(Metal-Organic Framework)-Polyaniline Sandwich structure
composites as Novel Hybrid Electrode Materials for
High-Performance Supercapacitor

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Abstract

Carbonized Zn-(Metal-Organic Framework)MOF- polyaniline composites for high performance of supercapacitor have been developed from zinc acetate, 8-Hydroxyquinoline, and aniline via a simple process. The as-synthesized product has been characterized by X-ray powder diffraction (XRD), Scanning electron microscopy(SEM), Fourier transform infrared spectra (FT-IR), Transmission electron microscope (TEM). The electrochemical properties of carbonized Zn-MOF/polyaniline electrode were investigated by current charge–discharge and cyclic voltammetry. The specific capacitance of MOF/PANI has been approach to be as high as 477 F g⁻¹ at a current density of 1A g⁻¹.

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1. Introduction

As the demand of the world of electric vehicles and hybrid electric (EV/HEV) is increasing year by year, energy problem is becoming more and more serious[1-9]. In order to solve the energy problem, the supercapacitors emerged[10-11].

Supercapacitor, as a kind of new energy storage device which combining the advantages of the high specific power of dielectric capacitors and the high specific energy of rechargeable batteries, has various advantages such as low internal resistance, fast charge/discharge, high power density, high energy density and long cycle life[10-16]. Furthermore, according to the energy storage mechanism, supercapacitor can be divided into electric double layer capacitor (EDLC) and pseudocapacitor[17-20]. EDLC as a new type of energy storage device can form double interfaces between the electrode material and the solution to store energy through the movement of positive and negative ions in the electrolyte under the action of the external force[21-27]. Furthermore, the energy storage mechanism of pseudocapacitor is that the electrode materials could show high storage energy density during the process of fast charge and discharge reaction [18, 28-30]. Therefore it is well known that the electrode material is the key to influence the

performance of supercapacitors and is becoming the research focus

Moreover, many materials **include** carbon material, metal oxide, and conducting polymers could be applied to electrode materials [26, 30-34]. Furthermore, polyaniline (PANI) as a desired candidate has become the optimum materials due to its simple process, low cost, high capacitance, desirable chemical stability and its unique protonic acid doping mechanism. However, the important factor of restricting the development of polyaniline materials is their low electrical conductivity and poor cycle life[21, 22, 35-38].

In order to conquer the problem, carbonized MOF/PANI composite material was used to apply for supercapacitor[39]. As well known, metal-organic frameworks (MOFs) built by metal ions and organic linker simultaneously could often cause fascinating structural topologies[40-45]. Moreover, MOFs porous materials also have the characters of well stability and ordered structures, high surface areas and tailored properties, which making MOFs porous materials distinguish for the synthesis of excellent membranes[31, 44, 46]. In the last decade, MOF membranes are widely used in various fields, such as gas separation, catalyst, optical device, sensor and so on[40, 47-50]. However, direct carbonized MOF has not been received much attention[51].

In our research, we **report** a simple method to fabricate carbonized MOF/PANI composite through in situ polymerization of aniline monomer

1 in the presence of carbonized Zn-MOF suspension. Carbonized Zn-MOF
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3 is synthesized from 8-hydroxyquinoline, zinc acetate and via calcination
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6 process.
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10 11 **2. Experimental Section**

12 13 **2.1. Materials.**

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17 8-hydroxyquinoline(C_9H_7NO) was purchased from Sinopharm
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19 Chemical Reagent Co., Ltd. Zinc(II) acetate dehydrate
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21 $[Zn(CH_3COO)_2 \cdot 2H_2O]$ was purchased from Sinopharm Chemical
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23 Reagent Co., Ltd. Aniline(C_6H_7N) was purchased from Shanghai
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25 Zhanyun Chemical Co., Ltd. Ammonium persulfate $[(NH_4)_2S_2O_8]$ was
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27 purchased from Shanghai Zhanyun Chemical Co., Ltd. Then all
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29 chemicals were used without further purification, and were received as
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31 analytical grade.
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38 39 **2.2. Preparation of MOF**

