

Research Article

Free-Standing Porous Carbon Nanofiber Networks from Electrospinning Polyimide for Supercapacitors

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Free-standing porous carbon nanofiber networks (CFNs) were synthesized by electrospinning method and carbonization procedure. We study the implementation of porous CFNs as supercapacitor electrodes and electrochemical measurements demonstrated that porous CFNs exhibit a specific capacitance (205 F/g at the scan rate of 5 mV/s) with high flexibility and good rate capability performance (more than 70% of its initial capacitance from 5 mV/s to 200 mV/s). Furthermore, porous CFNs exhibited an excellent cycling stability (just 12% capacitance loss after 10,000 cycles). These results suggest that porous CFNs are very promising candidates as flexible supercapacitor electrodes.

1. Introduction

With the continuous development of portable/wearable electronics such as wearable displays and hand-held electronic devices, the demand of sustainable and flexible energy storage devices has been increasing for last decade [1–5]. A variety of renewable green energy with intermittent characteristics, such as solar and wind power, requires corresponding energy storage systems [6, 7]. For the advantages of high power density, fast charge/discharge rates, long cycle life, and so on, supercapacitors (SCs) which have been researched for decades have demonstrated their promising potential applications including but not limited to personal multimedia, hybrid vehicles, and backup power [8–11].

Basically, SCs are classified into two categories according to the different charge storage mechanisms: electrochemical double-layer capacitors (EDLCs) which attract charges on the electrode-electrolyte interface of electrode materials electrostatically and the other is pseudocapacitors which store energy via fast redox reaction on/near electrode surface [12]. Compared with pseudocapacitors, EDLCs possess better rate capability and longer durability and are the most common SCs in practice [13–15]. As far as we know, the electrode material is one of the most important factors to

the EDLCs performance, which should provide advantages of high specific surface area, good electronic conductivity, outstanding physical and chemical stability, being environmentally friendly, low preparation cost, and so forth. Because carbon materials such as carbon onion, carbon nanotubes (CNTs), graphene [16], and carbon nanofibers (CFs) have the advantages mentioned above, they are the most important electrode materials for EDLCs and have been investigated widely for decades. However, most of the carbon-based EDLCs hardly acquire a specific capacitance more than 150 F/g so far [13, 17, 18]. Therefore, it is necessary to further study the carbon-based SCs for improving their performance.

At present, the main preparation method of carbon materials based SC electrodes is combining the active carbon materials with carbon black and insulated polymer binders, such as polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF). The additive insulated polymer binders will introduce contact resistance and extra preparation cost needlessly, which limit the EDLC's performance and thus applications in flexible and portable electronics [19]. Although the previously reported self-assembled CNTs films, graphene films prepared by vacuum filtration process, and onion carbon with high graphitization [20–22] were excellent candidates for high-performance flexible SC electrodes, the

high cost for CNTs, the elaborate procedure for graphene film, and onion carbon would hinder SCs further large-scale application in practice.

Electrospinning has been proved to be a simple, effective, and scalable technique to fabricate ultrathin and continuous nano- to micrometers fibers, especially for polymers or melts [23–25]. Moreover, it has been confirmed that carbon nanofiber networks (CFNs) can be prepared successfully using electrospinning followed by carbonization in an inert atmosphere [26, 27]. The as-fabricated free-standing CFNs fabrics show outstanding electrical interconnectivity, large surface area, and mechanical strength, making them potential candidates for high-performance flexible SC electrodes [28, 29]. Furthermore, the porous structure can not only increase the specific surface area, but also provide more transport channels for electrolyte ions. For this purpose, a few literatures have reported CFNs prepared by electrospinning polymer nanofibers such as polyacrylonitrile (PAN) as carbon precursor and polylactic acid (PLA) owing to their soluble feature. PAN nanofiber electrode based EDLCs were reported to have a specific capacitance of 175 F/g. However, polyimide-(PI-) derived CFs had a surprising higher yield of carbon and superior mechanical strength than those derived from PAN, which will be beneficial for the cycling stability and rate capability.

