



# Soluble Covalent Organic Polymer for the Flexible Electrode of Supercapacitors

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Covalent organic polymer (COPs) have emerged promising potentials for the fabrication of flexible supercapacitors. Numerous efforts are devoting to the promotion of processability of COPs and broaden their applications in practical devices. Herein we have developed a fully conjugated two-dimensional COP material (COP<sub>BTC</sub>-Mn) with nitrogen coordinated metal centers. The unique structures of COP<sub>BTC</sub>-Mn endow it with high solubility via an *in-situ* exfoliation pathway and the capability to adsorb onto carbon-based matrix by electrostatic force. COP<sub>BTC</sub>-Mn demonstrated superior processability, reliability, and repeatability for the fabrication of flexible electrodes of supercapacitors. Besides, superior to the electrodes based on traditional COPs, our as-prepared flexible electrodes exhibited a specific capacitance as high as 325 F g<sup>-1</sup> with the current density of 0.2 A g<sup>-1</sup> and excellent stability after charge/discharge cycles.

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## INTRODUCTION

Flexible supercapacitors are vital for the development of portable energy storage devices such as wearable electronics, bendable displays, and electronic papers (Lu et al., 2014; Chen et al., 2015). Recently, numerous efforts have been paid to explore the flexible supercapacitors with high power density, fast charge/discharge rate, and long lifetime (Peng et al., 2016; Wu et al., 2018). As the crucial part of flexible supercapacitors, the flexible electrodes determine the energy storage capability, working performance, and the fabrication of flexible devices (Chen and Dai, 2016). During the past research, various kinds of materials have been used to prepare the flexible electrode through methods such as *in-situ* growth method, tablet method, smear method etc. (Chen and Dai, 2014; Yu et al., 2014; Choi et al., 2016; Zhou et al., 2018). Despite the extensive efforts in the fabrication of electrodes, the rational design of supercapacitive electrodes material that meet large capacitance, high energy density, outstanding stability, and simple efficient processing method remains a substantial challenge (Kou et al., 2011; Chen et al., 2014, 2017; Li et al., 2017).

Covalent organic polymer (COPs) are a class of porous frameworks which have been identified as promising electrode materials for supercapacitors (DeBlase et al., 2015; Diercks and Yaghi, 2017; Ma et al., 2017; Wang et al., 2017). The long range ordered arrangement with high accessible surface area and tunable elemental compositions of COPs are beneficial for ion transport between the interface of electrode and electrolyte solution. Besides, the regular network structures of COPs lead to explicit incorporation of redox-active functionalities, holding great potentials for pseudocapacitive energy storage (Kandambeth et al., 2019). The common usage of COPs materials during the fabrication of flexible electrodes is daubing or *in-situ* growing active material on the support (Xu et al., 2015). During these years, COPs materials have enriched the relevant literature

as promising supercapacitors, their superior processability, reliability, and repeatability for the fabrication of flexible electrodes are still limited (Halder et al., 2018). Therefore, a new kind COP show high performance electrode material with sizable electrolyte-accessible surface areas remains a huge challenge (Wang et al., 2019).

In our previous work, we have developed a fully conjugated two-dimensional COP material with rigid structure and uneven charged coordination single-atomic centers which demonstrated great solubility in many solutions through an *in-situ* charged exfoliation pathway (Peng et al., 2019a). Based on our previous outcomes, we synthesized through the assembly of benzene-1,2,4,5-tetracarboxitrile (BTC) with Mn riveted in the center and finally constructed into a fully closed conjugated planar COP system (termed as COP<sub>BTC</sub>-Mn). As expected, the COP<sub>BTC</sub>-Mn could be exfoliated into thin layers with positive charged metal centers. Driven by the intermolecular interactions, the COP<sub>BTC</sub>-Mn was able to be riveted on the carbon fiber through electrostatic adsorption with uniform distribution which could be directly used as flexible electrodes in supercapacitors (Peng et al., 2019b). Our approach to preparation flexible electrode much more convenient than the commonly used spin-casting method, *in-situ* synthesis and squash technique, holding promising potentials for industrial preparation (Guo et al., 2018). Moreover, the as-prepared flexible electrodes demonstrated outstanding capacitive performance (325 F g<sup>-1</sup>) and considerable galvanostatic charge/discharge (GCD) cyclic stability, exceeding 3,000 cycles without compromising the capacitance.