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42 In a typical synthesis, an ethanol solution (50mL) of
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44 8-hydroxyquinoline(C_9H_7NO , 1.8782g) was added into a redistilled
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46 water (150mL) of Zinc(II) acetate dehydrate $[Zn(CH_3COO)_2 \cdot 2H_2O]$,
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48 4.3708g] drop by drop slowly using a constant pressure funnel in an oil
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50 bath. The mixture was heated to 100°C and was stirred for 4h. After then,
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52 the reaction process was kept at room temperature without any
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54 interruption for 24h. Then, the resulting product was centrifuged and
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1 washed several times with distilled water and ethanol. Finally the
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3 samples were dried under oven at 80 °C before putting into a tube
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5 furnace. Then, after the as-prepared product being exposed to a flow of
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7 N₂ at room temperature for 15 min, the furnace was heated to 800 °C
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9 within 480 min. Afterwards, the resulting product was washed by 4M
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11 HCl to remove residual Zn component. Followed that, the product was
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13 further washed three times with distilled water and finally dried under
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15 oven at 80°C. The product was referred to as the carbonized Zn-MOF.
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22 **2.3 Synthesis of MOF/PANI**

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25 Carbonized Zn-MOF/PANI composites were synthesized by in situ
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27 chemical oxidative polymerization. In a typical synthesis, 4.6g of aniline,
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29 25mL of 2M H₂SO₄ and 0.1g carbonized Zn-MOF were dispersed in
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31 200mL of redistilled water with agitated stirring in an ice-bath to obtain a
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33 uniform solution. After stirring for 2h, 50mL of 0.8M (NH₄)₂S₂O₈ was
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35 added into the above-mentioned mixture with 1h drop by drop in an
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37 ice-bath. The polymerization was carried out for 4h in an ice-bath with
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39 continuous stirring. Next, the resulting mixture was kept at room
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41 temperature for 24h without disrupting. After that, the suspension was
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43 centrifuged and rinsed several times with distilled water and ethanol until
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45 the solution was changed to be colorless and transparent. The obtained
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47 product was dried under oven at 60°C for 24h to gain the carbonized
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49 Zn-MOF/PANI-0.1 composite. To give further evidence for different
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amount of MOF, carbonized Zn-MOF/PANI composites with approximate 0.02g and 0.04g MOF are signified as carbonized ZMP-0.02, carbonized ZMP-0.04 composites, respectively. Also, pure PANI was synthesized without using MOF by the same synthesis process. What's more, the carbonized Zn-MOF/PANI is short for MOF-PANI.

2.4 Characterization.

XRD patterns were obtained with a diffractometer on Rigaku, Japan, RINT 2500 V using Cu K α radiation. Raman spectra were carried out by a Horiba Jobin Yvon LabRAM using a 100 $\times$ objective lens with a 532 nm laser excitation. Fourier transform-infrared (FT-IR) spectra were recorded in KBr pellets with Bruker FTIR. Transmission electron microscopy (TEM) observations were obtained using a JEM-2100F microscope with Cs correction. Field-emission scanning electron microscopy (FESEM) observations were obtained using a Hitachi S4800.

2.5. Preparation of electrodes and electrochemical measurement

The MOF/PANI composite was prepared by mixing active materials, polyvinylidene fluoride (PVDF) (dissolved in the N-methylpyrrolidone (NMP)), acetylene black in a mass ratio of 8:1:1 to form uniform slurry. Furthermore, the slurry was coated onto titanium mesh(1cm $\times$ 1cm) as the working electrode, and dried in an oven at 80 $^{\circ}$ C for 12h. Then, the all electrochemical measurements were carried out using an electrochemical workstation (Chenhua CHI660E, China), on account of a three electrode

system. Furthermore, 1M H₂SO₄ was used as an electrolyte solution. Then, a Pt sheet and Ag/AgCl were applied as the counter electrode and reference electrode, respectively.

The electrochemical performance of the specimen was studied using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD). The voltage window of CV was from -0.2 to 0.8V at different scan rates from 5 mVs⁻¹ to 200 mVs⁻¹, and GCD was measured between -0.2 and 0.8 V with different current densities rang from 0.3 A g⁻¹ to 10 A g⁻¹. The specific capacitances of the samples were calculated from cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) curves according to the following equation[22]:

$$C_s = \frac{\int Idv}{vm\Delta V} \quad 1$$

$$C_s = \frac{I\Delta t}{m\Delta V} \quad 2$$

Where C_s is the specific capacitance (F g⁻¹), $\int Idv$ is the integrated area under the CV curve loop; v is the scan rate (V s⁻¹); m is the mass of the electroactive material (g); ΔV is the voltage window (V); I is the discharge current (A); Δt is the discharge time (s).

