

Ultramicroporous carbon cloth for flexible energy storage with high areal capacitance



Haiyan Wang, Jiang Deng, Chunmei Xu, Yiqing Chen, Fan Xu, Jing Wang, Yong Wang*

Advanced Materials and Catalysis Group, ZJU-NHU United R & D Center, Center for Chemistry of High-Performance and Novel Materials, Department of Chemistry, Zhejiang University, Hangzhou 310028, PR China

ARTICLE INFO

Keywords:

Supercapacitors
Flexible electrodes
High areal capacitance
Ultramicroporous carbon cloth

ABSTRACT

Most advances towards flexible supercapacitors (SCs) have been focused on porous carbon materials. However, the poor flexibility and low areal capacitance impede their industrial application. While carbon cloth is generally regarded as improper electrode material due to its poor electrochemical performance, here, we demonstrate the capacitance of carbon cloth can be boosted to three orders of magnitude higher (2900 mF cm^{-2}) with a simple high-temperature annealing process. The improvement stems from ultramicropores effects in the range of $0.46\text{--}0.64 \text{ nm}$ besides superhydrophilicity and high specific surface area. Remarkably, direct implementation for flexible solid-state SCs (SSCs) provides areal capacitance and energy density for the stack of 920 mF cm^{-2} and $128 \mu\text{W h cm}^{-2}$, respectively. In addition, these devices are bendable, durable and easy to be any dimensions, hence, holding great promise for large-scale production of flexible electronics.

1. Introduction

Flexible electronics are toward being low cost, environmentally benign, portable, light-weight, roll-up and even wearable [1], thus offering many promising applications including flexible circuits, mobile devices, roll-up displays, smart garments and implantable devices [2–5]. Among the various energy storage technologies, SCs are promising candidates owing to high power density, quick charge-discharge capability, long cycle life and good safety [6–8]. Their energy densities (typically $4\text{--}5 \text{ W h kg}^{-1}$) are often determined by the electroactive surface area and pore size distribution of carbon materials [6,9,10]. As a result, porous carbon with large surface area, such as activated carbon [11,12], mesoporous carbon [13], nitrogen-doped carbon [14–16] and pseudocapacitive particles [17–20] were proven appealing, but the use of current collector or flexible substrate, conductive additive and the elaborate procedures for powder to be films significantly hampered their use for flexible devices. Hence, much advances on flexible SCs have been focused on the development of carbon nanotubes (CNTs) [13,21–23], graphene [24–31] films and hydrogels [32], polymer films [33,34] and their composites [35], because of the full utilization of the entire electrode. The main obstacle, however, was the complicated manufacture, the limited areal capacitance ($10^0\text{--}10^2 \text{ mF cm}^{-2}$) for pure CNTs and graphene electrodes, or the poor cyclic stability for polymer electrodes. Therefore, the pursuit of electrode materials integrating high areal capacitance with robust flexibility should not case.

Carbon cloth (CC), made up of numerous uniform carbon fibers, has always been neglected though it meets the basic demands for flexible SCs such as high flexibility, good electric conductivity and easy synthesis of any dimensions. The reason can be attributed to its intrinsically small specific surface area (SSA) ($\sim 5 \text{ m}^2 \text{ g}^{-1}$), leading to poor capacitive performance with specific capacitance of $1\text{--}2 \text{ F g}^{-1}$ [36]. Although activation of carbon fabric had been an old topic in the early days [37–40], CC was generally regarded as proper flexible substrate rather than electrode material for flexible SCs up to now. In this regard, various active materials such as graphene [41], Co_3O_4 [42], MnO_2 [43], $\beta\text{-FeOOH}$ [44], TiN [45], and NiCo_2O_4 [46] have been coated on CC for fabricating flexible SCs. But most of their capacitances were limited by a low loading of electroactive materials and a high ratio of inert CC, which went against the electrochemical (EC) performance for the whole stack [47,48]. Therefore, the improvement of the intrinsic properties of CC is challengeable but increasingly vital. Recently, chemical activated [49] and electrochemical activated [50,51] CC, as well as plasma functionalized CC [52] have successfully been used as flexible electrodes for SCs and shown enhanced electrochemical performance. Nevertheless, those limited SSA and areal capacitance of activated CC still need to be improved or the use of toxic, flammable reagents impedes their large-scale industrial application for safe flexible devices.

