Electronic Doping of Metal-Organic Frameworks for High-Performance Flexible Micro-Supercapacitors

Yafei He, Sheng Yang, Yubin Fu, Faxing Wang, Ji Ma, Gang Wang, Guangbo Chen, Mingchao Wang, Renhao Dong, Panpan Zhang,* and Xinliang Feng*

The combination of high specific surface areas, well-defined porous structures, and redox-active sites renders the organic frameworks as promising electrode materials for next-generation energy storage devices. Despite the recent advancements in the fabrication of conductive metal-organic frameworks (MOFs), they generally require tedious synthesis procedures, which hinder their energy-related applications. Herein, a doping strategy using electron acceptor molecules is demonstrated to tune the ohmic electrical conductivity of MOF thin-film electrodes. For instance, the conductivity of MOF Cu$_3$(BTC)$_2$ film is enhanced over 40 times after doping with 7,7,8,8-tetracyanoquinodimethane (TCNQ). Thereby, asymmetric in-plane micro-supercapacitors (MSCs) are constructed utilizing in situ-grown TCNQ@Cu$_3$(BTC)$_2$ as the cathode and activated carbon as the anode, which delivers remarkable areal capacitance of 95.1 mF cm$^{-2}$ at a scan rate of 5 mV s$^{-1}$, superior to those of the reported MSCs (0.1–50 mF cm$^{-2}$). Moreover, the fabricated devices show long-term stability with 94.1% capacitance retention up to 5000 charge-discharge cycles at 10 mA cm$^{-2}$. The molecular doping engineering of organic framework materials with excellent electronic properties for energy storage and conversion applications is inspired.

1. Introduction

Metal-organic frameworks (MOFs) are constructed by coordinating metal ions or clusters to organic ligands. They are a new class of coordination polymers that exhibit high porosity and crystallinity. Importantly, they feature flexible structural designability as well as densely accessible redox-active sites, making MOFs promising materials toward high-performance electrochemical energy storage applications.

To date, significant efforts have been devoted to improving the electrical conductivity of MOFs. On the one hand, pristine MOFs are generally mixed with conductive additives and binders to improve the overall conductivity in energy storage devices. However, this strategy does not enhance the inherent electrical properties of MOFs but rather decrease the accessible surface areas. On the other hand, conductive MOFs with high electrical conductivity and permanent porosity have emerged in the past few years, which exhibited improved electrochemical performance in supercapacitors. Despite the recent achievements, the synthesis of conductive MOFs and their thin-film fabrication remain tedious. Therefore, developing an efficient and straightforward approach toward conductive and redox-active MOF thin films is highly attractive for on-chip energy storage devices.

In this work, we demonstrate an efficient strategy for the in situ fabrication and doping of Cu$_3$(BTC)$_2$ (BTC = benzene-1,3,5-tricarboxylate) thin-film electrodes. Doping of Cu$_3$(BTC)$_2$ thin films with electron acceptor molecules (such as 7,7,8,8-tetracyanoquinodimethane [TCNQ], benzoquinone [BQ], and pyromellitic diimide [PMDI]) is found to largely improve the ohmic electrical conductivity up to over 40 times; and the achieved maximum conductivity is 0.46 mS m$^{-1}$. Thereby, the high conductivity, the large specific surface area of 655 m$^2$ g$^{-1}$ together with excellent flexibility of TCNQ@Cu$_3$(BTC)$_2$ thin film facilitate the fabrication of on-chip energy storage devices. As a result, flexible asymmetric micro-supercapacitors (MSCs) based on TCNQ@Cu$_3$(BTC)$_2$ cathode and activated carbon (AC) anode deliver a remarkable areal capacitance of 95.1 mF cm$^{-2}$ at a scan rate of 5 mV s$^{-1}$, 3.4 times higher than MSCs based on undoped MOF thin films. This value is also superior to those of state-of-
the-art MSCs based on various types of hybrid material systems (0.1–50 mF cm⁻¹). Moreover, the fabricated device displays superb electrochemical stability and great promise in flexible electronics.