2. RESULTS AND DISCUSSIONS

TG analysis of Zn-MOF was analyzed at a heating rate of 10 °C /min under nitrogen conditions, and the result was shown in Figure S1. The first step of weight loss starts from 100 °C to 200 °C, which may be

1 related to adsorbed air and H₂O. The second weight loss from 350 °C to
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3 500 °C may be associated with the decomposition of the framework. On
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5 the basis of TGA results, the Zn-MOF was carbonized at 800 °C for 8h
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7 with a heating rate of 5 °C /min under nitrogen flowing.
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11 X-ray diffraction (XRD) was used to characterize the composite
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13 MOF-PANI. Figure 1 exhibits the XRD patterns of (a) MOF, (b)
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15 Pure-PANI, (c) ZMP-0.02, (d) ZMP-0.04, (e) ZMP-0.02, respectively.
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17 The carbonized Zn-MOF exhibits similar diffraction peaks with a broad
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19 peak at about $2\theta=25^\circ$ corresponding to carbon materials (002) diffraction.
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21 Pure-PANI shows three broad intense peaks at $2\theta=15.1^\circ$, 21° , 26° related
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23 to (011), (020), (200) planes, respectively. For the carbonized
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25 Zn-MOF-PANI composites, these materials have similar diffraction peaks
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27 to PANI. Notably, the XRD pattern of MOF-PANI-0.04 also has similar
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29 peak to that of carbonized Zn-MOF, which is obviously different from
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31 other materials.
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42 Figure 2 shows Raman spectra for (a) carbonized Zn-MOF, (b)
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44 Pure-PANI, (c) ZMP-0.02, (d)ZMP-0.24, (e) ZMP-0.1. As we know, the
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46 characteristic peak of the graphitic layers is called G band, while the D
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48 band is the characteristic peak of deficient graphitic structure or
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50 disordered carbon. It is general that the relative intensity ratio I_D/I_G of the
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52 D band and G band is used to estimate the defects in the pure
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54 grapheme[51]. The I_D/I_G for the carbonized Zn-MOF is 1.09, suggesting
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that high concentration of defects in the carbonized Zn-MOF and defects are helpful to the growth of polyaniline on carbonized Zn-MOF. At the same time, it should be noted that the higher I_D/I_G in the carbonized Zn-MOF may be induced by the doped nitrogen, which three types of N can be found in XPS of carbonized Zn-MOF (Figure S) The characteristic peak of 415cm^{-1} can be attributed to the stretching vibration of C-N-C bond between the adjacent benzenoid and quinoid rings in PANI[52]. From the Raman spectra of ZMP -0.02, ZMP-0.04, ZMP-0.1, Pure-PANI, it is obviously observed that the spectral features of ZMP -0.02, ZMP-0.04, ZMP-0.1 do not change obviously with adding the carbonized Zn-MOF compared to the Pure-PANI. But, the characteristic peaks of carbonized Zn-MOF have a minor change, which indicates that carbonized Zn-MOF has an interaction with PANI and indicates charge transfer between carbonized Zn-MOF and PANI.

The interaction between carbonized Zn-MOF and PANI is shown in Figure3. The peaks of 1115cm^{-1} , 1302cm^{-1} , 1490cm^{-1} , 1581cm^{-1} are the characteristics of PANI[23]. From the spectra, it can be found that (a) carbonized Zn-MOF, (b) ZMP-0.02, (c) ZMP-0.04, (d) ZMP-0.1 have similar characteristic peaks, implying that they have similar molecular structure. From Figure3, the peak of 1115cm^{-1} can be assigned to the N=Q=N stretching (Q is the quinonoid ring). Moreover, the characteristic peaks of 1302cm^{-1} , 1490cm^{-1} , 1583cm^{-1} reflect C-N

stretching vibration , C=C stretching of benzenoid ring, C=C stretching of quinonoid ring[53] respectively. But, it can be seen that (b) ZMP-0.02, (c) ZMP-0.04, (d) ZMP-0.1 have a red shifts in some degree, which could suggest that MOF-PANI composites are in doping state. This structure is benefit for the transformation of the free movement of electrons, and also improving the free movement of electrons in molecular chains and the ability of transport charge. It is hinted that MOF-PANI composites have the high electrical conductivity.

