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Flexible supercapacitors with high areal capacitance based on hierarchical carbon tubular nanostructures

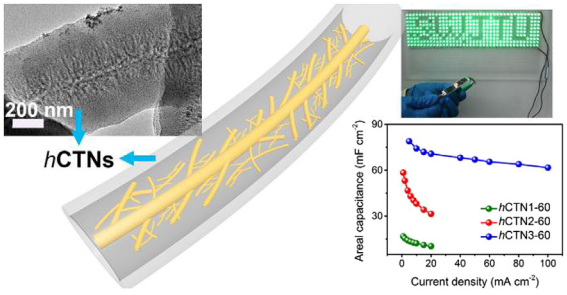
Haitao Zhang [a, **], Hai Su [a], Lei Zhang [a], Binbin Zhang [a], Fengjun Chun [a], Xiang Chu [a], Weidong He [b], Weiqing Yang [a, *]

[a] Key Laboratory of Advanced Technologies of Materials (Ministry of Education), School of Materials Science and Engineering, Southwest Jiaotong University, Chengdu 610031, China
[b] School of Energy Science and Engineering, University of Electronic Science and Technology, Chengdu, Sichuan 611731, China

HIGHLIGHTS

- *h*CTNs are synthesized through direct conversion of carbon dioxide.
- Environmentally-friendly and simply preparing method.
- *h*CTNs can be effectively constructed on various substrates.
- *h*CTN electrodes show the maximum areal capacitance of ~320 mF cm^{-2}.
- *h*CTNs based flexible supercapacitors possess superior electrochemical properties.

GRAPHICAL ABSTRACT



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ABSTRACT

Hierarchical structure design can greatly enhance the unique properties of primary material(s) but suffers from complicated preparation process and difficult self-assembly of materials with different dimensionalities. Here we report on the growth of single carbon tubular nanostructures with hierarchical structure (*h*CTNs) through a simple method based on direct conversion of carbon dioxide. Resorting to in-situ transformation and self-assembly of carbon micro/nano-structures, the obtained *h*CTNs are blood-like multichannel hierarchy composed of one large channel across the *h*CTNs and plenty of small branches connected to each other. Due to the unique pore structure and high surface area, these *h*CTN-based flexible supercapacitors possess the highest areal capacitance of ~320 mF cm^{-2}, as well as good rate-capability and excellent cycling stability (95% retention after 2500 cycles). It was established that this method can control the morphology, size, and density of *h*CTNs and effectively construct *h*CTNs well anchored to the various substrates. Our work unambiguously demonstrated the potential of *h*CTNs for large flexible supercapacitors and integrated energy management electronics.

1. Introduction

The recent explosive development of flexible, portable, and wearable electronic devices has being inspired rapid development of their counterpart energy storage systems for providing efficient energy management [1,2]. Supercapacitors, also known as

* Corresponding author.
** Corresponding author.
E-mail addresses: haitaozhang@swjtu.edu.cn (H. Zhang), wqyang@swjtu.edu.cn (W. Yang).

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electrochemical capacitors, have recently garnered intense interest as one kind of emerging flexible energy storage technologies [3–6]. Depending on different storage principles, supercapacitors can be divided into electrical double layer capacitors (EDLCs) represented by Helmholtz interface capacitor, and psuedocapacitors based on Faradaic reaction [7,8]. EDLCs based on electrostatic charge storage mechanism have high power density (>10 kW kg^{-1}) and an outstanding cycling stability. Consequently, supercapacitors complement or can even sometimes replace batteries in applications from microelectronics to transportation and the electrical grid, in which high-power delivery or uptake and super long cycle life are required [9,10].

Since EDLCs store the energy at the electrolyte/carbon interface by charging EDL capacitance, they suffer from low specific capacitance and low energy density (5–10 Wh kg^{-1}). These properties are largely determined by ion-accessible surface area, electrical conductivity, and pore structure of carbon materials [11–13]. Usually, through micro/nano-structural design to avoid the aggregation, provide efficient electron and ion transport pathways, and adjust the pore structure of carbon materials, superior capacitive performance and high energy density can be anticipated. And it is critical to further improve the properties of supercapacitors to achieve high specific capacitance and energy density for practical application.

Hierarchical structure design can greatly enhance unique properties of primary material(s) and has recently attracted great attention for fundamental investigations and potential applications in diverse technologies [14–20]. Inspired by the hierarchical structure in plants, carbon materials with hierarchical structure have been created through partial π–π stacking interactions to form a 3D macrostructure with interconnected pores, which possesses a wide pore size distribution (PSD) *via* self-assembly of multi-dimension carbon materials [21–23]. The unique hierarchical structures feature high ion-accessible surface area, and superior carbon–electrolyte interface for efficient adsorption of ions from the electrolyte. They can ideally be used as supercapacitor electrodes with excellent specific capacitance, rate capability, and cycling stability. For example, a hierarchically structured carbon microfiber made of an interconnected network of carbon nanotubes and graphene with PVA/H_3PO_4 electrolyte exhibit a specific volumetric capacitance of 300 F cm^{-3} and a volumetric energy density of 6.3 mWh m^{-3} [24].