Here, we report a simple high-temperature annealing route in the absence of any additives to prepare treated carbon cloth (TCC) from commercial CC. TCC shows high SSA of $500\text{--}819 \text{ m}^2 \text{ g}^{-1}$. Specifically,

* Corresponding author.

E-mail address: chemwy@zju.edu.cn (Y. Wang).

after high-temperature treatment, the capacitance of CC is boosted to three orders of magnitude higher of 2900 mF cm^{-2} (224 F g^{-1}) by making use of the superhydrophilicity and high porosity especially ultramicropores in the range of $0.46\text{--}0.64 \text{ nm}$. Direct implementation of TCC as freestanding electrode for flexible SSCs provides areal capacitance and energy density for the stack up to 920 mF cm^{-2} and $128 \mu\text{W h cm}^{-2}$, respectively.

2. Experimental

2.1. Synthesis of TCC from commercial CC

TCC was synthesized from commercial CC (Shanghai Hesen Electric Co. Ltd., China, HCCP330) using a high-temperature annealing method. Before annealing, a piece of commercial CC was cleaned with alcohol and distilled water. CC was heated at $600\text{--}1200 \text{ }^\circ\text{C}$ for 1 h at $5 \text{ }^\circ\text{C min}^{-1}$ in industry nitrogen (99% purity) and then dried at $70 \text{ }^\circ\text{C}$. The resultants were donated as $\text{TCC}_{\text{temperature}}$, such as TCC_{1000} . The yield of the obtained TCC after once annealing was 78–94%. The mass of TCC_{1000} is 15.6 mg cm^{-2} and the thickness is 0.34 mm . TCC finally exhibited excellent flexibility and good electric conductivity was retained. TCC-4h was prepared via annealing at $1000 \text{ }^\circ\text{C}$ for 4 h (14.8 mg cm^{-2}). TCC@2 was synthesized by annealing at $1000 \text{ }^\circ\text{C}$ for 1 h and repeating this procedure again. The yield for TCC@2 is 68% (12.9 mg cm^{-2}).

2.2. Synthesis of contrast samples

To further study the significant role of ultramicropores in TCC which match well with the size of solvated K^+ on its EC performance, different contrast samples were synthesized. Specifically, at first, CC (HCCP330) was annealed at $1000 \text{ }^\circ\text{C}$ for 1 h to synthesize TCC. The obtained TCC was dipped in 4 M KHCO_3 solution for 30 min, then taken out and dried at $70 \text{ }^\circ\text{C}$ in an oven. This dipping process was repeated three times to assure full adsorption. This material dipped with KHCO_3 was heated at $1000 \text{ }^\circ\text{C}$ for 1 h again and next was washed

with HCl, water for several times to remove the residual alkali and other impurities. Then, KHCO_3 activated material was obtained and the final yield is 47% (8.9 mg cm^{-2}).

2.3. Characterization

SEM images and energy-dispersive X-ray (EDX) spectra were taken on a SU-70 microscope. High-resolution TEM (HRTEM) was performed on Tecnai G2 F30 S-Twin at an acceleration voltage of 300 KV. The X-ray photoelectron spectra (XPS) were collected with an ESCALAB MARK II spherical analyzer using an aluminum anode (Al 1486.6 eV) X-ray source. A Raman spectrometer (JY, HR 800) using 514-nm laser excitation at room temperature was employed to obtain Raman spectra. FT-IR spectra were recorded on a Nicolet Fourier transform infrared spectroscopy. N_2 adsorption analysis was performed at 77 K using a Micromeritics ASAP 2020 to investigate the surface area and pore distributions. Porosity analysis was carried out with N_2 at 77.4 K and with CO_2 at 273.2 K. The specific surface area (SSA) was calculated by Brunauer-Emmette-Teller (BET) method. The Pore size distribution (PSD) was recorded by density functional theory (DFT) pore model. N_2 sorption was commonly used to measure pore structure and CO_2 sorption was done to analyze a small amount of micropores, which are not accessible by N_2 . Since no significant difference between N_2 and CO_2 pore volume was exist, most of results were used based on N_2 adsorption analysis.

