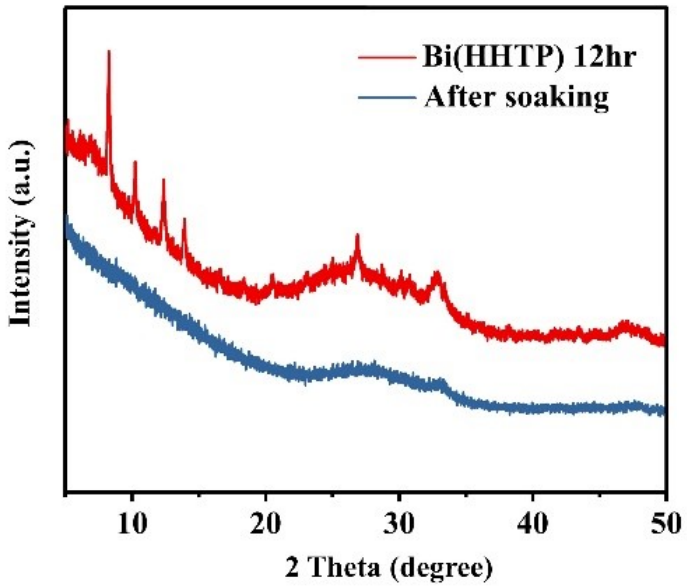

Figure S8. XRD pattern before and after soaking into 3M KOH aqueous electrolyte of Bi(HHTP) 12hr sample.

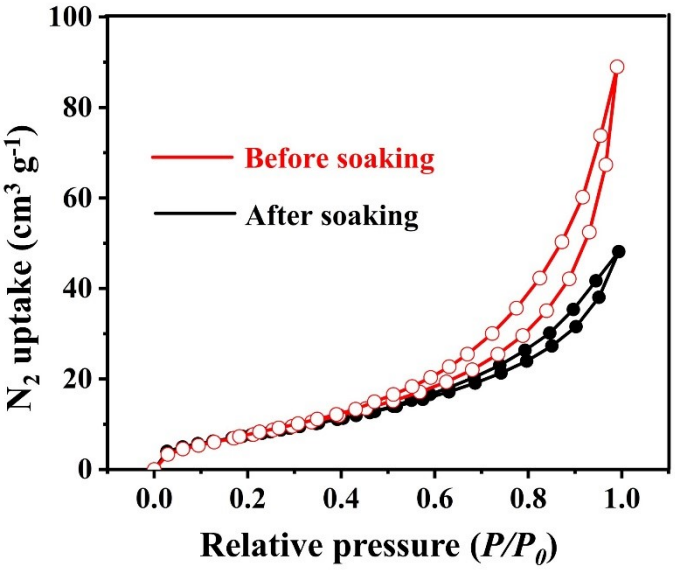

Figure S9 N_2 adsorption and desorption isotherm of Bi(HHTP) 12hr after soaking 3M KOH.

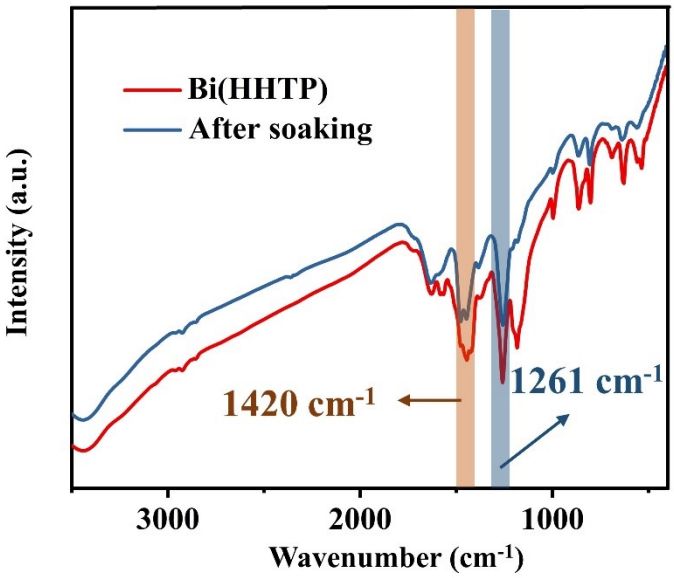

Figure S10 FT-IR of Bi(HHTP) 12hr before and after soaking 3M KOH.

