

Atomic layer deposition-induced integration of N-doped carbon particles on carbon foam for flexible supercapacitor

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ABSTRACT

Flexible devices have attracted abundant attention in energy storage systems. In this paper, we presented a novel approach for fabricating flexible supercapacitor based on metal organic frameworks-derived material. In this approach, a uniform zeolitic imidazolate frameworks-8 layer with a high mass loading was deposited on a flexible carbon foam (CF) skeleton efficiently by the induction of a uniform ZnO nanomembrane prepared via an atomic layer deposition technique. A flexible N-doped carbon particle-carbon foam (N-CP-CF) composite with a hierarchically porous structure and a large specific surface area (i.e., 538 m² g⁻¹) was obtained in a subsequent pyrolysis process. The resultant materials have the excellent electrochemical performance (i.e., a high specific capacitance of 300 F g⁻¹ and a high energy density of 20.8 W h kg⁻¹). The N-CP-CF composite can provide a stable capacitance (i.e., 250 F g⁻¹) and an energy density (i.e., 17.36 W h kg⁻¹) under large deformation (25% of original thickness). This work could propose a promising strategy in fabrication of flexible electrode with a large potential towards energy storage applications in the future.

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1. Introduction

With the scarcity of fossil energy, the demands for searching environmental-friendly as well as high power providing energy storage systems become more and more urgent in recent years [1,2]. Supercapacitors have received vast research interests due to their high power density, fast charge/discharge rate and good rate performance that can endure large current charging [3,4]. Compared to the conventional supercapacitors, flexible supercapacitors hold a great electrochemical performance and deliver a good flexible property like large deformation toleration and lightweight, making them a promising device for wearable electronics [5]. Many efforts have been devoted to the development of flexible supercapacitors so far [6–9], and some pseudocapacitive materials like conducting polymers are widely applied in flexible supercapacitors electrodes [10,11]. However, it is still a challenge due to

the high cost, complex fabrication process (e.g., wet chemical polymerization), and unsatisfied performance [12]. Application of double-layer capacitive materials such as carbon particles and nanofibers in flexible electrodes also needs further exploration and optimization [13,14]. For instance, Chen et al. [15] incorporated ruthenium oxide nanoparticles uniformly on carbon-based microfibers consisting of holey reduced graphene oxide and single-walled carbon nanotubes to enhance the energy density of the device.

As is known, the electrode materials are the most crucial part of supercapacitors [16]. Carbon-based materials are widely used for electrodes because of their abundant porosity, excellent electrical conductivity, and chemical stability [17–19]. Commonly, the capacitance of carbon materials is closely related to its pore structure and specific surface area [3]. Therefore, among versatile carbon materials, porous carbon particles derived from metal organic frameworks (MOFs) with large surface area, large pore volume, and rich nitrogen contents are widely engaged in electrodes [20]. However, MOFs as well as pyrolyzed carbon structures have narrow pore distributions and low ion transport efficient, thus restricting their electrochemical applications in supercapacitors [3]. Furthermore, the individual rigid particles hinder their

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application in flexible electronics. In order to solve these problems, flexible foam-like open-porous materials with high conductivity and 3D interconnected structures as substrates have been taken into consideration. The so-called carbon foam (CF) is one of ideal substrate materials with a good deformation toleration property that is prepared *via* directly pyrolysis from melamine foam [21]. However, it is still challenging in combining MOFs with CF to achieve high mass loading of active materials, intimate adhesion, and large specific surface area *via* a uniform integration approach.

This paper reports a recent work on a novel method, taking advantages of atomic layer depositions (ALD), which could deposit nanomembrane conformally and uniformly [22], to integrate a high mass loading as well as a uniform MOF layer with flexible substrate [23]. The MOFs used was zeolitic imidazolate frameworks-8 (ZIF-8), which consisted of Zn ions and imidazole frameworks [24]. N-doped carbon particle-carbon foam (N-CP-CF) composite was fabricated in a subsequent pyrolyzed process. In the resultant hierarchically porous composite, N-CP derived from ZIF-8 provided high surface area and nitrogen dopant, and conductive CF provided 3D interconnected networks for fast ion transportation. The N-CP-CF composite can endure large deformation with outstanding flexible property. The N-CP-CF as electrodes for a symmetric supercapacitor exhibited excellent electrochemical performance (i.e., a large capacitance of 300 F g⁻¹ at a current density of 0.5 A g⁻¹, a high energy density of 20.8 Wh kg⁻¹, as well as a high power density of 10000 W kg⁻¹). The composite had a relatively stable rate performance, and the capacitance remained to be 72 F g⁻¹ at a high current density of 20 A g⁻¹. At a severe compression rate of 25%, the N-CP-CF electrode showed a slight decline in capacitance. Thus, the N-CP-CF composite could facilitate an efficient route for the fabrication of new generation flexible electrode in energy storage field.

