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Electrochemical capacitive properties of CNT fibers spun from vertically aligned CNT arrays

Gengzhi Sun · Jinyuan Zhou · Feng Yu · Yani Zhang · John Hock Lye Pang · Lianxi Zheng

Abstract Due to their lightweight, large surface area; excellent electrical conductivity; and mechanical strength, carbon nanotube (CNT) fibers show great potentials in serving as both electrode materials and current collectors in supercapacitors. In this paper, the capacitive properties of both as-spun CNT fibers and electrochemically activated CNT fibers have been investigated using cyclic voltammetry and electrochemical impedance spectroscopy. It is found that the as-spun CNT fibers exhibit a very low specific capacitance of $2.6 \ F g^{-1}$, but electrochemically activated CNT fibers show considerably improved specific capacitance. The electrochemical activation has been realized by cyclic scanning in a wide potential window. Different electrolytes have also been examined to validate the applicability of our carbon materials and the activation mechanism. It is believed that such an activation process can significantly improve the surface wetting of the CNT fibers by electrolyte (aqueous Na_2SO_4 solution). The cycling stability and rate-dependence of the capacitance have been studied, and the results suggest practical applications of CNT fibers in electrochemical supercapacitors.

Keywords Supercapacitor · Carbon · Nanotube · CNT fiber · Electrochemical activation

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Introduction

Carbon nanotubes (CNTs) are light-weight and chemically inertial, have large surface area, and possess excellent electrical and mechanical properties, making them promising electrode materials for supercapacitors [1–3]. Several methods have been proposed to prepare CNT-based electrodes [4–8], and in most cases, CNTs were prepared in the form of >films or pastes and then coated on conductive substrates. In these cases, a conductive substrate like nickel foam or foil is always necessary to function as current collectors and support the electroactive materials [5–7]. Significant progress has been made, but the improvement is limited by the compromise of CNTs' electrical properties, because the preparation processes of CNT films usually involves the chemical treatments for CNT dispersion and the use of binders in electrode structure. In order to realize the full utilization of CNTs' excellences, the electrode material is better as a macro-assembly that could retain the most of CNT's intrinsic properties.

CNT fiber, as a macro-CNT assembly, has recently demonstrated its superior capability on retaining CNT's mechanical and electrical properties. Super strong, tough, and stiff CNT fibers with low mass density and good electrical conductivity have been successfully fabricated [9–18]. Electrochemical properties of CNT fibers have also been studied, and the electrochemical actuation has been achieved [19, 20]. In addition, CNT fibers are very flexible and thus could allow us to fabricate them into any shape, such as unidirectional films, woven mats, or muscle-like bundles, to meet the specific application requirements. These features encourage scientists to explore their applications in energy

storage devices such as supercapacitors. Previous studies on capacitive performance of CNT fibers mainly focused on composite fibers or fibers spun from CNT dispersions [9, 19, 21]. Only a few papers reported the capacitive properties of pure CNT fibers or fiber-equivalent "CNT solid" [4, 20], which are directly originated from vertically aligned CNT arrays without any chemical treatments and have high potentials to preserve CNT's capacitive properties without compromising CNT's electrical and mechanical properties.

In this paper, the capacitive properties of CNT fibers, which were spun from vertically aligned CNT arrays, were extensively studied, and an electrochemical activation method was introduced to improve the capacitance. The CNT fibers function as both current collector and electrochemical active materials in these studies. It is found that the capacitance of as-spun fibers is small. However, after cycles of electrochemical activation in a wide potential window, the capacitance of activated CNT fibers has been increased significantly. The possible mechanism has also been discussed.

Experimental

Materials and methods

Vertically aligned CNT arrays were synthesized by chemical vapor deposition [16, 22, 23]. CNT fibers were spun from CNT arrays with a micro-spindle mounted on a motor. Ethanol was used during spinning for fiber densification. Figure 1a shows a schematic of fiber spinning process. The mass of CNT fibers was measured by using a microbalance with a very high resolution of 0.001 mg. As the fiber could be spun from CNT array continuously, a totally 6-m-long CNT fiber with an average diameter of 3.3 μm was weighed for 10 μg. Then the density of CNT fibers was calculated for around 0.2 g cm^{-3}, which is similar to our previous result [15]. The specific capacitance of CNT fibers measured could then be normalized by gram according to this density combined with fiber length and diameters.