Herein, the free-standing flexible, collapsible, carbon nanofiber networks were successfully fabricated by carbonization of electrospinning PI and SiO₂ hybrid composite nanofibers. The porous structures could be obtained by carbonization process and removing the SiO₂ additive. The porous carbon nanofiber networks (CFNs) as SC electrode material exhibit an enhanced electrochemical energy storage property compared with those solid fibers. A rate capability of more than 70% with the scan rate from 5 mV/s to 200 mV/s is obtained by porous CFNs electrodes.

2. Experimental

2.1. Materials and Chemicals. Polymer solution of polyamic acid (PAA) was purchased from Changzhou Sunchem High Performance Polymer Co. Ltd. The N,N-dimethylacetamide (DMAc) was purchased from Aladdin Chemical Reagent Co. Ltd., and tetraethoxysilane (TEOS, SiO₂ content P28%) was purchased from Alfa Aesar. All chemicals in the present work were used as received without any further purification.

2.2. Synthesis of Porous Carbon Nanofiber Networks. The electrospinning precursor was prepared as the following procedure: firstly, 20 mL PAA solution was added to 50 mL DMAc and magnetically stirred for 5 h to dissolve completely. Then PAA/DMAc solution was obtained. Secondly, TEOS (5 mL) and HCl (0.05 mL, 1.18 g/mL) were added to the as-received PAA/DMAc solution under continuous stirring for 20 h. Finally the electrospinning precursor of homogeneous PAA/SiO₂ mixture was obtained (as shown in Figure 1).

The electrospinning technique was employed to prepare PAA/SiO₂ hybrid nanofiber networks (PAA/SiO₂ HFNs). The electrospinning precursor was ejected into a stainless steel



FIGURE 1: The photograph of free-standing carbon nanofiber networks.

capillary (25 kV, 2 mL/h). The electrospinning parameters such as distance between the capillary and collector, the temperature, and relative humidity were 18 cm, 30°C, and 40~50%, respectively. The PAA/SiO₂ HFNs were collected on a rotating aluminum drum. The PAA/SiO₂ HFNs were treated by an imidization process. Then they were carbonized at 750°C for 1 h in Ar atmosphere to obtain CFNs/SiO₂. After removing the SiO₂ nanoparticles by HF acid for 20 h [30], CFNs with porous nanostructures can be obtained.

2.3. Fabrication of Flexible SCs Electrodes. The 1 M sulfuric acid (H₂SO₄) electrolyte was prepared as follows: 9.8 g H₂SO₄ was dropped into 100 mL deionized (DI) water slowly and magnetically stirring to obtain a uniform solution. A three-electrode cell was introduced for investigating the performance of the porous CFNs based SCs electrode. The porous CFNs, a Pt sheet, and a saturated Ag/AgCl electrode were used as working electrode, counter electrode, and reference electrode, respectively.

2.4. Characterization. Field-emission scanning electron microscopy (FE-SEM, FEI Nova 450 Nano) and transmission electron microscopy (TEM, FEI Tecnai G20) were employed to analyze the morphology and the porous structure of PAA/SiO₂ HFNs and CFNs. The degree of graphitization of the as-prepared CFNs was characterized by high-resolution transmission electron microscopy (HRTEM, FEI Titan probe corrected microscopy) and selected-area electron diffraction (SAED). Raman spectrum was recorded on a Renishaw-inVia Raman spectrometer with an excitation of 514.5 nm line of an Ar⁺ laser.

