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Nitrogen doped carbon derived from polyimide/multiwall carbon nanotube composites for high performance flexible all-solid-state supercapacitors

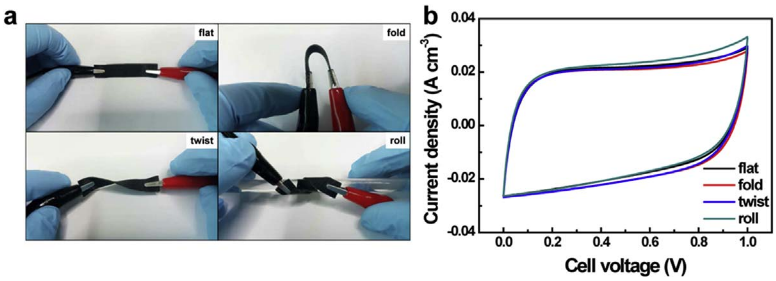
Dae Kyom Kim[a], Nam Dong Kim[c], Seung-Keun Park[a], Kwang-dong Seong[a], Minsik Hwang[a], Nam-Ho You[c,**], Yuanzhe Piao[a,b,*]

[a] *Program in Nano Science and Technology, Graduate School of Convergence Science and Technology, Seoul National University, 145 Gwanggyo-ro, Yeongtong-gu, Suwon-si, Gyeonggi-do, 443-270, Republic of Korea*
[b] *Advanced Institutes of Convergence Technology, 145 Gwanggyo-ro, Yeongtong-gu, Suwon-si, Gyeonggi-do, 443-270, Republic of Korea*
[c] *Carbon Composite Materials Research Center, Institute of Advanced Composites Materials, Korea Institute of Science and Technology, Chudong-ro 92, Bondong-eup, Wanju-gun, Jeollabuk-do, 565-905, Republic of Korea*

HIGHLIGHTS

- Nitrogen doped carbon was derived for flexible symmetric supercapacitors.
- The electrodes deliver high specific capacitances of 333.4 F g^{-1} at 1 A g^{-1}.
- The fabricated device shows excellent flexibility and mechanical stability.
- The device presents the volumetric energy density of 0.5 mWh/cm^3.

GRAPHICAL ABSTRACT



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ABSTRACT

Flexible all-solid-state supercapacitors are desirable as potential energy storage systems for wearable technologies. Herein, we synthesize aminophenyl multiwall carbon nanotube (AP-MWCNT) grafted polyimide precursor by *in situ* polymerization method as a nitrogen-doped carbon precursor. Flexible supercapacitor electrodes are fabricated via a coating of carbon precursor on carbon cloth surface and carbonization at high temperature directly. The as-obtained electrodes, which can be directly used without any binders or additives, can deliver a high specific capacitance of 333.4 F g^{-1} at 1 A g^{-1} (based on active material mass) and excellent cycle stability with 103% capacitance retention after 10,000 cycles in a three-electrode system. The flexible all-solid-state supercapacitor device exhibits a high volumetric capacitance of 3.88 F cm^{-3} at a current density of 0.02 mA cm^{-3}. And also the device can deliver a maximum volumetric energy density of 0.50 mWh cm^{-3} and presents good cycling stability with 85.3% capacitance retention after 10,000 cycles. This device cell can not only show extraordinary mechanical flexibilities allowing folding, twisting, and rolling but also demonstrate remarkable stable electrochemical performances under their forms. This work provides a novel approach to obtain carbon textile-based flexible supercapacitors with high electrochemical performance and mechanical flexibility.

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[*] Corresponding author. Program in Nano Science and Technology, Graduate School of Convergence Science and Technology, Seoul National University, 145 Gwanggyo-ro, Yeongtong-gu, Suwon-si, Gyeonggi-do, 443-270, Republic of Korea.

[**] Corresponding author. Carbon Composite Materials Research Center, Institute of Advanced Composites Materials, Korea Institute of Science and Technology, Chudong-ro 92, Bondong-eup, Wanju-gun, Jeollabuk-do, 565-905, Republic of Korea.

E-mail addresses: polymer@kist.re.kr (N.-H. You), parkat9@snu.ac.kr (Y. Piao).

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1. Introduction

Recent rapid developments in wearable technology have attracted significant demand for flexible electronics such as in mobile phones, flexible displays, and smart textiles. In order to achieve all-in-one flexible systems, the development of light-weight, wearable and high performance power sources is necessary. Supercapacitors are potential candidates for flexible power sources because of their quick charge-discharge capability, long cycle life and safety [1]. Compared to conventional supercapacitors, flexible supercapacitors have advantages in their low weight, small size, ease of handling, excellent reliability, and wide range of operating temperatures [2]. Many efforts have been made to realize flexible supercapacitors with robust mechanical properties and excellent electrochemical performance, to ensure operation in extreme conditions. Possible flexible substrates for supercapacitors include polyethylene-terephthalate films [3], carbon material integrated office paper [4], carbon nanofibers [5], graphene paper [6], carbon nanotube fibers [7], and graphene fibers [8]. Among these, textile-based substrates show great promise for use as flexible supercapacitor substrates. Carbon cloth (CC) is particularly attractive in this regard, as CC is a textile of carbon fiber bundles approximately 5 μm in diameter, granting it light weight, flexibility, mechanical strength, thermal stability, electrical conductivity, and chemical resistance [9]. However, it is still a significant challenge to achieve high energy density and long cycle life in flexible supercapacitors. A typical fabrication of all-solid-state flexible supercapacitor cells needs an additional binder or other additive to integrate the active materials on current collector surfaces, resulting in large contact resistance and dead surface areas on the electrode materials [10]. In response to this, researchers have begun developing direct fabrication processes of active materials onto CC surfaces using *in situ* growth strategies. Various methods, including electrodeposition of conductive polymers [11] or metal oxides [12], hydrothermal growth of metal oxides [13,14], *in situ* chemical polymerization of conducting polymers [15], and surface activation of CC [9,16], have been demonstrated to achieve binder-free fabrication of active materials in such systems. However, control over the loading mass of active material on the CC surface is a challenge for commercialization, especially in regards to high specific capacitance and large scale production.