The morphologies of the ZMP-0.04 composites are examined by SEM. The image of MOF-PANI-0.04 shows that PANI is between the layers of carbonized MOF. From the low-resolution SEM images as shown in Figure 4b, it can be easily observed that ZMP-0.04 shows the layered structure. Then, ZMP-0.04 is indeed the layered structure in Figure 4a. From the high-resolution SEM images as shown in Figure 4c and 4d, it can be observed that the thickness of carbonized MOF layer is about 50nm. As shown in Figure 5a, 5b, the TEM images further indicate the coexisting structure of MOF-PANI, which could be identified that PANI is between the layers of carbonized Zn-MOF.

The electrochemical performances of ZMP-0.04, ZMP-0.1, ZMP-0.02 and pure-PANI as electrode materials for supercapacitor are carried out using a three-electrode cell in 1M H₂SO₄. Figure 6 shows the cyclic voltammetry curves in the potential window from -0.2 to 0.8V.

Two pairs of redox peaks are found on the CV curves, which are attributed to the redox transitions of PANI between a semiconducting state (leucoemeraldine form) and a conducting state (polaronic emeraldine form), the benzoquinone and aminoquinone couple, respectively.[42]

From the Cyclic voltammetry curves shown in Figure 6a, it is notable that the CV area of pure-PANI was smaller than those of other samples, and even was smaller than ZMP-0.02. The enhancement electrochemical performance of the composites attributed to the synergistic effect of the two components, as follows: (1) the carbonized Zn-MOF has excellent electrical conductivity, which can enhance the electrical conductivity of the composites [51]. (2) Sandwich-like carbonized Zn-MOF/PANI reduces the transmission distance of the electron and also reduces the diffusion resistance of electrolyte. (3) In the process of charge and discharge, carbonized Zn-MOF can keep the overall structure of the polyaniline was not damaged. Therefore, it suggests that ZMP-0.04 has the largest capacitor than others. Based on this, it is concluded that the calcined MOF can improve electrical conductivity of the composite and enhance the capacitance of composite. Figure 6b shows the CV curves of ZMP-0.04 at different scan rates from 10 to 200mVs⁻¹ respectively. It is clear that the composites could show high redox current increased with increasing scan rate, indicating an

excellent rate capability.

To reveal the electrochemical capacitive performances of the composites, the galvanostatic charge-discharge experiment was employed. Figure 7a shows the GCD potential curves of the composites range from -0.2 to 0.8 V with different composites at same current density of 1 A g⁻¹. It is well known that the symmetric and linear charge-discharge curves indicate that the electrodes would show high performance supercapacitor behavior. It is observed that the composite of ZMP-0.04 has the largest specific capacitance with 477 F g⁻¹ at a current density of 1 A g⁻¹. However, the specific capacitance of ZMP-0.1, ZMP-0.02 and pure-PANI were lower than that of ZMP-0.04. Notably that the pure-PANI has the lowest specific capacitance than all kinds of composites. Moreover, the superior specific capacitance of ZMP-0.04 could be promoted due to the carbonized MOF containing a small quantity of nitrogen, which can not only ameliorate the wettability of the composite in the electrolyte but also improve the conductivity of the composite. Figure 7b shows the galvanostatic charge-discharge curves of ZMP-0.04 at a current density over range of 0.3 to 10 A g⁻¹. The specific capacitance of ZMP-0.04 is as high as 500 F g⁻¹ at a current density of 0.3 A g⁻¹. However, with the increase of current density, the specific capacitance of ZMP-0.04 would be only decrease to 281 F g⁻¹ at a current density of 10 A g⁻¹. All of the above suggest that ZMP-0.04 composite is best choice for

1 electrochemical capability.