Material characterization

The morphologies of as-spun CNT fibers were acquired by field emission scanning electron microscopy (FESEM).
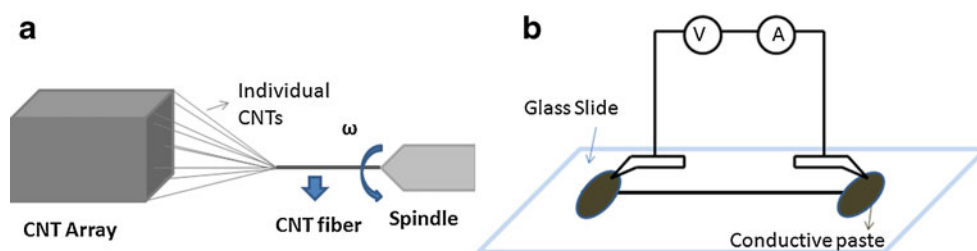
High-resolution transmission electron microscopic (HRTEM) imaging was performed on a JEOL 2010 TEM for CNT's structure study. The electrical measurements of CNT fibers were performed on a probe station to evaluate their resistivity (as shown in Fig. 1b) using a two-probe technique. The alignment of CNTs within fibers was characterized by Raman scattering with a 633-nm He–Ne laser source. The electrochemical activation was conducted in a three-electrode system (Pt wire as counter electrode and Ag/AgCl-saturated KCl solution as reference electrode, respectively) using cyclic voltammetry (CV) in the potential window between 0 and 1.5 V in 1 M Na_2SO_4 aqueous solution for 100 cycles. The CV technique was also used to characterize the capacitive behavior of CNT fibers in 1 M Na_2SO_4 aqueous solution. Electrochemical impedance spectroscopy (EIS) was conducted by applying an AC voltage with 5 mV amplitude in a frequency range from 0.1 to 100 kHz. The DC potential was always set up at 0 V. All the electrochemical characterizations were carried out with a CHI 760 C Electrochemical Work Station (CH Instruments, USA) at room temperature, and the potential reported below are all referred to Ag/AgCl (saturated KCl).

Results and discussion

SEM and TEM were used to characterize the morphology and structure of CNT fibers. As shown in Fig. 2a of a FESEM image and a magnified image in the red area, it is found that there are plenty of wrinkles on the surface of the CNT fiber, and CNTs in the fiber are well orientated in the same direction. The morphology of CNT fiber is similar to a cylinder with circular periphery. The top-right inset of Fig. 2a shows a HRTEM image, indicating that the diameter of individual CNTs is about 12 nm. The CNT fiber was fixed by Ag conductive epoxy which could offer high electrical conductivity and strong conductive bonding. Figure 2b shows a typical I-V curve measured from the CNT fiber. The linear relationship between current and voltage indicates the metallic feature of multi-walled CNTs and good electrical contacts between CNT fibers and conductive epoxy. The resistivity has been measured along one CNT fiber at different segments to check the uniformity of the CNT fiber, and the results are shown in Fig. 2c. The
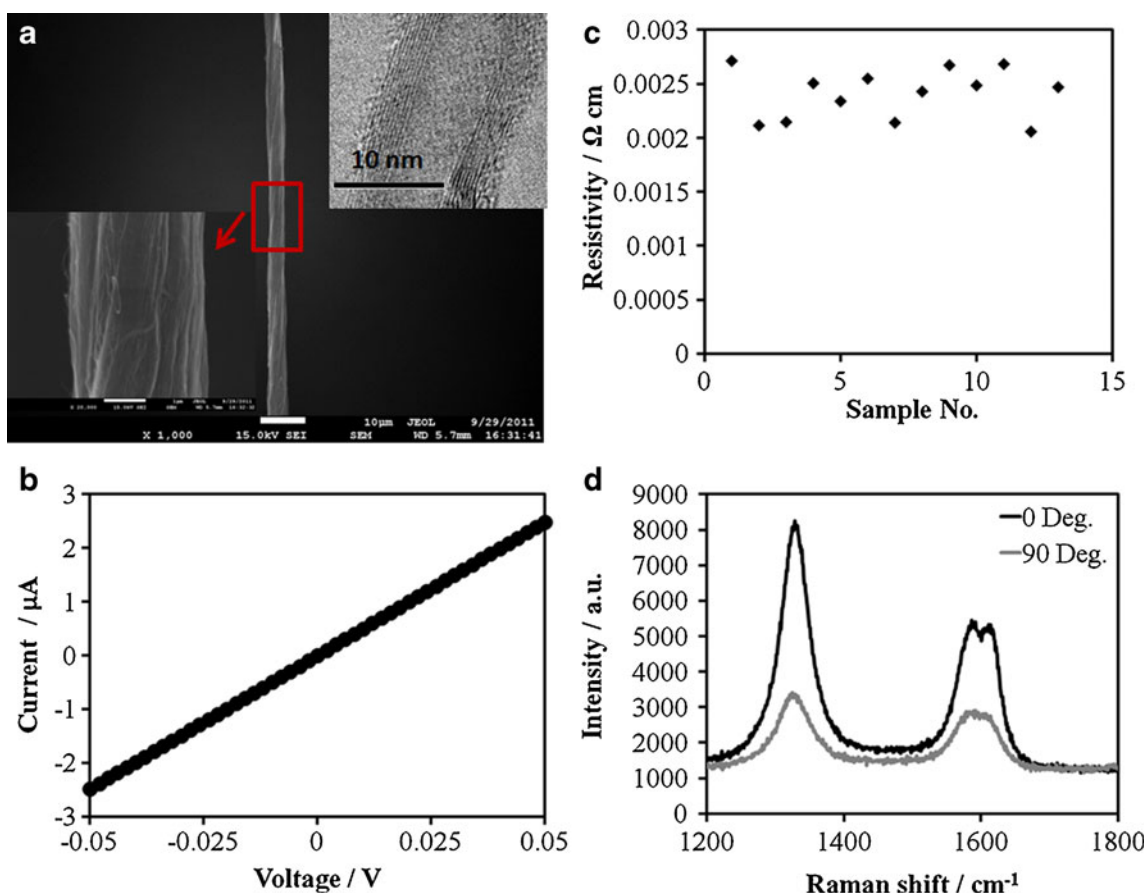
Fig. 1 a Schematic of CNT fiber spinning process and b schematic of electrical measurement of CNT fibers