The electrochemical measurements of this work were carried out on the electrochemical workstation (EC-lab VMP-300). For a typical three-electrode measurement, a piece of CFNs, Ag/AgCl (CHI, USA), YP-50 (Kuraray Chemical, USA), and Celgard (Celgard, USA) were used as work electrode, reference electrode, counter electrode, and separator, respectively. All of the electrochemical tests were performed in Swagelok cells (Swagelok, USA). Electrochemical

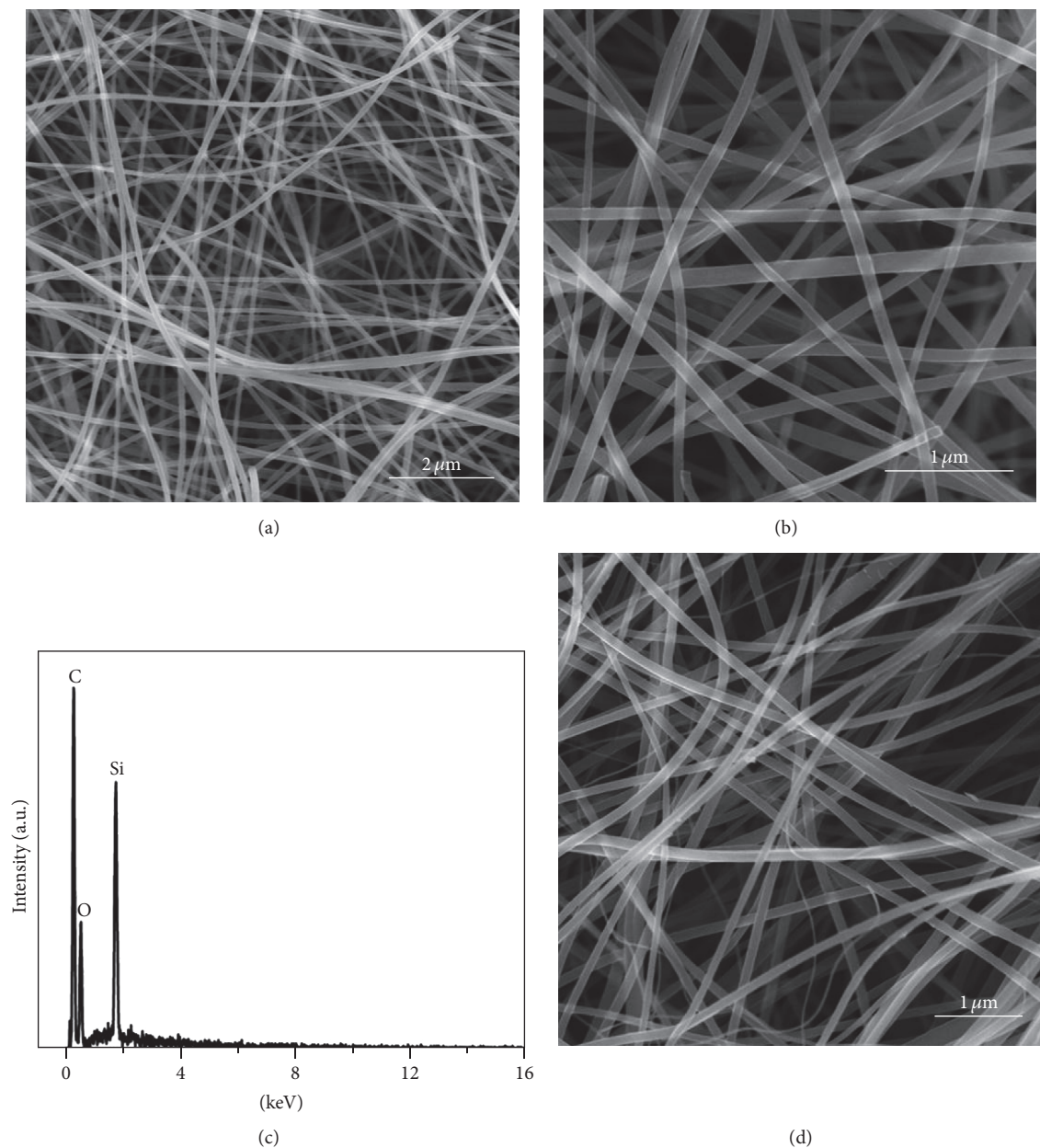


FIGURE 2: The SEM images of (a) PAA-SiO₂ fibers, (b) CFN-SiO₂ fibers, and (d) porous CFNs and (c) the energy spectra of CFN-SiO₂ fibers.

impedance spectroscopy (EIS) measurement was taken from 1 MHz to 10 mHz, and the potential amplitude was set as 10 mV.