2.4. Electrochemical measurements

The electrochemical performance of the TCC were investigated by cyclic voltammetry (CV), galvanostatic charge/discharge tests (GCD) and electrochemical impedance spectroscopy (EIS). The GCD measurements were performed using a LAND CT2001A workstation. The CV tests were conducted on CHI electrochemical workstation. The EIS measurements were recorded on a Gamry Reference 600 electrochemical workstation over a frequency range of $0.01 \text{ Hz--}100 \text{ kHz}$ at the open-circuit potential. For a three-electrode cell, platinum sheet and

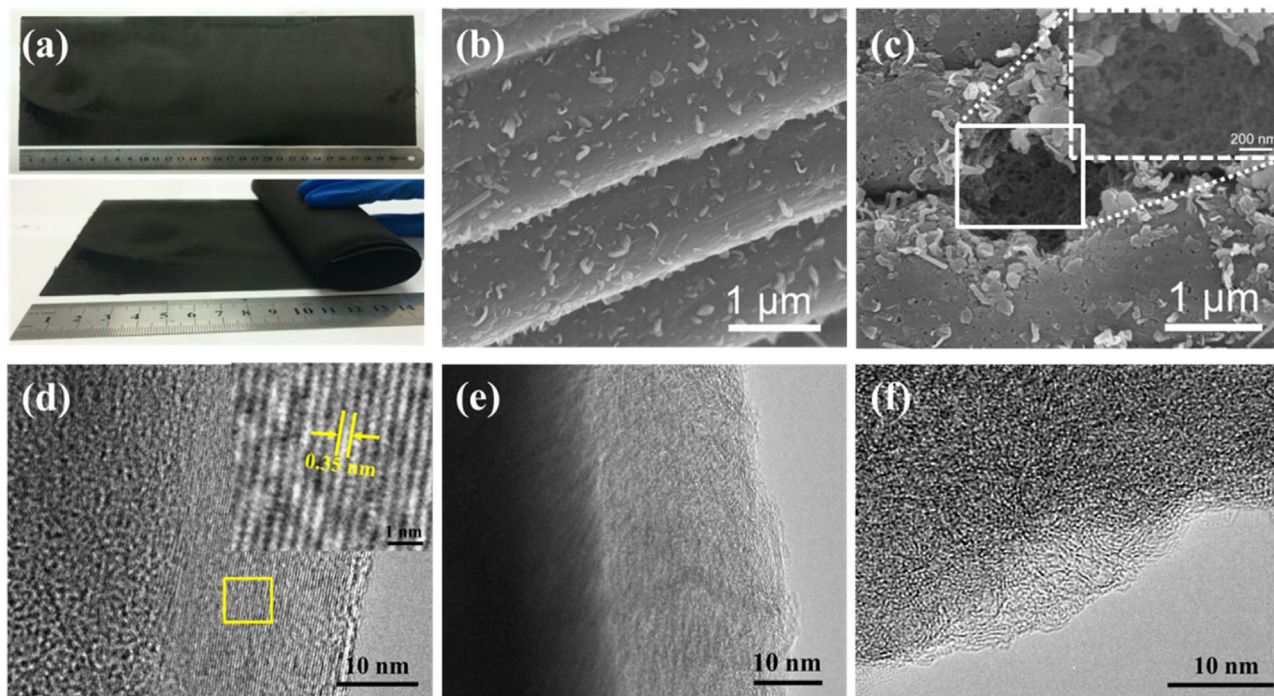


Fig. 1. Characterizations of CC and TCC. (a) Digital photographs of TCC_{1000} with an area of 512 cm^2 ($16 \times 32 \text{ cm}^2$) and excellent flexibility. (b) SEM images of CC. (c) SEM image of TCC_{1000} , with a corresponding higher magnification for internal carbon fibers in the inset. (d) High-resolution TEM (HRTEM) image of CC; scale bar, 10 nm. (Inset) a magnified HRTEM image; scale bar, 1 nm. Average lattice space of $\sim 0.35 \text{ nm}$ corresponds to (002) planes of graphitic materials. (e) HRTEM image of TCC_{1000} with a core-shell structure and (f) without a shell structure, scale bar, 10 nm.

Download English Version:

<https://daneshyari.com/en/article/5453699>

Download Persian Version:

<https://daneshyari.com/article/5453699>

[Daneshyari.com](https://daneshyari.com)