Fig. 2 **a** SEM image of as-spun CNT fiber (the *insets* are an HRTEM image of individual CNT and a magnified SEM image in the *red* area); **b** a typical *I-V* curve of CNT fibers; **c** resistivity measurements of different segments from the same CNT fiber, and **d** Polarized Raman spectra of a CNT fiber with laser polarization *parallel* (0°) and *perpendicular* (90°) to the fiber axis

resistivity is in the range of 0.002~0.003 Ω cm with an average resistivity of ~0.0025 Ω cm (corresponding to a conductivity of ~400 S cm^{-1}). These results are very similar to our previous values on untreated CNT fibers [18]. The alignment of CNTs in the fiber was investigated by polarized Raman spectroscopy with a laser polarized parallel and perpendicular to the fiber axis. The results are shown in Fig. 2d. Evidently, the intensities of G-band and D-band for polarization parallel (0°) to fiber axis are much stronger than those for polarization perpendicular (90°) to fiber axis, suggesting the fiber has good alignment [16]. These structure and material features suggest the potentials of our CNT fibers in application of supercapactiors: The wrinkles formed on the surface of CNT fibers supply a larger accessible area which is beneficial for high capacitance, and the good conductivity allows the CNT fibers being used as both the electrode material and the current collector. The good electrical property is a reasonable consequence of good alignment of CNTs in the fiber evidenced by FESEM and Raman results.

The electrochemical measurement was conducted in a three-electrode system as shown in Fig. 3a. For easy handling, the CNT fiber was mounted on a glass slide using conductive epoxy as working electrode without any conductive substrate. It is found that, comparing to the as-spun fiber, the activated fiber exhibits larger capacitive current (Fig. 3b), where the capacitance of as-spun fiber was only 2.6 F g^{-1}. In order to find out the underlying enhancing mechanism of fiber's capacitance, the morphology of activated fiber was firstly characterized by FESEM (Fig. 4a). The magnified SEM image in red area shows significant difference in morphology compared with as-spun fiber shown in Fig. 2a. The bottom-left inset of Fig. 4a shows the activation process of the CNT fiber. No obvious redox peak was observed in the curves. The EDS measurements on as-spun and activated fibers were performed. All the elements inside the fiber almost maintain the same (as-spun fiber—C 71.81%, O 23.61%, Al 0.44%, and Si 4.14%; activated fiber—C 71.25%, O 23.56%, Al 0.43%, and Si 4.76%. Al Si signals are from substrate), giving further evidence that no functionality was generated on the surface of the CNT fiber. To further investigate the underlying mechanism, EIS was also performed, and the Nyquist plots were shown in Fig. 4b. It is found that the impedance of the activated fiber is much smaller than that of the as-spun fiber.