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3 To further characterize the performance of the supercapacitors, the
4 long-term cycle stability of the electrodes was investigated by repeating
5 CV testing in 1 M H₂SO₄ electrolyte at a scan rate of 100 mV s⁻¹ for 100
6 cycles. As shown in Figure 8a, ZMP-0.04 presents good cycling behavior
7 and only a slight capacitance loss (<10%) after 100 cycles. The special
8 sandwich structure of ZMP-0.04 is also helpful for the relaxation of the
9 volume expansion during the doping/dedoping process.
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22 Figure 8 (b) shows the Nyquist plots in the frequency range of 100k
23 to 0.01Hz for ZMP-0.04, ZMP-0.1, ZMP-0.02, Pure-PANI. As we all
24 know, the electrochemical impedance spectroscopy (EIS) is very
25 important in analyzing the basic behavior of electrode material for
26 supercapacitor. As shown in Figure 8 (b), the Nyquist plot of carbonized
27 MOF-PANI shows a short Warburg-line, indicating that the composites
28 have fast ion diffusion as electrode material for supercapacitor. The
29 low-frequency part of the composites was almost vertical, suggesting that
30 the composites have a pure capacitor behavior. The resistance of
31 ZMP-0.04, ZMP-0.1, ZMP-0.02, Pure-PANI are 0.22Ω, 1.147Ω, 1.054Ω,
32 4.569Ω, respectively. Therefore, it is concluded that moderate carbonized
33 Zn-MOF would enhance the conductivity of the electrode material.
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55 3. Conclusion

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57 In summary, the electrode material for supercapacitor of carbonized
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MOF-PANI composite was synthesized by a novel and facile route. The Zn-MOF was calcined at 800°C and washed with 4M HCl. In the process of polymerization of aniline, the carbonized MOF can be applied as the skeleton to carbonized MOF-PANI sandwich structure composites. ZMP-0.04 exhibits a specific capacitance of 477 F g⁻¹ at a current density of 1 A g⁻¹. The carbonized MOF could show a good electrical conductivity to improve the electrical conductivity of carbonized MOF/PANI composite, and also enhances the ability of PANI storage electrolyte and electrochemical activity. Moreover, the carbonized MOF plays a key role to improve the performance electrode material.

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Scheme 1.

Figure 1.

Figure 2

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Figure 8.

Scheme 1. Schematic Illustration of synthesizing sandwich structure of carbonized Zn-MOF/PANI composites.

Figure1. XRD patterns of (a) carbonized Zn-MOF, (b) Pure-PANI, (c) ZMP-0.02, (d) ZMP-0.04, (e) ZMP-0.1.

Figure2. Raman spectra of (a) carbonized Zn-MOF, (b) Pure-PANI, (c) ZMP-0.02, (d) ZMP-0.24, (e) ZMP-0.1.

Figure3. FTIR spectra of (a) carbonized Zn-PANI , (b) ZMP-0.02 , (c) ZMP-0.04 , (d) ZMP-0.1

Figure4. SEM images of composite (a-d) ZMP-0.04.

Figure5. TEM images of composite (a-b) ZMP-0.04.

Figure6. (a) Cyclic voltammetry curves of a) ZMP-0.04 , b) ZMP-0.1, c) ZMP-0.02, d) pure PANI at the scan rate of 10mVs^{-1} in $1\text{M H}_2\text{SO}_4$. (b) Cyclic voltammetry curves of ZMP-0.04 at the scan rate range of $10\text{-}200\text{mVs}^{-1}$ in $1\text{M H}_2\text{SO}_4$.

Figure7. (a) Glvanostatic charge discharge curves of (a) ZMP-0.04,(b) ZMP-0.1 , (c) ZMP-0.02, (d) pure-PANI at a current density of 1 A g^{-1} . (b) Galvanostatic charge discharge curves of ZMP-0.04 at a current density range of $0.3\text{ to }10\text{ A g}^{-1}$.

Figure8. (a) Cycling performance of ZMP-0.04 composites at a current density of 1 A g^{-1} . (b) Nyquist plots of (a) ZMP-0.04, (b) ZMP-0.1, (c) ZMP-0.02, (d) Pure-PANI from 100 kHz to 0.01Hz (the high frequency regions shown in the inset picture).