## EXPERIMENTAL SECTION

### Materials and Methods

All used chemicals in this work are analytical reagents without further treatment. Carbon fiber is supplied by Shanghai Hesun Company. Manganese(II) chloride (MnCl<sub>2</sub>) is bought from Saan chemical technology (Shanghai) Co., Ltd. Benzene-1,2,4,5-tetracarboxitrile (BTC) is got from Ark Pharm, Inc. N,N-Dimethylformamide (DMF), Ethylene glycol, and Sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) are both bought from Shanghai Macklin Biochemical Co., Ltd. Elemental analysis is performed on CARLO ERBA 1106. ICP-OES is performed on ICAP7400. X-ray photoelectron spectroscopy (XPS) analysis is performed on Thermo VG ESCALAB 250 equipped with an Al K $\alpha$  X-ray source. Scanning electron microscopic (SEM) images are obtained from a S4700 SEM instrument equipped with an energy dispersive spectrometer (EDS) analyzer. Fourier Transform Infrared Spectroscopy (FTIR) is tested by a Bruker AC-80 MHz. Solid State Nuclear Magnetic Resonance (SSNMR) is measured on a Bruker AV300 spectrometer operating at 75.5 MHz for <sup>13</sup>C.

### Electrochemical Measurements

The electrochemical tests are performed in the standard three-electrode system using a CHI 660e electrochemistry workstation at room temperature. All potentials are calibrated. The obtained carbon felt and COP<sub>BTC</sub>-Mn/CF are directly used as working electrode. Platinum (Pt) loop is used as the counter electrode and silver chloride electrode is used as the reference electrode. The

electrolyte is 1 M Na<sub>2</sub>SO<sub>4</sub> (pH = 7). During the test, working electrode is performed by Cyclic Voltammetry (CV) with the potential set between -1 and 0 V at different sweep rate (10, 20, 50, 100, 200, and 400 mV/s, respectively). Galvanostatic charge/discharge (GCD) is used to evaluate the electrochemical performance of the developed flexible electrodes at different current density (0.2, 0.5, 1.0, 2.0, 5.0, and 10 A g<sup>-1</sup>, respectively).

## Synthesis

### Synthesis of COP<sub>BTC</sub>-Mn

Benzene-1,2,4,5-tetracarboxitrile is used as the monomers via a mild microwave process (150°C for 20 min) with 1,8-Diazabicyclo(5,4,0)undec-7-ene (DBU) as the catalysts. Typically, BTC, manganese (II) chloride, and DBU are dissolved in ethylene glycol and kept at 150°C for 20 min in a Discover SP-microwave synthesizer.