2. Results and Discussion

The in situ synthesis process of Cu₃BTC₂ thin film on Cu foil is schematically shown in Figure 1a. First, the pretreated Cu foil was placed onto the home-made spin coating holder and heated to 120 °C. Then, the solution containing H₃BTC (benzene-1,3,5-tricarboxylic acid) and AgNO₃ was spin coated with a speed of 300 rpm on the Cu foil for 5 min. During this process, Ag⁺ reacted with Cu foil and generated Cu²⁺ and Ag (2Ag⁺ + Cu = 2Ag + Cu²⁺). Ag deposited onto Cu foil and act as collector. Afterward, the generated Cu²⁺ coordinated with H₂BTC and formed the Cu₃BTC₂ thin film, which was adhered by Ag layer on the Cu foil. The achieved Cu₃BTC₂ thin film was dried in vacuum at 180 °C to remove the coordinated water molecules. The thin film was then immersed into the solution containing electron acceptors (e.g., TCNQ, BQ, and PMDI) for 1 week. Because TCNQ, BQ, and PMDI have the specific functional groups that can coordinate with metal atom, showing the possibility to react with centered metal atom of Cu₃BTC₂.

Moreover, the pore size of Cu₃BTC₂ (1.17 nm) is large enough concerning the molecular diameters of electron acceptors (TCNQ: 0.92 nm, BQ: 0.54 nm, PMDI: 0.87 nm), the latter can reconcile into the pores of Cu₃BTC₂ for the efficient doping. Thereby, the as-prepared doped Cu₃BTC₂ thin films are denoted as TCNQ@Cu₃BTC₂, BQ@Cu₃BTC₂, and PMDI@Cu₃BTC₂, respectively. The details about the synthesis process are shown in the Experimental Section in Supporting Information. As shown in Figure 1b,c, the obvious color changes from blue to green visually confirm the strong electronic interaction between Cu₃BTC₂ and acceptor molecules.

The morphologies and structures of the fabricated Cu₃BTC₂, TCNQ@Cu₃BTC₂, BQ@Cu₃BTC₂, and PMDI@Cu₃BTC₂ thin films on Cu foils are characterized by scanning electron microscope (SEM), X-ray diffraction (XRD), Raman spectroscopy, infrared reflection absorption spectroscopy (IRRAS), X-ray photoelectron spectroscopy (XPS), Brunauer–Emmett–Teller (BET) method, and thermal gravimetric analyzer (TGA). Figure 2a,b show that Cu₃BTC₂ thin film consists of densely stacked nanoparticles with diameters ranging from 80 to 120 nm. After doping, the side-view SEM images of TCNQ@Cu₃BTC₂ thin film indicate that the thickness is about 3 μm, and no apparent changes in the morphology were noticed (Figure 2c and Figure S1–S3, Supporting Information). The corresponding energy-dispersive spectroscopy (EDS) elemental mapping analysis implies the distinct elemental distribution. Furthermore, the homogeneous distribution of the N element suggests that electron acceptor molecules are well incorporated into Cu₃BTC₂ thin film.

The XRD patterns in Figure 2d show the polycrystalline structure of doped Cu₃BTC₂ thin films. Especially, the positions of (333) peak in TCNQ@Cu₃BTC₂, BQ@Cu₃BTC₂, and PMDI@Cu₃BTC₂ thin films all shifted to the lower degree compared with that of undoped Cu₃BTC₂ thin film. This shift corresponds to the gap distance increase of (333) crystal facet, revealing the incorporation of acceptor molecules into the pores of Cu₃BTC₂.

Raman spectrum of TCNQ@Cu₃BTC₂ discloses the peak at 2205 cm⁻¹, which is attributed to the nitrite stretch (C≡N) vibration of TCNQ (Figure 2e). In addition, the C= C stretching frequency of TCNQ@Cu₃BTC₂ shifts from 1447 cm⁻¹ (TCNQ) to 1438 cm⁻¹ and the peaks at 1392 and 1249 cm⁻¹ indicate the strong electronic interaction between TCNQ (guest) and the available coordination sites of the Cu²⁺ ions in the Cu₃BTC₂ framework (host). IRRAS spectra (Figure S4, Supporting Information) also present that the C≡N stretch of TCNQ is influenced by the infiltration into the Cu₃BTC₂ framework, with a shift from 2223 to 2179 cm⁻¹.
accompanied by peak broadening. This result supports the conclusion based on Raman spectroscopic studies. The Raman and IRRAS spectra of BQ@Cu$_2$(BTC)$_2$ and PMDI@Cu$_3$(BTC)$_2$ are presented in Figure S5 and S6, Supporting Information.