2. Experimental

2.1. Materials

The melamine foam used was obtained from BASF basotect Co., China. Zinc Acetate Dihydrate (Zn(CH₃COO)₂·2H₂O), 2-methylimidazole (2-MI), and Methanol (AR, ≥99.5%) were obtained from Sinopharm Chemicals Co., China. All the reagents were used as received without further purification. The de-ionized (DI) water used throughout all the experiments was purified through a Millipore system.

2.2. Fabrication of CF

CF was fabricated by a one-pot carbonization method. Melamine foam was cut into small blocks with the size of 50 × 30 × 20 mm³, washed with fresh ethanol and acetone under ultrasonication for 30 min, and dried in vacuum at 60 °C for 12 h. Dried melamine foam blocks were then heated at 800 °C in N₂ atmosphere for 2 h, and CF was obtained after being cooled to room temperature. The CF was washed with 0.5 M HNO₃ solution for 1 h to remove impurities, and then washed with DI water for several times.

2.3. ZnO nanomembrane deposited on CF by ALD

ZnO nanomembrane was prepared by an ALD-based technology. The deposition of ZnO nanomembrane on the skeletons of CF was performed at 150 °C in a homemade reactor. Diethylzinc (DEZ) and DI water were used as precursors. A typical ALD cycle included DEZ pulse (50 ms), waiting time (5 s), N₂ purge (30 s), DI water pulse (30 ms), waiting time (5 s), and N₂ purge (30 s). 300 ALD cycles were adopted in the experiments.

2.4. Growth of ZIF-8 layer on carbon foam

Zn(CH₃COO)₂·2H₂O (2.7 g) was dissolved in methanol of 40 mL (i.e., solution A) and 2-MI (6 g) was dissolved in methanol of 112 mL (i.e., solution B). Several blocks of CF were then fully immersed in a vessel containing solution A. Then solution B was added and the mixture was aged at room temperature for 24 h, leading to the growth of ZIF-8. After ZIF-8 growth, the CF blocks were washed with fresh ethanol for several times and dried in vacuum at 60 °C for 12 h. The CF with ZIF-8 on it was denoted as ZIF-8-CF.

2.5. Synthesis of N-CP-CF composites

The ZIF-8-CF was heated at 800 °C for 2 h. After cooling down, the obtained N-CP-CF was washed with ethanol and dried in vacuum at 60 °C for 12 h.

2.6. Synthesis of N-CP powders

For comparison, ZIF-8 powders were obtained by mixing solutions A and B directly. The fabricated ZIF-8 powders were heated in a N₂ atmosphere at 800 °C for 2 h to fabricate N-CP powders. After cooling down, the N-CP powders were washed with ethanol to remove impurities and dried in vacuum at 60 °C for 12 h.

2.7. Microstructural characterizations

The morphologies of all the products were measured by a VEGA TS 5136 MM field-emission scanning electron microscopy (SEM, TESCAN Co., Czech). The composition of the samples was analyzed by a X-Max 80T energy dispersive spectrometer (EDS, Oxford Instrument Co., Ltd., UK). The X-ray diffraction (XRD) patterns were measured by an X'Pert Pro X-ray diffractometer (PANalytical Co., Netherlands) equipped with Cu K_α radiation (λ = 0.1542 nm) at a current of 40 mA and a voltage of 40 kV. The nitrogen sorption/desorption properties were measured by a Quadrasorb adsorption instrument (Quantachrome Instruments Co., US). The specific surface areas were calculated using a multi-point Brunauer-Emmett-Teller (BET) method. The pore size distributions were calculated based on nitrogen sorption data using the Barrett Joyner Halenda (BJH) equilibrium model method for slit, cylinder, and sphere pores provided by the Quantachrome data reduction software named ASiQ win Version 4.01. The electrical properties of the samples were carried out by a Keithley 4200 semiconductor parameter analyzer (Tektronix Co., US). The sample was tailored into thin blocks with the size of 10 × 10 × 4 mm³ for electrical measurement.