3. Results and Discussion

Figure 2 displays the morphologies of the as-electrospun free-standing PAA/SiO₂ HFNs, carbon/SiO₂ fibers, and porous CFNs. It can be observed that all of fibers of the three samples are randomly oriented forming an interconnected and porous network. In addition, their diameters all vary from tens to hundreds of nanometers and lengths are several hundreds of microns, as shown in Figures 2(a), 2(b), and 2(d). After

imidization and carbonization procedures, the carbon/SiO₂ fibers were obtained with a nonwoven structure; the corresponding energy spectra demonstrated the existence of Si and O, as shown in Figure 2(c). Porous structure could be achieved by removing SiO₂ using HF etching treatment, and the average diameter of porous CFNs is slightly smaller than that of PAA/SiO₂ HFNs, for the reason of weight loss of SiO₂ and densification caused by high temperature treatment.

TEM was introduced to further analyze the detailed microstructure of the as-prepared porous CFNs. Figures 3(a) and 3(b) display the low-magnification TEM image, clearly demonstrating that the average diameter of the porous fibers is ~100 nm and the surface is slightly rough. The disperse rings in the corresponding SAED pattern (Figure 3(c)) and

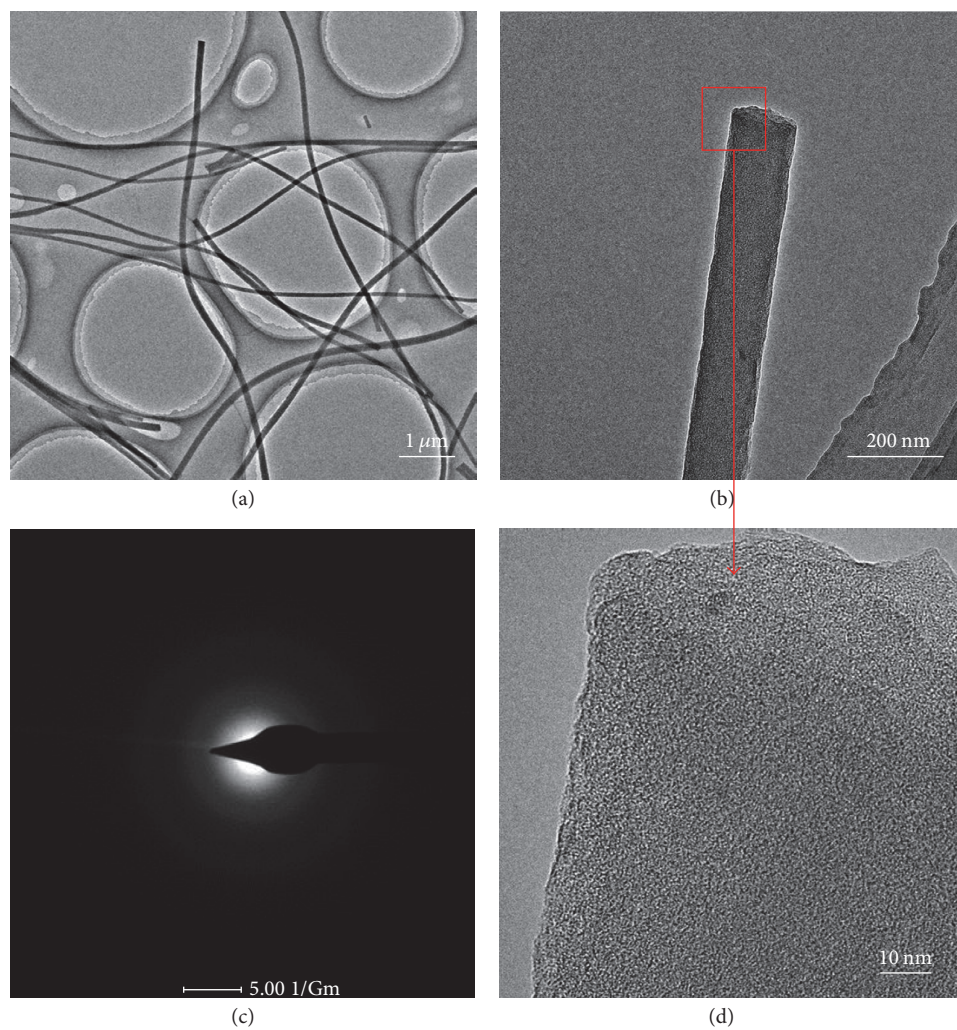


FIGURE 3: (a, b) TEM image and (d) HRTEM image of porous CFNs and (c) the corresponding SAED of (b).

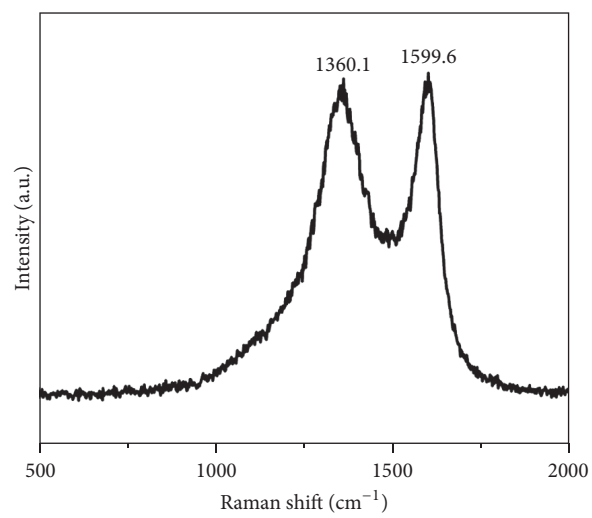


FIGURE 4: The Raman spectrum of porous CFNs.