### Synthesis of Flexible Electrode COP<sub>BTC</sub>-Mn/CF

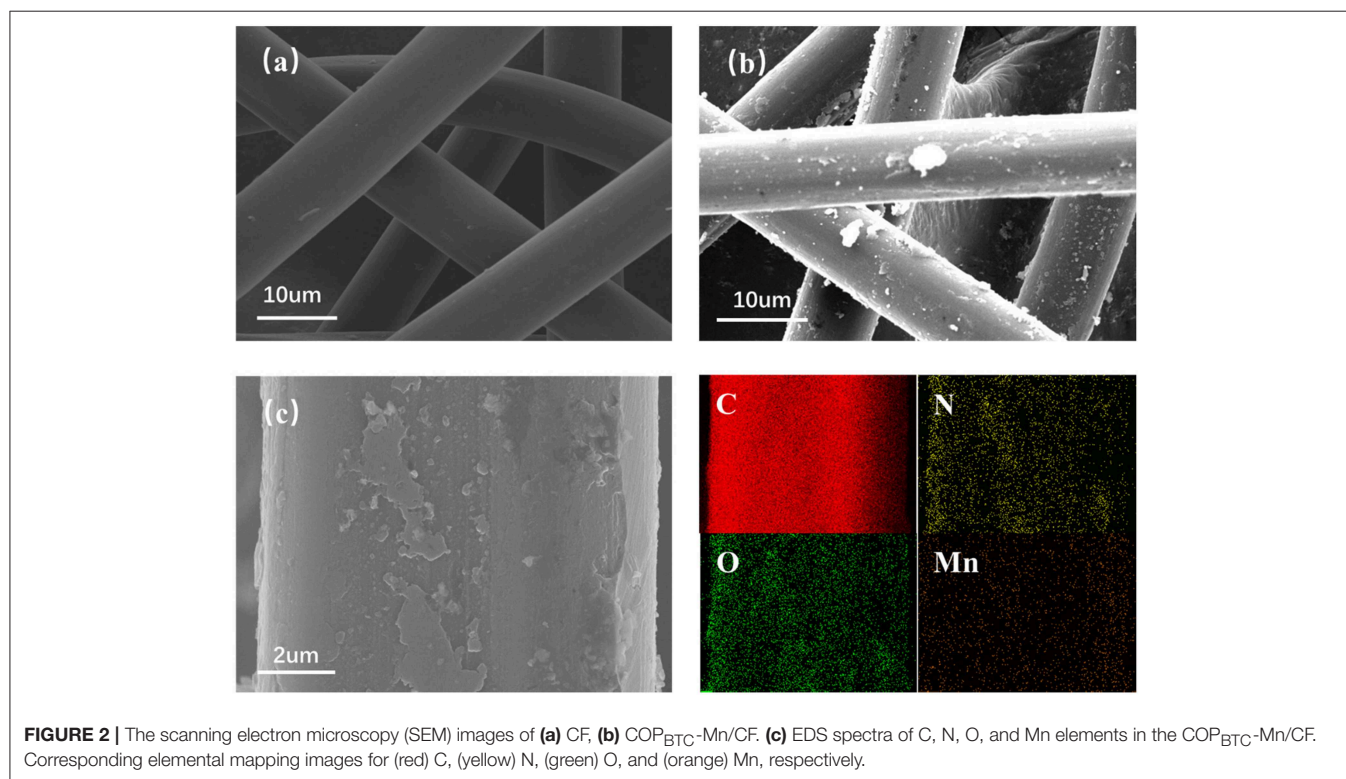
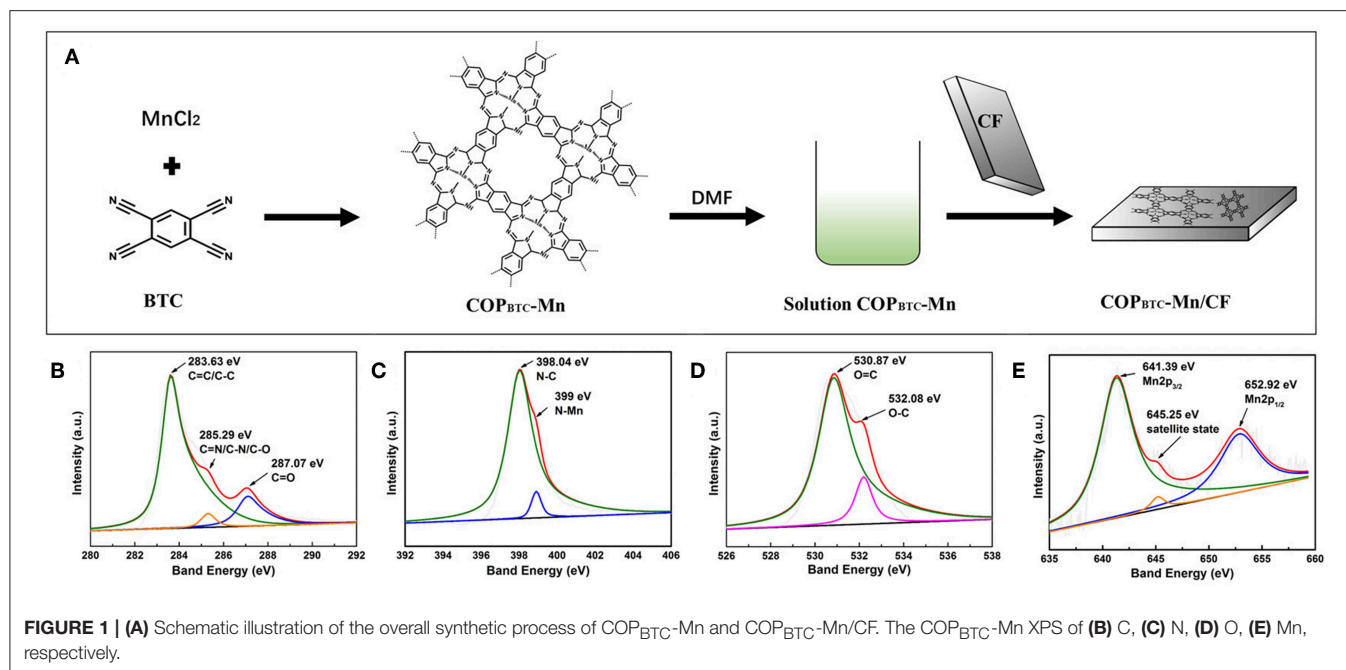
Commercial carbon felt (CF) is trimmed into small pieces with the size of 1.5 × 1.0 cm. Then the CF pieces are immersed in ethyl alcohol under ultrasonication for three times. The cleaned CF pieces are dried at 75°C overnight. During the process of the electrodes, the CF was soaked into the DMF solution with COP<sub>BTC</sub>-Mn dissolved at different content. The flexible electrodes (termed as COP<sub>BTC</sub>-Mn/CF) were then obtained after evaporating the solvent (Figure 1A).