2.8. Electrochemical measurement

The electrochemical performances were evaluated in a Shanghai Chenhua CHI 660E electrochemical workstation. Two-electrode symmetric supercapacitors were fabricated and characterized. The more details can be found in Supplementary data.

3. Results and discussion

The synthesis process of N-CP-CF composites is shown in Fig. 1a-c. In Fig. 1a, CF as a flexible supporter is prepared *via* a directly carbonization of melamine foams in N₂. Although the shrinkage of the sample appears in our experiment, the 3D inter-connected structure of the foam demonstrates no apparent variety after carbonization, and the flexibility remains well. The corresponding SEM image in Fig. 1d displays a fiber like branch with the smooth surface. A ~50 nm-thick ZnO nanomembrane was coated on the surface of CF after ALD pretreating (see Fig. S1) [25]. ZnO

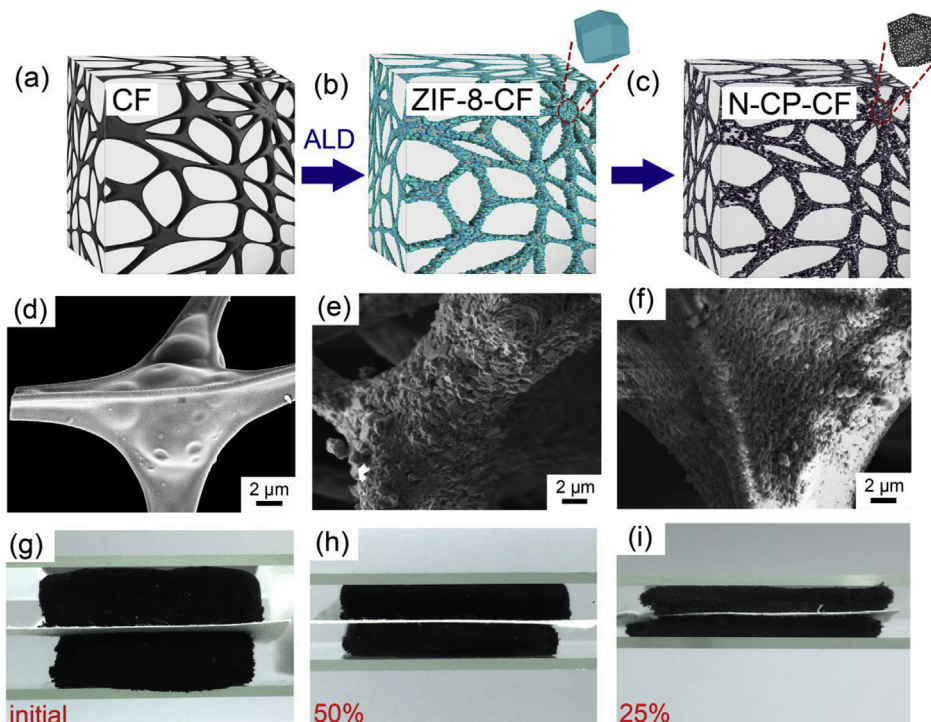


Fig. 1. (a)–(c) Schematic of the fabrication process of N-CP-CF composite; (d)–(f) SEM images of CF, ZIF-8-CF, and N-CP-CF, respectively; (g)–(i) Photographs of the N-CP-CF composites with different compression rates; The compression rates (defined as the ratio of the thicknesses of the sample after and before compression) are labelled.