Another strategy to improve the energy density and cycle life of these systems involves the modification of surface functionality of the carbon materials, using elements such as nitrogen, oxygen, boron, or phosphorous. Heteroatom-doped carbon can enhance the capacitance and induce surface faradaic reactions by improving the charge mobility of negative charges on the carbon surface, while maintaining the high rate capability and long cycle life [17,18]. Among these elements, nitrogen doping in carbonaceous electrode materials has received much attention in recent years due to its effect on capacitance and ease of preparation. Nitrogen-doped carbon materials can be prepared as active materials in one of two ways: post-treatment or *in situ*. The post-treatment pathway involves attaching nitrogen-containing functional groups such as urea [19], ammonia [20] and nitrogen plasma [21], but this pathway leads to relatively low nitrogen contents on the surface and an inhomogeneous nitrogen distribution. In the *in situ* pathway, nitrogen-containing precursors such as polypyrrole [22,23], polyaniline [24–26], melanine [27], polyacrylonitrile [28] and nitrogen-containing ionic liquids undergo pyrolysis at high temperatures [29], directly converting them to nitrogen-doped carbon materials. Compared to post treatment, this method can realize homogeneous incorporation of nitrogen, and is a more simple and facile way to utilize various precursors. Aromatic polymers have excellent thermal stability and high carbon yield after pyrolysis compared to small organic precursors, making them useful nitrogen-containing precursors in this field. Recently, nitrogen-doped porous carbon nanofibers were prepared by carbonization of carbonaceous nanofibers coated with polypyrrole [30] and polyaniline [31] using a direct polymerization method.

Aromatic polyimides (API), having conjugated aromatic rings in the polymer backbone, are widely used in display, microelectronic, and aerospace technologies because of their high mechanical stability, thermal stability, chemical resistance, and low dielectric constants [32]. Moreover, API is an effective carbon precursor due to its high carbon yield and ease of carbonization [33]. Carbonized PIs, obtained by pyrolysis of API at high temperature, can be an alternative means to obtain nitrogen-doped carbon materials for energy storage applications due to nitrogen atoms in the PI backbone. To date, several reports have shown the capacitive performance of API as a nitrogen-doping source. Le et al. reported the preparation of microporous carbon nanofibers derived from PI and polyvinyl pyrrolidone, using electrospinning followed by pyrolysis [34]. Li et al. prepared nitrogen-doped carbon membranes using electrospun carbon nanofibers comprised of heterocyclic PIs [35]. In et al. fabricated a flexible all-solid-state micro supercapacitor using direct laser writing on PI film surfaces to convert porous carbon on the surface [36]. However, further investigation is needed into flexible binder-free nitrogen-doped carbon materials derived from PI precursors for high energy density, long cycle life, and mechanical durability.

Here, we report a nitrogen-doped carbon derived from polyimide/MWCNT composites (C-MWCNT-PI) for flexible all-solid-state symmetric supercapacitors. As a nitrogen-doped carbon precursor, aminophenyl multiwall carbon nanotube (AP-MWCNT) grafted PI precursor was synthesized by *in situ* polymerization method. The synthesized PI precursor solution was dropped to the CC surface which was served as the flexible substrate and current collector and coating followed by direct carbonization at high temperature. These suggested drop, paste and pyrolysis process for the fabrication of electrodes effectively solved the technical problems of the control of the loading mass of active material on the CC surface, and the difficulty of large scale production. The obtained electrode shows a high specific capacitance of 333.4 F g^{-1} at 1 A g^{-1} (based on active material mass) in a three electrode system. We also fabricated an all-solid-state flexible supercapacitor device, which exhibits a high volumetric capacitance of 3.88 F cm^{-3} at a current density of 0.02 mA cm^{-3}. This flexible supercapacitor can deliver the maximum volumetric energy density of 0.50 mWh cm^{-3} and presents a good cycling stability with capacitance retention of 85.3% after 10,000 cycles. Furthermore, this device displays superior flexibility with stable electrochemical performance and good capacitance retention.

2. Experimental

2.1. Synthesis of MWCNT-PI nanocomposite precursor via in situ polymerization

Aminophenyl functionalized MWCNT (AP-MWCNT) was prepared according to a procedure reported in our previous works [37]. The as-prepared AP-MWCNT (36 mg) were dispersed in N,N-dimethylformamide (DMF, 15 mL) and the solution subjected to ultrasonication for 1 h. Then, 4,4′-oxydianiline (0.59 g, 2.75 mmol) was added to the solution and stirred for 30 min. Subsequently, pyromellitic dianhydride (0.60 g, 2.75 mmol) was added to the mixture with stirring for 24 h at room temperature, yielding the MWCNT-PI precursor with the desired viscosity.

2.2. Fabrication of CC/C-MWCNT-PI electrodes

In order to form a conformal coating of precursor solution, Carbon cloth (CC) (CeTech Co. Ltd. W0S1002) was treated with DI water/ethanol (7/3 v/v) at 80 °C in a water bath overnight. The treated CC was dried in a vacuum oven at 60 °C for 2 h. A desired amount of MWCNT-PI precursor solution was dropped uniformly on a 1 cm × 1 cm area of the CC surface. Thermal treatment was performed by increasing the temperature at a rate of 3 °C min^{-1} and maintained at