Fig. 3 **a** Schematic of the set-up for electrochemical test and **b** CV results of as-spun and activated CNT fibers
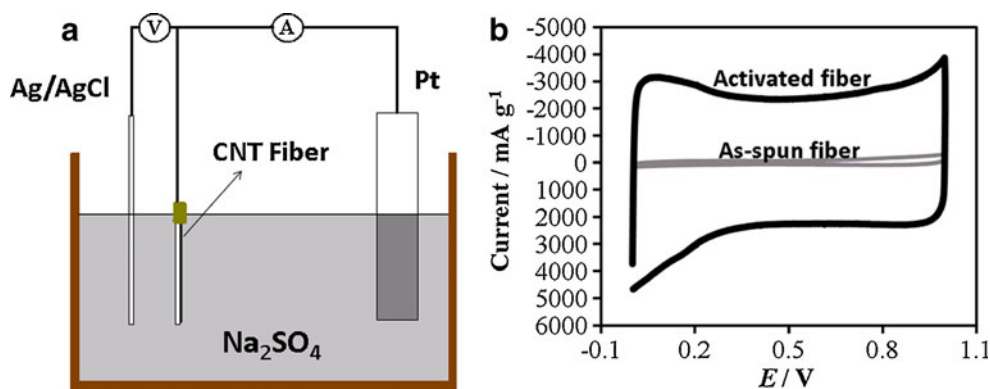
Similar improvement by electrochemical activation was observed in carbon fibers and was explained by the increase of surface area due to the surface roughing [24]. Since we have not found obvious change in the composition of CNT fiber (structures), and the near-rectangular shape of CV curves (Fig. 3b) without any obvious redox peak [25], together with the hydrophobic nature of our CNT material [26], we believe that the enhanced specific capacitance after activation in our case could be attributed to the improved-wetting effect of CNTs by electrolyte (Na_2SO_4 aqueous solution) during potential scanning in a large window, leading to a larger accessible area. This is supported by EIS results in Fig. 4b: The impedance is composed of resistance and capacitance, so the impedance decrease is a result of increase in capacitance.

Since local pH change induced by non-buffered Na_2SO_4 may be one of the possible reasons of the voltammogram distortion, H_2SO_4 (1 M) was selected as a comparison electrolyte. As shown in Fig. 5a, the specific capacitances of several activated and inactivated CNT fibers were tested and compared as a function of cycle numbers: (1)

inactivated CNT fiber tested in Na_2SO_4, (2) inactivated CNT fiber tested in H_2SO_4, (3) Na_2SO_4-activated CNT fiber tested in Na_2SO_4, (4) Na_2SO_4-activated CNT fiber tested in H_2SO_4, and (5) H_2SO_4-activated CNT fiber tested in H_2SO_4. In the cases of inactivated (as-spun) fibers, the capacitances are quite low either in Na_2SO_4 or in H_2SO_4. After the activation in Na_2SO_4, the capacitance of CNT fiber tested in H_2SO_4 is larger than that tested in Na_2SO_4. Moreover, the capacitance of CNT fiber 5 is the largest among all the situations, and there are obvious redox peaks in the CV results (as shown in Fig. 5b). From the comparison, it could be concluded that: (1) additional rapidly rechargeable functionalities start to contribute when CNT fiber is cycled in H_2SO_4 in potential range between 0 and 1 V; (2) the specific capacitances of all activated CNT fibers show slight decrease according to the cycling number, indicating good durability; (3) the enhancement of fiber's capacitance can result from better wetting of CNTs and also from pseudocapacitance increase.