nanomembrane completely wraps the skeleton of CF, and no obvious defect occurs due to the advantage of the conformal and uniform deposition process of ALD. The complete ZnO coating is benefit for the nucleation of ZIF-8 layer in the next solution-based growth step. In the SEM images of ZIF-8-CF (see Fig. 1e and S2), a dense and uniform ZIF-8 layer clearly appears on CF. The mass loading calculated based on the change of mass of the sample is ~55%. The growth mechanism of ZIF-8 layer can be described as follows: The ZnO nanomembrane by ALD reacts with zinc acetate to form (Zn, Zn) hydroxy double salts (HDS) [26–28]. Then, the combination of organic linkers (2-MI) with (Zn, Zn) HDS leads to a rapid production of target ZIF-8 layer [26]. During the next carbonization process, organic linkers transform into carbon composition, and Zn^{2+} is reduced to Zn [3]. ZIF-8 layer is thus converted into N-doped carbon layer and N-CP-CF composite is obtained (see Fig. 1c). However, the polyhedron shape of ZIF-8 becomes vague after carbonization due to the strong adhesion between ZIF-8 layer and CF substrate (see Fig. 1e). For comparison, the morphology of ZIF-8 powders prepared in solution and the corresponding N-CPs derived from ZIF-8 powders are shown in Fig. S3. The ZIF-8 powders display a polyhedron shape with a particle size of ~2 μm (see Fig. S3a). In the pyrolysis process, the ZIF-8 powders turn into N-CPs (see Fig. S3b). It is seen that the polyhedron shape remains well although particle size reduces to ~500 nm, which is different from the cases in N-CP-CF (see Fig. 1e). Furthermore, Fig. 1g–i shows the flexibility of N-CP-CF. The sample can be compressed to 25% of the initial thickness with a perfect structural integrity.

Fig. 2a shows the XRD patterns of the samples. The CF exhibits an amorphous nature without any sharp peak. Some sharp peaks attributed to crystallized ZnO appear (plot ALD-ZnO-CF) after the CF is coated with ZnO nanomembrane. When ZIF-8 layer is grown, the XRD pattern shows typical sharp peaks associated with ZIF-8 (plot ZIF-8-CF) [29,30], indicating the successful formation of ZIF-8 layer in the composite. The XRD pattern of N-CP-CF displays a

complete amorphous status, proving the complete pyrolysis of ZIF-8-CF after the high-temperature treatment. For comparison, the XRD patterns of ZIF-8 powder and the corresponding N-CP are shown in Fig. S4, which illustrates that the ZIF-8 powder completely transforms into amorphous state after the pyrolysis. This process exists in both N-CP and N-CP-CF. In addition, the EDS result of N-CP-CF is also shown in Fig. S5. An abundant N content of 9.2 wt% appears, which is beneficial to the enhancement of the electrochemical performance.

In order to further investigate the porous structures of the samples, the nitrogen adsorption/desorption isotherms of ZIF-8, N-CP, and N-CP-CF were carried out and the results are shown in Fig. 2b. The isotherms of ZIF-8 and N-CP display typical type I isotherms [31], indicating the absence of vast micropores. N-CP-CF shows both microporous and mesoporous characters. Fig. 2c shows the detailed pore size distributions. It is seen that ZIF-8 and N-CP both display typical microporous structures with the pore sizes of <2 nm, while N-CP-CF shows more complex structures with both microporous and mesoporous peaks in pore size distributions. After the pyrolysis process, N-CP-CF has an apparent mesopore peak at ~20 nm, which can be attributed to the close stack of particles in the N-CP layer. Meanwhile, some micropores with the pore sizes of <2 nm were effectively preserved in N-CP-CF, forming the hierarchically porous structures. Also, Fig. 2d shows the specific surface area of ZIF-8, N-CP, and N-CP-CF. N-CP-CF has a large specific surface area of 538 m² g⁻¹.

In order to investigate the practical application of N-CP-CF composite in supercapacitors, a typical two-electrode symmetric supercapacitor was fabricated utilizing the N-CP-CF as an electrode material. Fig. 3a shows typical CV curves at 10 mV s⁻¹ of N-CP-CF, compared to N-CP and CF. All the CV curves are a rectangular shape, indicating the ideal double-layer capacitance character [3]. The area surrounded by the CV curves of N-CP-CF is greater than that of CF or N-CP, implying the higher capacitance and largely enhancement of electrochemical performance. It is noticed that the CV curve of pure