The electronic interaction between TCNQ and Cu$_2$(BTC)$_2$ was further investigated by XPS spectroscopy. As shown in Figure 2f and Figure S7, Supporting Information, the C=O peak in C 1s and C≡N peak in N 1s were observed in TCNQ@Cu$_3$(BTC)$_2$, demonstrating the presence of TCNQ in the doped thin film. Moreover, the shift Cu 2p$_{3/2}$ from 933.8 to 934.7 eV was ascribed to the change of surface electronic state after the incorporation of TCNQ in the Cu$_2$(BTC)$_2$ framework. Subsequently, the TGA curves revealed that the weight ratio of TCNQ, BQ, and PMDI in the doped Cu$_2$(BTC)$_2$ thin films was estimated to be 17.9, 10.6, and 12.5 wt%, respectively (Figure S8, Supporting Information), which provided LUMO and highest occupied molecular orbital (HOMO) energy levels of Cu$_2$(BTC)$_2$, TCNQ@Cu$_3$(BTC)$_2$, BQ@Cu$_3$(BTC)$_2$, and PMDI@Cu$_3$(BTC)$_2$ thin films, respectively. This result demonstrates small molecules (TCNQ, BQ, and PMDI) could occupy some pores of Cu$_2$(BTC)$_2$ and slightly decrease its specific surface area. Although the specific surface areas of doped MOFs were reduced, the utilization rate of specific surface area can be improved by enhancing the conductivity.

To determine the energy levels of acceptor molecules and doped Cu$_2$(BTC)$_2$ thin films, the cyclic voltammetry (CV) measurements were performed in a standard three-electrode cell. Figure 3a and Figure S10, Supporting Information, display the first reversible reductions ($E_{\text{red}}$) of TCNQ, BQ, and PMDI at $-0.08$, $-0.54$, and $-0.46$ V (vs. Ag/AgCl), respectively. Cu$_3$(BTC)$_2$ shows the first reversible oxidation ($E_{\text{ox}}$) at $1.53$ V and the first reversible reduction ($E_{\text{red}}$) at $-1.35$ V. Thus, the lowest unoccupied molecular orbital (LUMO) energy levels of TCNQ, BQ, PMDI, and Cu$_3$(BTC)$_2$ are derived to be $-4.68$, $-4.22$, $-4.30$, and $-3.41$ V, respectively (Figure 3b). It is worth noting that the LUMO energy level of Cu$_3$(BTC)$_2$ is higher than those of TCNQ, BQ, and PMDI; thus, TCNQ, BQ, and PMDI can accept the electrons from Cu$_3$(BTC)$_2$. The CV curves of TCNQ@Cu$_3$(BTC)$_2$, BQ@Cu$_3$(BTC)$_2$, and PMDI@Cu$_3$(BTC)$_2$ further confirmed the electron transfer between Cu$_3$(BTC)$_2$ and acceptor molecules (Figure 3c and Figure S11, Supporting Information), which provided LUMO and highest occupied molecular orbital (HOMO) energy levels of $-4.8$ and $-6.34$ V, $-4.31$ and $-6.37$ V, $-4.26$ and $-6.35$ V, respectively.