CV measurements have also been performed in Na_2SO_4 under different scan rates ranging from 10 to 750 mV s^{-1} to
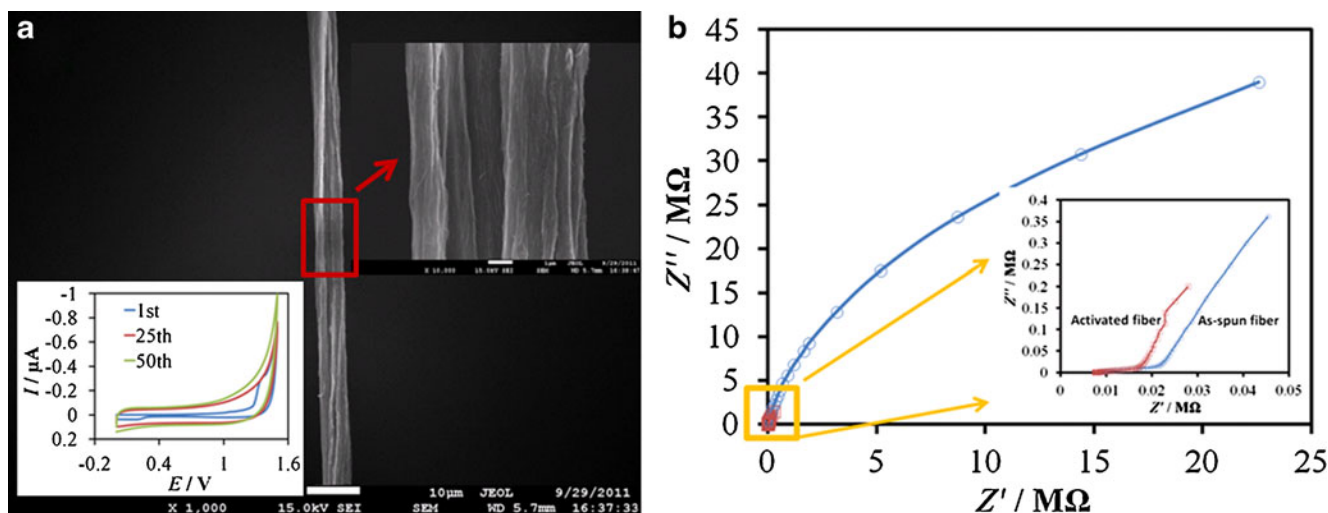