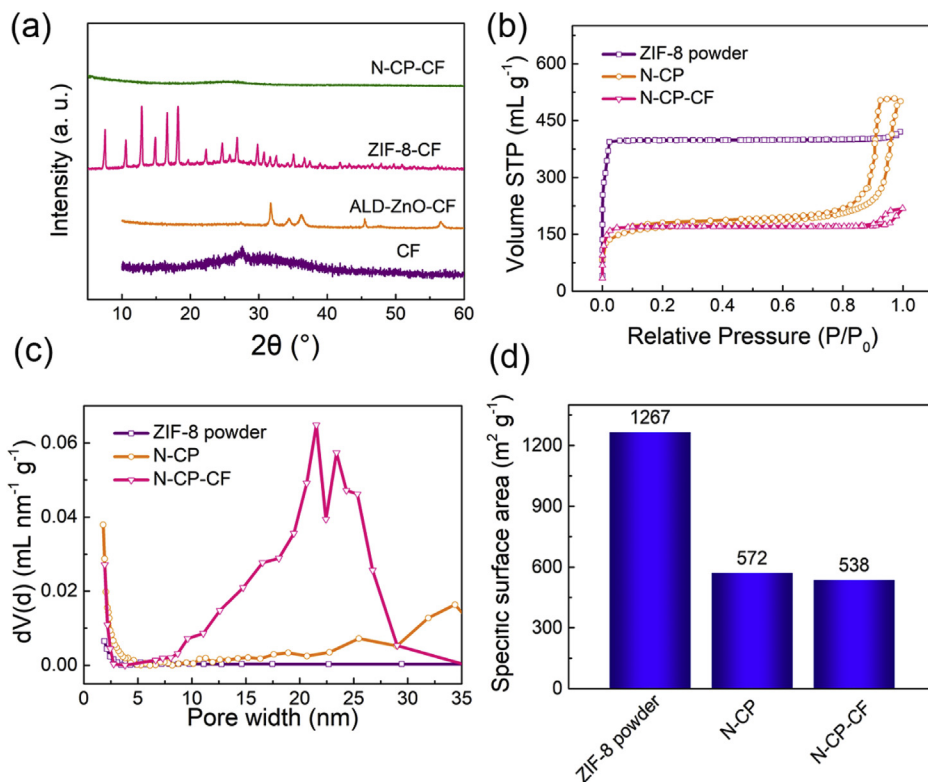


Fig. 2. (a) XRD patterns of the obtained samples; (b) Nitrogen adsorption/desorption isotherms of the samples; (c) Calculated pore size distributions; (d) Summary of specific surface areas of N-CP-CF, ZIF-8 powder and N-CP.

graphite paper at a scan rate of 10 mV s⁻¹ in Fig. S6 shows that the graphite paper contributes a negligible capacitance. Fig. 3b shows the CV curves of N-CP-CF at various scan rates. A relatively stable rate performance appears as the shapes of CV curves remain well at various scan rates. Even at a higher scan rate of 200 mV s⁻¹, the electrochemical performance of N-CP-CF is still stable in terms of only slight tilting of CV. Fig. 3c shows the galvanostatic charge/discharge curves in a potential range from 0 to 1 V of N-CP-CF. The N-CP-CF displays a linear curves in both charging and discharging cases, which means the unanimous charging and discharging characteristics. Also, there is no obvious IR drop during the discharging process due to the negligible internal resistance. Fig. 3d shows the EIS results to further illuminate the resistant characteristic of the samples. The Nyquist plots of all electrodes show a linear traits at a relatively low frequency area, and no semicircles can appear at a high frequency, indicating a low charge transfer resistance of all the electrodes. Moreover, N-CP-CF composite exhibits the highest slope at a low frequency, showing the fastest ion transfer rate and best electrolyte penetration, compared to N-CP and CF. It is indicated that the formation of hierarchically porous structure in N-CP-CF is since the introduction of mesopores (see Fig. 2c) enhances the ion transfer rates. Also, CF skeleton provides 3D inter-connected conductive pathway for fast ion transportation, which can improve the electrochemical performance. Fig. 3e shows the specific capacitance calculated from the galvanostatic charge/discharge curves of N-CP-CF, compared to N-CP and CF. It is seen that N-CP-CF exhibits a greater capacitance rather than CF and N-CP. At a current density of 0.5 A g⁻¹, N-CP-CF has an outstanding specific capacitance of 300 F g⁻¹, and the value is much greater than that of N-CP (i.e., 120 F g⁻¹) or CF (i.e., 160 F g⁻¹). At a high current density of 20 A g⁻¹, N-CP-CF achieves a specific capacitance of 52 F g⁻¹, which is also significantly higher than that of N-CP or CF. We also calculated the specific capacitances of N-CP-CF from the CV

curves. In Fig. S7, the composite electrode exhibits a high capacitance of 519 F g⁻¹ at 10 mV s⁻¹, and remains 116 F g⁻¹ at 200 mV s⁻¹, indicating a good electrochemical performance.