## RESULTS AND DISCUSSION

### Material Characterization of the COP<sub>BTC</sub>-Mn and COP<sub>BTC</sub>-Mn/CF

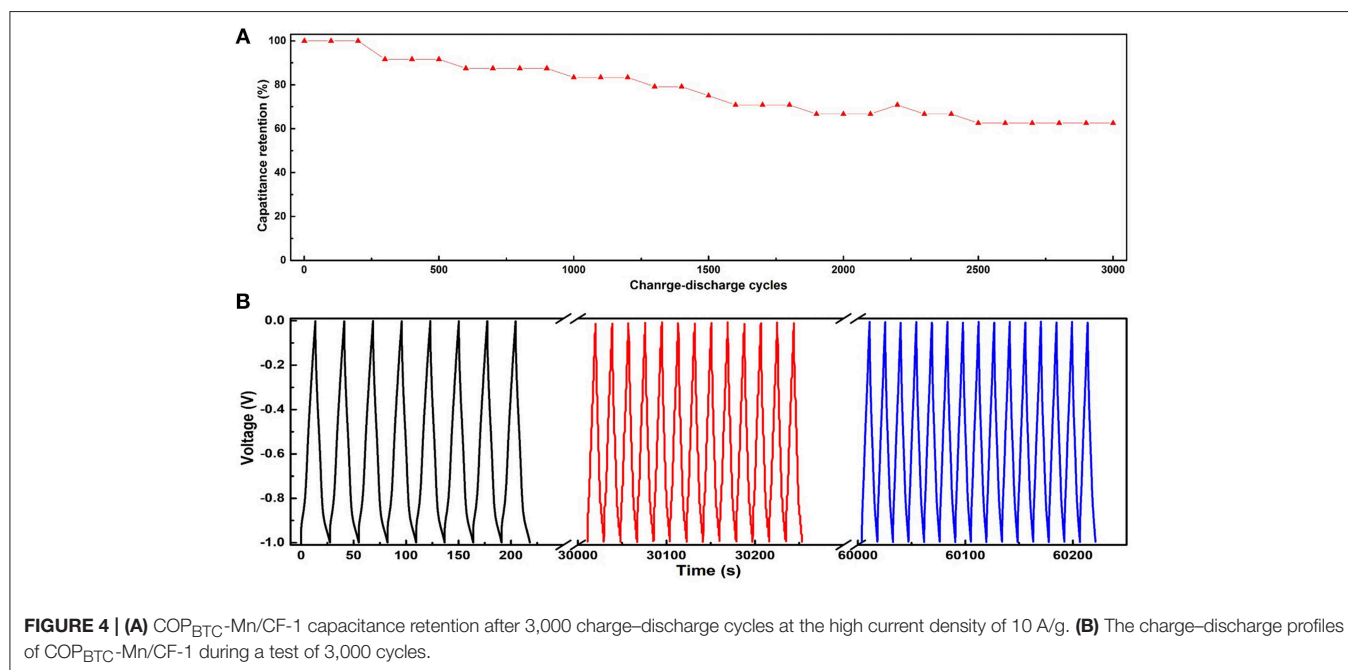
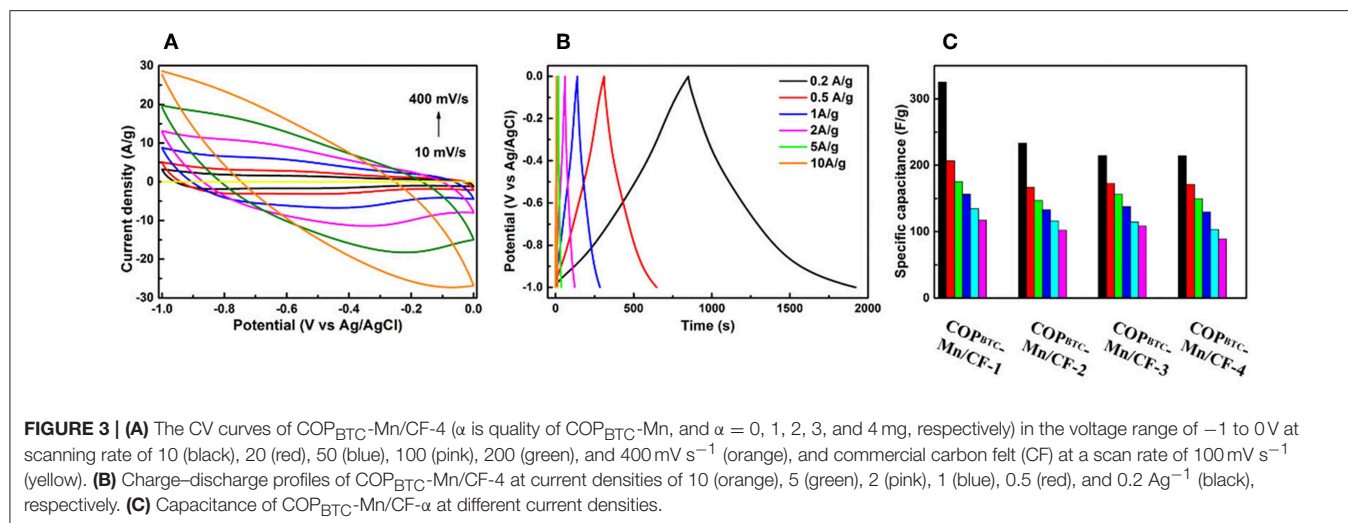
COP<sub>BTC</sub>-Mn was synthesized according our previous work with nitrogen coordinated Mn in the center (Figure 1A). The structure of the COP<sub>BTC</sub>-Mn was confirmed by the <sup>13</sup>C Solid-state NMR (Figure S1), which demonstrated four peaks at 44.43, 110.7, 137.52, and 168.11 ppm, attributing to the phthalocyanine macrocycles in the phthalocyanine-based conjugated polymer network. Fourier Transform Infrared Spectroscopy (FTIR) was also performed to further investigate the structure of the as-synthesized COP<sub>BTC</sub>-Mn (Figure S2), while the BTC monomer was used as the controlled sample. The peaks at 1,315, 1,616, and 1,760 cm<sup>-1</sup> were the stretching vibration peaks of C=C and C=N on the framework of aromatic ring. Compared with the BTC monomer, new peaks at 742, 1,060, 1,125 cm<sup>-1</sup> were found in the FTIR spectra of COP<sub>BTC</sub>-Mn, indicating the formation of phthalocyanine ring. Besides, cyano as the end group, the related characteristic peaks were found at 2,242 cm<sup>-1</sup> in both BTC monomer and COP<sub>BTC</sub>-Mn, which further proved the synthetic route of COP<sub>BTC</sub>-Mn.