Although hierarchical carbon materials show great potential in supercapacitor electrode materials, they commonly suffer from the disadvantages of complicate preparation methods, consisting of composite materials, and high ratio of macropores [25–28]. Recently, many investigations have focused on the use of wet processing routes such as colloidal solutions or suspensions of particles for the electrode preparation [29,30]. These methods also have the drawbacks of low mass production and therefore it is difficult to develop flexible supercapacitors integrated with printable electronics.

In this work, hierarchical carbon tubular nanostructures (*h*CTNs) with 3D framework, linear, spring-like structure are created through direct conversion of carbon dioxide and shaped on multiple flexible substrates. The *h*CTNs are blood-vessel-like multichannel hiberarchy structure with carbon micro/nano-structures and possess good mechanical flexibility. A “main artery” runs through the whole *h*CTNs and a large number of “capillary vessels” spread over carbon micro/nano-structures with abundant micro to meso-pores. Particularly, these *h*CTNs with unique structure are suitable and effective electrode/electrolyte materials, and preferable structural designs to develop flexible power sources with better electrochemical performance for integration into flexible electronics. As expected, *h*CTN-based solid-state flexible supercapacitors exhibit high areal capacitance (321 mF cm^{-2} at 5 mV s^{-1} with PVA/H_3PO_4 electrolyte and 316 mF cm^{-2} at 5 mA cm^{-2} with PVA/KOH electrolyte) and excellent cycling stability (95% retention after 2500 cycles). In addition, our patterned *h*CTN supercapacitors with excellent performance could be integrated in serial or parallel connections to expand the output voltage or total capacitance to operate various active devices in need of variable operation voltage and current. The superior performance of these *h*CTNs evidently demonstrated the promise for applications in energy storage and then expansive energy management electronics.

2. Experimental

2.1. Preparation of hCTNs

The *h*CTNs were synthesized by a simple method of Mg reaction with CO_2 gas. To fabricate different substrate supporting *h*CTNs, Mg powders with a purity of 99.5% are spread on substrate like stainless steel meshes (500 meshes), wires, springs, and silicon wafers. In a typical process, 4.0 g Mg powders were put into a high purity corundum boat with a size of 100 × 25 × 20 mm. Then the corundum boat was put into a tube furnace (GSL-1700X, Hefei Kejing Materials Tech. CO., Ltd., China) with a multichannel flow controller (GMF-2Z, AnHui BEQ Equipment Tech. CO., Ltd. China). And then Mg powders were heated to the aimed reaction temperature under the protection of Ar gas with flow rate of 20–200 sccm. Once the initial reaction temperature was achieved, the CO_2 gas with an equivalent volume of Ar was turned on. Through adjusting the position of the substrates and the reaction time, the morphology, size and density of *h*CTNs could be tailored. To emphasize the importance of some synthetic parameters, we named the samples as *h*CTN*X*-*Y*, where *X* represents different substrate positions and *Y* represents different reaction time. The detailed information of substrate positions was illustrated in Supporting Fig. S1 and all the sample parameters were summarized in Table 1. After the reaction, the samples were treated by 1 M HCl aqueous solution for eliminating the impurities including Mg and

Table 1
The sample names and their concrete preparing parameters.

Sample names	Substrates	Position[a]	Time (min)
*h*CTN1-5	stainless steel mesh	left	5
*h*CTN2-5	stainless steel mesh	middle	5
*h*CTN3-5	stainless steel mesh	right	5
*h*CTN1-30	stainless steel mesh	left	30
*h*CTN2-30	stainless steel mesh	middle	30
*h*CTN3-30	stainless steel mesh	right	30
*h*CTN1-60	stainless steel mesh	left	60
*h*CTN2-60	stainless steel mesh	middle	60
*h*CTN3-60	stainless steel mesh	right	60
*h*CTN1-90	stainless steel mesh	left	90
*h*CTN2-90	stainless steel mesh	middle	90
*h*CTN3-90	stainless steel mesh	right	90
*h*CTN1-120	stainless steel mesh	left	120
*h*CTN2-120	stainless steel mesh	middle	120
*h*CTN3-120	stainless steel mesh	right	120
*h*CTN2-30S	stainless steel spring	middle	30
*h*CTN2-60Si	silicon wafer	middle	60
*h*CTN30[b]	/	/	30
*h*CTN60	/	/	60
*h*CTN90	/	/	90
*h*CTN120	/	/	120

Note.
[a] The substrate positions are shown in Fig. S1, where the positions are defined as left, middle, and right along the direction of the airflow from the left to right.
[b] The *h*CTN30 was powder of carbon tubular nanostructures without using the substrates, as well as the *h*CTN60, *h*CTN90 and *h*CTN120.