Fig. 3f shows the Rogan plot for the energy density and power density of N-CP-CF composites. A symmetric supercapacitor used N-CP-CF as electrodes has an energy density of 20.8 W h kg⁻¹ at a power density of 250 W kg⁻¹. When the power density increases to 10000 W kg⁻¹, which still delivers an energy density of 3.6 W h kg⁻¹. Fig. 3f also shows the results from other MOF-based structures in the literature for comparison. Table 1 lists the detailed comparison of N-CP-CF with other MOF-based materials in terms of capacitance, electrolyte, as well as device configuration. Clearly, the current N-CP-CF composite exhibits a superior electrochemical performance. The capacitance property of the N-CP-CF composites can be attributed to its unique structure. In the resultant composite, N-CP-CF preserves the abundant micropores, and provides mesopores due to the stack of carbon particles. Micropores lead to exposure of more vast active sites, and meanwhile the existence of mesopores are beneficial to penetration of the electrolyte. The existence of hierarchically porous structure as well as the large surface area can enhance the specific capacitance. The formation of uniform N-CP layer fixes the active particles. The confinement of active particles prohibits the aggregation of N-CP, buffering the volume changes during charging and discharging process, leads to an increased structural stability. Also, an improved ion transportation due to the 3D inter-connected conductive frameworks may further promote the electrochemical performance. The conductivity of pure CF is measured by I-V test (see Fig. S8), and the calculated conductivity is 2.13 S m⁻¹.

The N-CP-CF composite exhibits an excellent flexibility due to the flexible support of CF, and thus we expect a good deformation-tolerant electrochemical performance of N-CP-CF composite. In this work, the electrochemical performance of the flexible electrode was