Figure 2. Characterizations of the fabricated Cu$_3$(BTC)$_2$, TCNQ@Cu$_3$(BTC)$_2$, BQ@Cu$_3$(BTC)$_2$, and PMDI@Cu$_3$(BTC)$_2$ thin films on Cu foils. a, b) Top-view SEM images of TCNQ@Cu$_3$(BTC)$_2$ thin film with different magnifications. c) Side-view SEM image of TCNQ@Cu$_3$(BTC)$_2$ thin film. d) XRD patterns of Cu$_3$(BTC)$_2$, TCNQ@Cu$_3$(BTC)$_2$, BQ@Cu$_3$(BTC)$_2$, and PMDI@Cu$_3$(BTC)$_2$ thin films on Cu foils. e) Raman spectra of TCNQ, Cu$_3$(BTC)$_2$, and TCNQ@Cu$_3$(BTC)$_2$, respectively. f) C 1s, N 1s, and Cu 2p spectra of TCNQ@Cu$_3$(BTC)$_2$. g) Nitrogen adsorption–desorption isotherms of Cu$_3$(BTC)$_2$, TCNQ@Cu$_3$(BTC)$_2$, BQ@Cu$_3$(BTC)$_2$, and PMDI@Cu$_3$(BTC)$_2$ thin films, respectively.
(Figure 3d). Clearly, after doping the Cu$_3$(BTC)$_2$ with acceptor molecules, the LUMO energy levels decreased obviously while the HOMO energy levels remained similar. Density functional theory (DFT) calculation also confirmed the decreased LUMO energy level (located at acceptor molecules) of doped Cu$_3$(BTC)$_2$ (Figure 3e,f and Figure S12–S15, Supporting Information), which supports the strong electronic communication between Cu$_3$(BTC)$_2$ and acceptor molecules. The matching energy level between Cu$_3$(BTC)$_2$ and electron acceptors is the essential factor to narrow MOF’s band gap, which is potentially to enhance its conductivity.

The conductivities of the Cu$_3$(BTC)$_2$, TCNQ@Cu$_3$(BTC)$_2$, BQ@Cu$_3$(BTC)$_2$, and PMDI@Cu$_3$(BTC)$_2$ were measured with van der Pauw method (Lakeshore Hall Testing System) at room temperature. Cu$_3$(BTC)$_2$ exhibited the highest slope in the voltage–current (V–I) curves (Figure 3g), whereas the slopes of TCNQ@Cu$_3$(BTC)$_2$, BQ@Cu$_3$(BTC)$_2$, and PMDI@Cu$_3$(BTC)$_2$ were much lower. According to the V–I curves, the electrical conductivities of Cu$_3$(BTC)$_2$, TCNQ@Cu$_3$(BTC)$_2$, BQ@Cu$_3$(BTC)$_2$, and PMDI@Cu$_3$(BTC)$_2$ were determined to be 0.0114, 0.463, 0.169, and 0.136 mS m$^{-1}$, respectively. Therefore, the conductivities of TCNQ@Cu$_3$(BTC)$_2$, BQ@Cu$_3$(BTC)$_2$, and PMDI@Cu$_3$(BTC)$_2$ are 41, 15, and 12 times higher than that of undoped Cu$_3$(BTC)$_2$, respectively (Figure 3h).

Encouraged by the enhanced electrical conductivity, large specific surface area, rich redox-active sites, and excellent flexibility of the doped Cu$_3$(BTC)$_2$ thin films, flexible asymmetric MSCs were assembled using TCNQ@Cu$_3$(BTC)$_2$, BQ@Cu$_3$(BTC)$_2$, or PMDI@Cu$_3$(BTC)$_2$ as the positive electrode and AC as the negative electrode in polyvinyl alcohol (PVA)/LiCl gel electrolyte (Figure S16, Supporting Information). The corresponding devices are denoted as TCNQ-MOF-MSC, BQ-MOF-MSC, and PMDI-MOF-MSC, respectively. A benchmark MSC using the same AC anode but undoped Cu$_3$(BTC)$_2$ cathode was also fabricated for comparison and named as MOF-MSC. The electrochemical behavior of the AC anode and the Cu$_3$(BTC)$_2$ (TCNQ@Cu$_3$(BTC)$_2$, BQ@Cu$_3$(BTC)$_2$, or PMDI@Cu$_3$(BTC)$_2$) cathode were investigated by CV in the three-electrode cell (Figure S17, Supporting Information). Figure 4a clearly shows that the integral area of CV curve for TCNQ-MOF-MSC presents the maximum value compared with other MSCs. Furthermore, at the same current density of 2 mA cm$^{-2}$ in galvanostatic charge-discharge (GCD) measurement (Figure S18–S21, Supporting Information), TCNQ-MOF-MSC requires the most charge/discharge duration, indicating the highest delivered capacitance. In addition, the CV curves of these devices display redox peaks associated with their pseudocapacitance from ligand-based redox activity.$^{[60]}$ As shown in Figure 4b,c the areal
capacitances of MOF-MSC, TCNQ-MOF-MSC, BQ-MOF-MSC, and PMDI-MOF-MSC were calculated to be 28.3, 95.1, 77.2, and 69.2 mF cm$^{-2}$, respectively, at a scan rate of 5 mV s$^{-1}$. Apparently, the improved conductivities of doped Cu$_3$(BTC)$_2$ thin films benefited to the significant increase in the capacitances of the corresponding devices. Remarkably enough, the capacitance of TCNQ-MOF-MSC is 3.4 times higher than that of MOF-MSC and is also superior to those of the recently reported MSCs based on coordination polymer framework,[10] carbon nanotube/graphene,[11] graphene/conductive MOF,[12] graphene/carbon nanotube,[13] graphene/V$_2$O$_5$,[14] graphene/thiophene,[15] and graphene/phosphorene[16] (0.1–50 mF cm$^{-2}$, Table S1, Supporting Information).