Fig. 4 **a** SEM image of a CNT fiber after activation (the *insets* show the activation process and a magnified SEM image in the *red* area) and **b** Nyquist plots of as-spun and activated CNT fibers (the *inset* shows the magnified plots in the *red* area)
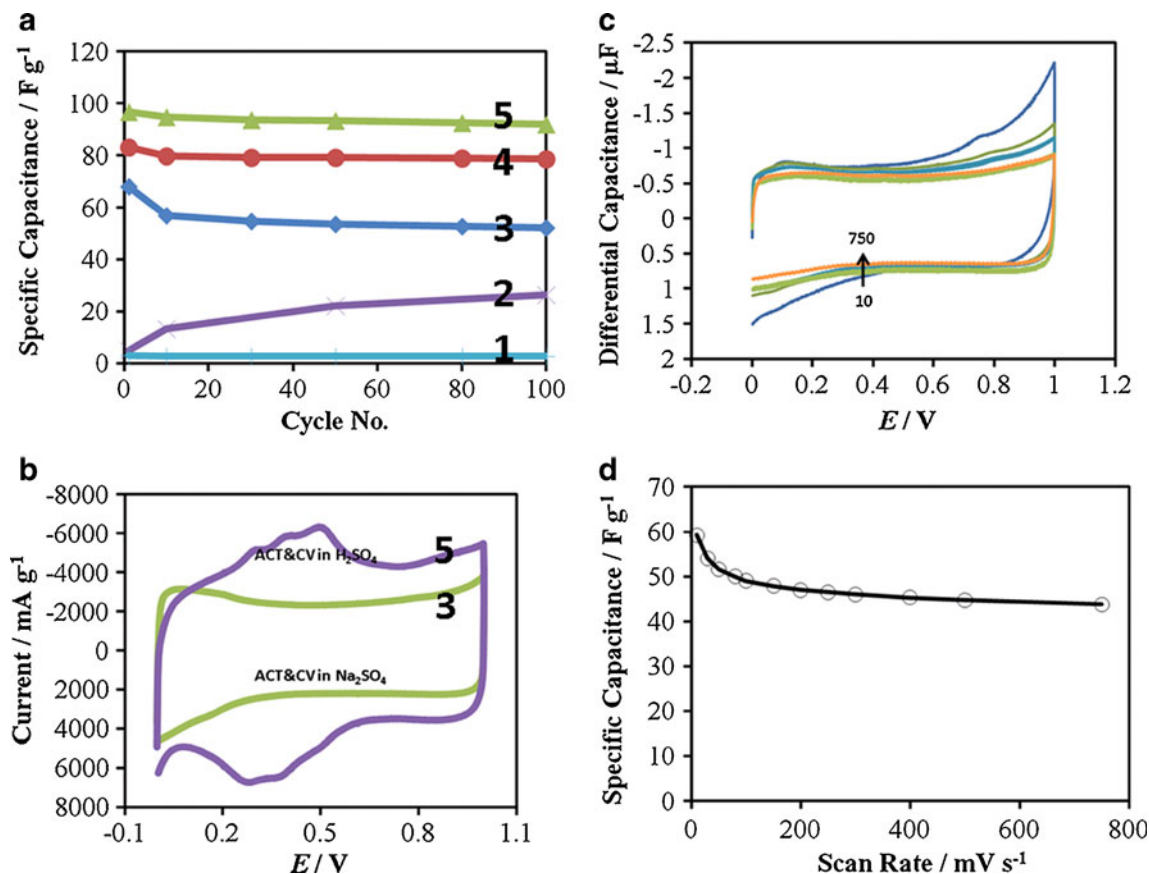
Fig. 5 **a** Dependence of specific capacitance of CNT fibers activated in different electrolyte on cycle numbers (*1*: as-spun CNT fiber tested in Na_2SO_4, *2*: as-spun CNT fiber tested in H_2SO_4, *3*: CNT fiber activated and tested in Na_2SO_4, *4*: CNT fiber activated in Na_2SO_4 and then tested in H_2SO_4, *5*: CNT fiber activated and tested in H_2SO_4. Scan rate, 50 mV s^{-1}); **b** typical CV behaviors of CNT fibers in Na_2SO_4 and in H_2SO_4; **c** CV results of the activated CNT fiber in Na_2SO_4 at different scan rate, and **d** specific capacitance of in Na_2SO_4-activated CNT fibers as a function of scan rate (10 to 750 mV s^{-1}), respectively

examine the high rate performance of the activated CNT fibers. As shown in Fig. 5c, the rectangular shapes of the CV curves are almost maintained even at high potential scan rates. Because the rate-dependent CV curve demonstrates the typical charging–discharging performance, the specific capacitance of the activated CNT fiber is compared as a function of the scan rate (the results are shown in Fig. 5d). As expected, the capacitance decreases with increasing the scan rate and saturates when the scan rate is higher than 100 mV s^{-1}. All the above evidences show that CNT fibers are applicable in different electrolyte and exhibit good capacitive performance after activation.

Comparing to other carbon materials working in Na_2SO_4 [27–31], the capacitance of our fibers is slightly lower, which could be attributed to not having a current collector (metal substrate) employed. However, there are some merits which could compensate this disadvantage: First, fiber's performance could be further optimized by adding other functionalities; second, texture-like structures could be woven from CNT fibers, offering minimization of practical devices and high volumetric power density.

Conclusions

In conclusion, the capacitance properties of pure CNT fibers were investigated, and an electrochemical activation method was introduced. Different electrolytes have also been examined to validate the applicability of our carbon material and the activation mechanism. Based on the analysis of CV and EIS results, it is found that the capacitance of as-spun CNT fiber is low. However, after activation in a potential window between 0 and 1.5 V for 100 cycles, the electrolyte (Na_2SO_4 aqueous solution) could wet the surface of CNT fiber better, leading to a larger accessible area, and the capacitance of activated CNT fiber could be increased 20 times from 2.6 to 52 F g^{-1}. The capacitance increase in Na_2SO_4 is mainly from better wetting of CNTs, and further improvement has been realized by adding more functionalities to CNTs in H_2SO_4 electrolyte (~95 F g^{-1}). Because of the low resistivity and the large accessible area, the activated CNT fibers exhibit good electrochemical capacitance performance, fast charge–discharge property, and cycling durability, indicating that CNT fibers are a promising material for supercapacitor applications.

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