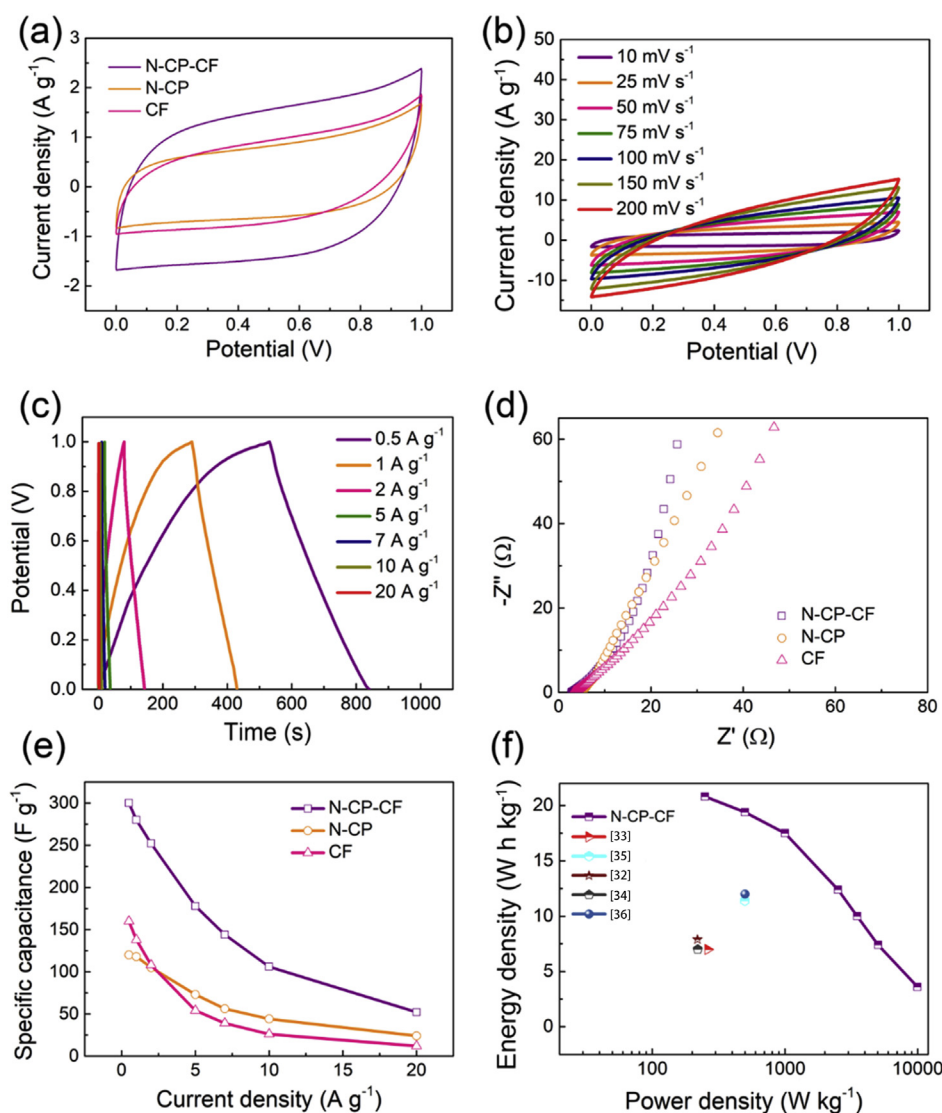


Fig. 3. (a) CV curves of electrodes made from N-CP-CF, N-CP, and CF at a scan rate of 10 mV s^{-1} ; (b) CV curves of electrode made from N-CP-CF at various scan rates ranging from 10 to 200 mV s^{-1} ; (c) Galvanostatic charge/discharge curves of N-CP-CF electrode at various current densities; (d) EIS curves of electrodes made from N-CP-CF, N-CP, and CF; (e) Specific capacitance of N-CP-CF, N-CP, and CF electrodes at various current densities; (f) Ragone plot of N-CP-CF electrode; Results from other MOF-based structures in previous literature are also plotted for comparison.

Table 1
Summary of electrodes made from MOF-based structures.

Material and structure	Electrolyte	Device configuration	Specific capacitance (F g^{-1})	Ref
N-NFC	1 M H_2SO_4	Three-electrode	387.3 at 1 A g^{-1}	[32]
CZ-6	6 M KOH	Two-electrode	204 at 1 A g^{-1}	[33]
S-3DCN	6 M KOH	Two-electrode	190 at 1 A g^{-1}	[34]
ZM-C-800	6 M KOH	Two-electrode	118.5 at 0.5 A g^{-1}	[35]
CoP-NPC/RGO	1 M H_2SO_4	Two-electrode	352.8 at 1 A g^{-1}	[36]
NCPs	6 M KOH	Two-electrode	170 at 1 A g^{-1}	[3]
MWCNT/NPCs	6 M KOH	Two-electrode	112 at 0.5 A g^{-1}	[37]
PC1000@C	6 M KOH	Three-electrode	225 at 0.5 A g^{-1}	[30]
Carbon-ZS	6 M KOH	Three-electrode	285.8 at 0.1 A g^{-1}	[38]
N-CP-CF	6 M KOH	Two-electrode	300 at 0.5 A g^{-1}	This work

investigated at various compression rates. For the sake of simplicity, the N-CP-CF composites compressed to 75%, 50%, and 25% of its initial thickness are denoted as N-CP-CF-75, N-CP-CF-50, and N-CP-CF-25, respectively. In Fig. 4a, the CV curves of N-CP-CF at various compression rates exhibit negligible difference, indicating the stable capacitance under large deformation. Fig. 4b shows the EIS curves of

the electrode at different compression rates. There is only slightly decay of the slope in low frequency region with deformation. The results indicate a stable charge transportation even under severe compression. The observed negligible decay can be ascribed to the fact that the pores in CF shrink under compression, thus slightly affecting the ion penetration therein. Fig. 4c shows the specific