To further reveal the excellent performance of our fabricated devices, the electrochemical impedance spectra (EIS) were analyzed (Figure S22, Supporting Information). At low frequency, the straight line of TCNQ-MOF-MSC with much larger slope suggested the enhanced mass transfer inside electrode material, resulting from the improved electrical conductivity. At high frequency, the much smaller semicircle of TCNQ-MOF-MSC indicated the decreased charge transfer resistance, due to the fully accessible electrode surface in the electrolyte. Moreover, TCNQ-MOF-MSC exhibited excellent cycling stability, with 94.1% of capacitance retention after 5000 charge/discharge cycles (Figure S23, Supporting Information).

Concerning the limited mass loading of active materials, it is rational to calculate the energy and power densities based on area and volume of the electrode, other than its weight. To determine the overall performance of our devices, Ragone plots of volumetric energy density and power density are shown in Figure 4d. Notably, our TCNQ-MOF-MSC delivers an ultrahigh energy density of up to 46 mWh cm$^{-3}$ at 1.67 W cm$^{-3}$, which considerably exceeds those of the state-of-the-art in-plane MSCs (0.1–10 mWh cm$^{-3}$, Table S1), e.g., MOF-based MSCs,[11,12] graphene-based MSCs,[15,16] conducting polymer-based MSCs,[10] Ti$_3$C$_2$T$_x$ MSCs,[18] and carbon-based MSCs.[19] In addition, the obtained high power density of 33.3 W cm$^{-3}$ at 20 mWh cm$^{-3}$ is superior to those of state-of-the-art MSCs (0.01–10 W cm$^{-3}$) based on various electrode materials such as laser-scribed graphene,[20] MXene/graphene,[21] poly(3,4-ethylenedioxythiophene),[17a] and coordination polymer frameworks.[10] Furthermore, the high areal energy density ($E_A$, max = 13.8 μWh cm$^{-2}$) and power density ($P_A$, max = 10 mW cm$^{-2}$) are achieved for TCNQ-MOF-MSC, which is much better than other reported MSCs (Figure S24, Supporting Information). On the other hand, good flexibility and variable working window are crucial for portable and wearable energy storage devices. To demonstrate the excellent flexibility of the fabricated devices, we evaluated the CV at different bending angles (Figure 4e and Figure S25, Supporting Information). No obvious changes in CV curves were observed, highlighting the great electrochemical stability. Moreover, the connection of single MSCs in series and parallel could achieve higher voltage and capacitance. For example, three serially connected TCNQ-MOF-MSCs could reach 3.0 V and light up a red LED (Figure S26 and S27, Supporting Information).
3. Conclusion

In summary, we demonstrate a novel strategy for the in situ growth and doping of Cu₄(BTC)₂ thin-film electrodes. The doping of Cu₄(BTC)₂ thin films with electron acceptor molecules significantly improves the electrical conductivity. The mechanism behind is elucidated by the electrochemical investigations and supported by DFT calculations. As a result, flexible MSCs assembled with TCNQ@Cu(BTC)₂ as the cathode and AC as the anode delivers a remarkable areal capacitance of 95.1 mF cm⁻², superior to those of the reported MSCs (0.1–50 mF cm⁻²). Our work sheds light on the molecular doping strategy as an efficient approach for tailoring the electronic properties of organic framework materials for energy storage and conversion applications.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

acceptor molecules, electrical conductivity, flexible micro-supercapacitors, in situ growth, metal-organic frameworks

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