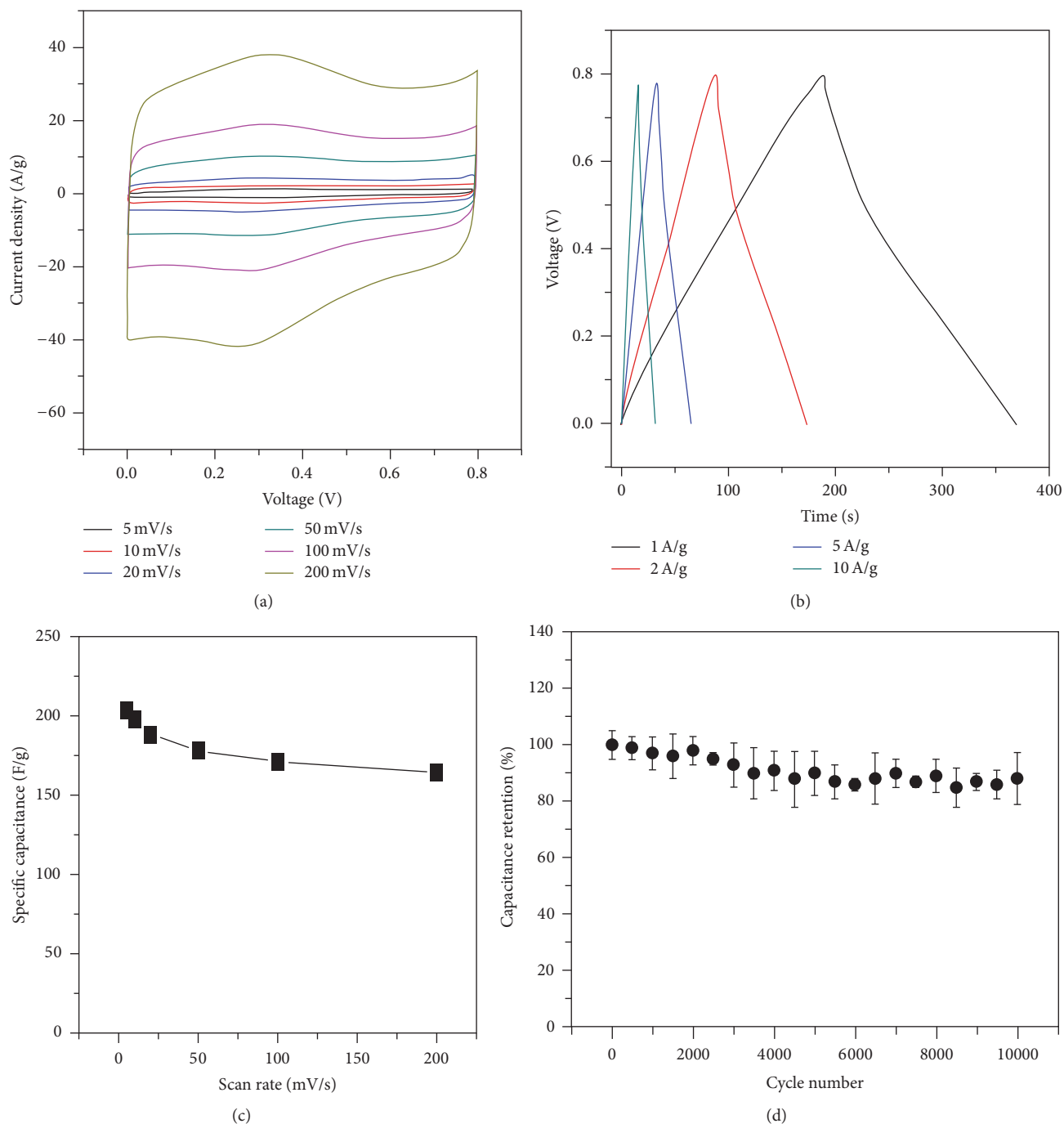


FIGURE 5: (a) Cyclic voltammogram curves, (b) galvanostatic charge-discharge curves, (c) specific capacitance, and (d) capacity retention of porous CFNs, respectively.

the HRTEM image (Figure 3(d)) both indicate that the CFNs are characteristic of amorphous structures. A lot of micropores which derived from the removal of SiO₂ nanoparticles were also observed via HRTEM image, as shown in Figure 3(d).

Raman spectrum of the porous CFNs was introduced in order to further analyze their degree of graphitization. In Figure 4, two sharp peaks at 1599.6 cm⁻¹ and 1360.1 cm⁻¹

can be observed, which are known as the G peak and the D peak, respectively. According to the previous research results, the G band can be assigned to the response of the in-plane stretching motion of symmetric sp² C-C bonds, whereas the D band results from the disruption of the symmetrical hexagonal graphitic lattice [27, 31]. The intensity ratio of the D peak and G peak (I_D/I_G), which is considered as a measure of the graphitization degree of porous CFNs [31], was

calculated as 0.9849. This I_p/I_G value suggests that the porous CFNs exhibit typical amorphous characteristic structures, in agreement with the SAED and HRTEM measurements well.

Cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) measurements were carried out in a three-electrode electrochemical cell to investigate the electrochemical properties of porous CFNs electrode. A piece of Pt foil, a saturated Ag/AgCl electrode, and 1 M H_2SO_4 aqueous solution were used as counter electrode, reference electrode, and electrolyte, respectively. As shown in Figure 5(a), all of the CV curves using different sweep rates from 5 to 200 mV/s in a potential window of 0 to 0.8 V exhibit the quasirectangular approximately symmetrical shape about the zero-current line and almost significantly change along with the increasing sweep rates, demonstrating a good reversible capacitive behavior [32, 33]. The sharp changes at 0 V and 0.8 V suggest the good electrical conductivity, while the notable and reversible hump, which located at 0.3 V, can be ascribed to the pseudocapacitive contribution of oxygen groups [32, 34].