The Residual Impurity in Bi(HHTP) Nanobelts and Its Influences

Figure S1a and b depict the XRD patterns of bismuth acetate standard sample and a well-mixed sample of $Bi(C_2H_3O_2)_3$ and Bi(HHTP) 12hr with a mass ratio of 2:1. The amount of the impurity ($Bi(C_2H_3O_2)_3$) in Bi(HHTP) 12hr is evaluated according to the area ratio of peak located in 6.74° and 8.25° of the mixture sample. In Figure S1b, the area ratio of peak located in 6.74° and 8.25° of the mixture sample of $Bi(C_2H_3O_2)_3$ and Bi(HHTP) 12hr with a mass ratio of 2:1 is 96.52:1, thus, their relative response factor

of XRD diffraction intensity is 48.26 because of the much lower density of Bi(HTTP). And the area ratio of peak located in 6.74° due to $Bi(C_2H_3O_2)_3$ and 8.25° in Bi(HHTP) 12hr pattern is 1:2.82, hence the mass ratio of $Bi(C_2H_3O_2)_3$ and pure Bi(HHTP) 12hr in Bi(HHTP) 12hr pattern is estimated to be about 0.0073:1. Obviously, the mass of $Bi(C_2H_3O_2)_3$ in Bi(HHTP) 12hr is very, very low, such a diffraction peak at 6.74° due to $Bi(C_2H_3O_2)_3$ is still observed. As the referee mentioned, that's because the peak at 8.25° is indicated to be the planes of heavy Bi atoms and the density of Bi atoms in Bi(HHTP) 12hr is far lower than those of in $Bi(C_2H_3O_2)_3$. In addition, we also prepared the mixed sample of $Bi(C_2H_3O_2)_3$ and Bi(HHTP) 12hr with a mass ratio of 0.25:1 to evaluate the electrochemical impact of the impurity. Figure S1b shows the XRD pattern of the mixture sample of $Bi(C_2H_3O_2)_3$ and Bi(HHTP) 12hr with a mass ratio of 0.25:1. And it's very reasonable that the relative intensity of peak at 8.25° due to Bi(HHTP) 12hr is lower than peak at 6.74° due to $Bi(C_2H_3O_2)_3$. And the GCD curves of $Bi(C_2H_3O_2)_3$ and the mixture samples of $Bi(C_2H_3O_2)_3$ and Bi(HHTP) 12hr are showed in Figure S5 to evaluate the influence of the $Bi(C_2H_3O_2)_3$ impurity on the electrochemical properties of the samples. The specific capacitances of $Bi(C_2H_3O_2)_3$ electrode and the mixture sample of $Bi(C_2H_3O_2)_3$ and Bi(HHTP) 12hr with a mass ratio of 0.25:1 are calculated to be 36 F g^{-1} and 222 F g^{-1}, respectively. With much less impurity inside, on the contrary, the specific capacitance of Bi(HHTP) 12hr increased to 234 F g^{-1}. These results strongly implied that very little residual $Bi(C_2H_3O_2)_3$ might be present in Bi(HHTP) 12hr although a small XRD diffraction pattern for it was found, such little impurity almost has no any influence on the electrochemical performance of Bi(HHTP) nanobelts.

Soaking of 3M KOH in Bi(HHTP) materials

To verify the integrity of Bi(HHTP) materials after being soaking in 3M KOH, XRD, are performed. As shown in Figure S8, the diffraction peaks of heavy Bi atom planes were greatly weakened after being soaked into 3M KOH aqueous electrolyte and the diffraction pattern corresponding to Bi atoms plane almost disappear. It's known that the peak intensities of XRD patterns depend on the sample density and the content of Bi ions is low in porous Bi(HHTP) frameworks with a low density. Because a large amounts of potassium-containing compounds are randomly adsorbed inside according to N_2 adsorption isotherms (Figure S9), it is rational to observed the disappearance of the XRD pattern of Bi atom planes.[1] Nevertheless, the diffraction peak at 33° corresponding to benzene ring backbones of Bi(HHTP) still exists, likely implying the integrity of Bi(HHTP) materials. In Figure S10, the IR of Bi(HHTP) 12hr before and after being soaked in 3M KOH are showed. Obviously, they both display characteristic bands around 1420 cm^{-1} and 1261 cm^{-1} assigned to bidentate catechol coordination, which eventually implied the integrity of Bi(HHTP) materials after being soaked in 3M KOH.[29]

References

[1] X. W. Wu, Y. L. Hong, B. Q. Xu, Y. Nishiyama, W. Jiang, J. W. Zhu, G. Zhang, S. Kitagawa, and S. Horike, J. Am. Chem. Soc., 2020, 142, 14357–14364.