According to the previous reports, the abundant nitrogen coordinated Mn centers endowed the COP<sub>BTC</sub>-Mn with the capability to be dissolved and form intermolecular interactions with the carbon matrix. As analyzed by the X-ray photoelectron spectroscopy (XPS), the peaks for C, N, and Mn were generated during the synthesis (Figures 1B-E). The fitting curves in C 1s spectrum were deconvoluted into three peaks



corresponding to the typical “C-C/C=C” (283.63 eV), “C=N/C-N/C-O” (285.29 eV), and “C=O” (287.07.8 eV) bonds. The fitted peaks of N 1s at 398.04 and 399 eV were attributable to “N-C” and “N-Mn,” respectively. The Mn 2p spectra demonstrated obvious peaks at 641.39, 645.25, and 652.92 eV, assigned to Mn 2p<sub>3/2</sub>, satellite state Mn, and Mn 2p<sub>1/2</sub>, which indicating

the formation of nitrogen coordinated Mn as the centers. As controlled examinations, the chemical valence state of  $\text{COP}_{\text{BTC-Mn/CF}}$  and CF were also performed (Figures S3, S4). The thermal stability of  $\text{COP}_{\text{BTC-Mn}}$  was performed in Figure S5. The survey spectra revealed that CF only contains three elements of C, N, O while the C, N, O, Mn were found in  $\text{COP}_{\text{BTC-Mn/CF}}$ ,



suggesting that the COP<sub>BTC</sub>-Mn was successfully introduced to the system. Elemental analysis (EA) and inductively coupled plasma (ICP) were performed to specifically explore the contents of CF and COP<sub>BTC</sub>-Mn/CF (Table S1). Consistently, the results proved that the COP<sub>BTC</sub>-Mn as the active sites were successfully riveted on the CF matrix and the COP<sub>BTC</sub>-Mn/CF electrodes were thus prepared.

The internal morphology and structure of the COP<sub>BTC</sub>-Mn/CF were revealed by SEM images. It was clear that the commercial carbon felt was composed of interconnected fibers, demonstrating a skeleton with smooth surface (Figure 2a). During the fabrication of electrodes, the COP<sub>BTC</sub>-Mn was adsorbed on CF through intermolecular interactions. Thus, the COP<sub>BTC</sub>-Mn/CF demonstrated a rough surface with uniformly distributed absorptions (Figure 2b). According to

the energy-dispersive X-ray spectroscopy (EDS) tests, COP<sub>BTC</sub>-Mn/CF electrodes presented a homogeneous dispersion of N and Mn elements (Figure 2c), suggesting the efficiency of our developed method for the fabrication of flexible electrodes.