The GCD test was carried out to further evaluate the capacitive performance of porous CFNs. Figure 5(b) shows the GCD curves of porous CFNs at different current densities from 1 A/g to 10 A/g. All of the charge curves and corresponding discharge curves exhibit relatively symmetric characteristic, suggesting the good reversibility and high coulombic efficiency. What is more, the IR drop related to the equivalent series resistance is slight, implying a good electrical conductivity, consistent with the measurement of CV curves. The specific capacitance of porous CFNs can be calculated by using the following equation [34]:

$$C = \frac{(\int j dV) / s}{V}, \quad (1)$$

where j is the current density (A/g), s is sweep rate, V is the voltage window, and C is specific capacitance (F/g). According to the above equation, the specific capacitances of porous CFNs at different scan rates were depicted in Figure 5(c). The specific capacitance retention is more than 70% while the scan rate increases from 5 mV/s to 200 mV/s, indicating good rate capability. The cycling stability performance of porous CFNs was performed at a sweep rate of 100 mV/s for 10,000 cycles, as shown in Figure 5(d). The capacitance retention was still over 91% even after 10,000 cycles, demonstrating the excellent stable performance.

EIS measurement was conducted to further investigate the as-electrospun free-standing porous CFNs electrode. Figure 6 shows the Nyquist plot of porous CFNs measured from 1 MHz to 10 mHz with a potential amplitude of 10 mV. There is only a semicircle located at the high-frequency region. The semicircle resistance (R_{semi}), which means the charge transfer resistance (R_{ct}) and contact resistance, is close to zero, as displayed in Figure 6 (inset). The low series resistance implies that porous CFNs electrode possesses good electrical conductivity. Meanwhile the sloping line is almost parallel to the y -axis in the low-frequency region indicating the good capacitance behavior. According to the analysis, it can be concluded that porous CFNs have a good capacitive

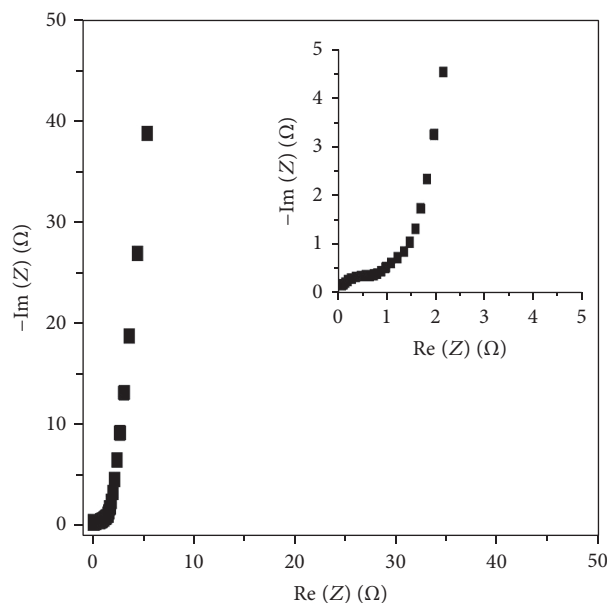


FIGURE 6: The Nyquist plot of porous CFNs. The inset is the enlarged view of the high-frequency region.

behavior, which is in consistency with the electrochemical measurement discussed above.

4. Conclusions

In summary, porous CFNs were successfully fabricated through a facile electrospinning method and carbonization procedure. The formation of porous nanostructure is beneficial for electrolyte ions transfer in the network, leading to a good rate capability. When the scan rate increases from 5 mV/s to 200 mV/s, the capacitance retention is more than 70% of its initial capacitance. What is more, for their good rate capability and high performance, porous CFNs are able to serve as scaffold to support other active electrode materials. The above results suggest that porous CFNs may be a promising candidate as flexible supercapacitor electrode.

Competing Interests

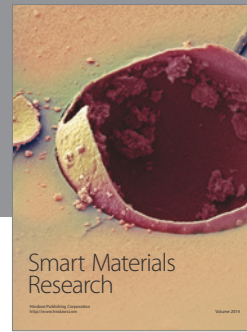
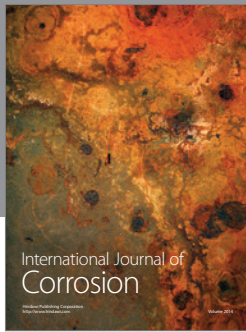
The authors declare that they have no competing interests.

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