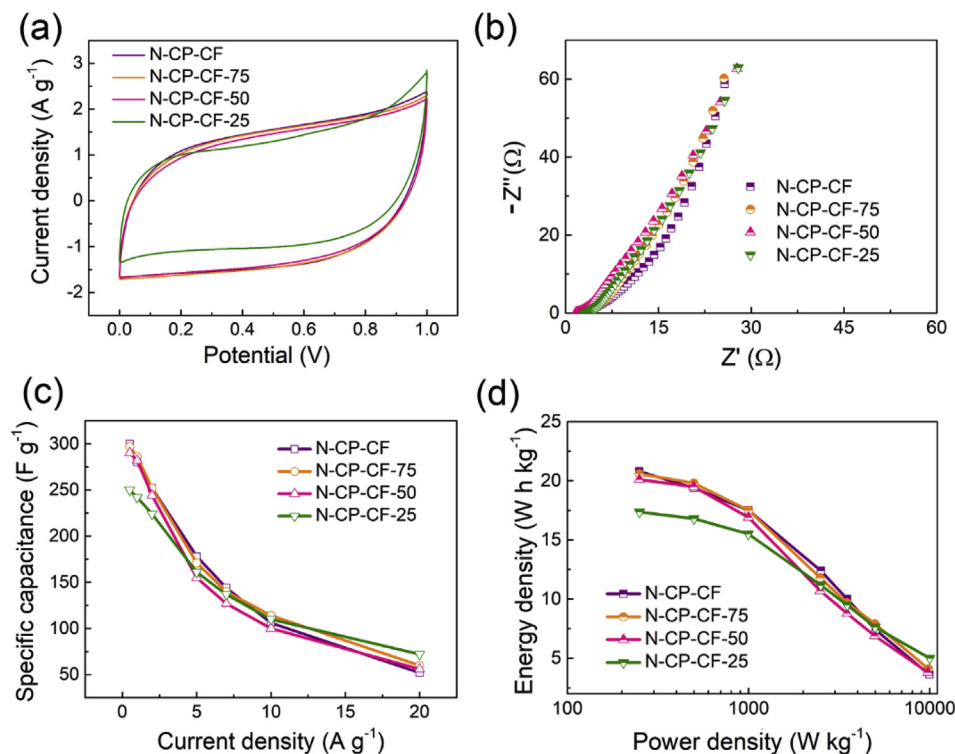


Fig. 4. (a) CV curves of electrode under different compression rates at a scan rate of 10 mV s^{-1} ; (b) EIS curves of the electrode under different compression rates; (c) Specific capacitances of electrode under different compression rates as function of current density; (e) Rogan plots of N-CP-CF under different compression rates.

capacitance under deformation calculated from the galvanostatic charge/discharge curves at different current densities. At various compression rates, the N-CP-CF electrode exhibits a slight decline of specific capacitance, i.e., the capacitances of N-CP-CF, N-CP-CF-75, N-CP-CF-50, and N-CP-CF-25 are 300, 297, 290, and 250 F g^{-1} , respectively, at a current density of 0.5 A g^{-1} . Also, the N-CP-CF composite at different compression rates shows no apparent variety in rate performance. At a high compression rate of 25%, the N-CP-CF-25 maintains a specific capacitance of 72 F g^{-1} at a current density of 20 A g^{-1} . As a flexible electrode, the N-CP-CF-25 with a large deformation also exhibits a high energy density of $17.36 \text{ W h kg}^{-1}$ at a power density of 250 W kg^{-1} . The energy density of N-CP-CF-25 remains 5 W h kg^{-1} at a high power density of 10000 W kg^{-1} (see Fig. 4d), indicating the outstanding stability of electrochemical properties of N-CP-CF composite under deformation. The superior flexible property of the current electrode can be ascribed to the following factors. First, flexible CF provides a firm support, and the adhesion between N-CP layer and CF leads to a good stability. Second, the hierarchically porous structure offers a large vacancy volume to accommodate the geometrical deformation. The as-obtained device can storage/deliver energy under severe compression, which is promising in flexible and wearable electronics related area.

4. Conclusion

A uniform ZIF-8 layer was integrated on the surface of CF with a high mass loading via efficient induction of ZnO nanomembrane by ALD. In the subsequent pyrolysis process, the N-CP-CF composite was fabricated with a hierarchically porous structure, which provided a large specific surface area of $538 \text{ m}^2 \text{ g}^{-1}$. The N-CP-CF composite electrode exhibited outstanding electrochemical performance and good flexibility due to the firm and flexible support of CF. At 0.5 A g^{-1} , the composite electrode had a large specific capacitance of 300 F g^{-1} , and a slight deterioration to 250 F g^{-1} was

noted at a large compression rate of 25%. This work could propose an efficient synthesis approach for the fabrication of flexible supercapacitor device, which could be promising in new generation energy storage devices.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jmat.2020.01.011>.

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