### Electrochemical Performance of Flexible Electrode COP<sub>BTC</sub>-Mn/CF

To evaluate the electrochemical performance of the developed flexible electrodes, we performed the cyclic voltammetry (CV) and GCD. The as-prepared COP<sub>BTC</sub>-Mn/CF were directly used as the working flexible electrodes. Electrodes with different mass ratio of COP<sub>BTC</sub>-Mn were tested as comparison (marked as COP<sub>BTC</sub>-Mn/CF- $\alpha$ , where  $\alpha$  was mass of COP<sub>BTC</sub>-Mn and equaled to  $0, 1, 2, 3,$  and  $4$  mg, respectively). The CV curves

of COP<sub>BTC</sub>-Mn/CF- $\alpha$  and CF in the voltage range of  $-1$  to  $0$  V with different scanning rates were presented in **Figure 3A** and **Figure S6**. It could be found that the current of CF barely changed during the test, suggesting that CF was inactive for capacitive energy storage. Another feature was that none of obvious redox peaks were observed in the CV circles, indicating that the pseudocapacitance effect was small. The GCD test was performed at various current density from  $0.2$  to  $10$  A  $g^{-1}$  to further illuminate the electrochemical properties of the flexible COP<sub>BTC</sub>-Mn/CF- $\alpha$  electrodes. In **Figure 3B** and **Figure S7**, the as-prepared electrodes displayed typical charge-discharge curves. The voltage linearly increased with time in the charging process, while linearly decreased with time in the discharging process. Thus, the electrodes demonstrated symmetrical charge and discharge curves. Besides, with the increase of current density, the charge-discharge time shortened obviously. It should be noted that all of the COP<sub>BTC</sub>-Mn/CF- $\alpha$  electrodes was capable to be used at high current density of  $10$  A  $g^{-1}$ . We further evaluated the specific capacitance from the discharge curve and found that the performance highly dependent on the mass of COP<sub>BTC</sub>-Mn, suggesting that COP<sub>BTC</sub>-Mn was the necessary active material (**Figure 3C**). Moreover, with COP<sub>BTC</sub>-Mn/CF- $\alpha$  as the electrodes, the capacitors demonstrated a superior specific capacitance to the state-of-art electrodes made up of COP and MOF (Xu et al., 2015; Khattak et al., 2016; Han et al., 2017; Sheberla et al., 2017; Sun et al., 2017; Halder et al., 2018; Liu et al., 2018; **Table S2**). The impedance plot of COP<sub>BTC</sub>-Mn/CF-1 was provided in **Figure S8**. The COP<sub>BTC</sub>-Mn/CF- $\alpha$  electrodes also demonstrated superiorly long stability. As shown in **Figure 4A**, during the cycling experiments, the COP<sub>BTC</sub>-Mn/CF-1 kept about 60% capacitance after 5,000 charge/discharge cycles with the current density as high as  $10$  A  $g^{-1}$ . Meanwhile, the linearity and symmetry of the charge/discharge curves were well-retained (**Figure 4B**).

## CONCLUSION

In this work, we have developed a soluble COP<sub>BTC</sub>-Mn for supercapacitors. Benefited from the abundant nitrogen coordinated Mn centers, the COP<sub>BTC</sub>-Mn could be dissolved

in DMF through an *in-situ* charge exfoliation pathway and form intermolecular interactions with the CF matrix. Combining the activity of COP<sub>BTC</sub>-Mn with the high surface area of carbon fiber skeleton, we developed a COP<sub>BTC</sub>-Mn/CF flexible electrode with considerable capacitance and superiorly long charge/discharge lifetime. Our findings paved a notable avenue to simply and repeatable prepare flexible electrodes for not only high-performance supercapacitors, but also many other flexible energy storage devices.

## DATA AVAILABILITY STATEMENT

The raw data supporting the conclusions of this manuscript will be made available by the authors, without undue reservation, to any qualified researcher.

## AUTHOR CONTRIBUTIONS

CM and PP performed synthesis, structural characterizations, electrochemical tests, and battery tests. CM wrote this paper. ZX supervised and led this project.

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## SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fmats.2019.00242/full#supplementary-material>

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**Conflict of Interest:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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