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Flexible quasi-solid-state SnO_2/CNT supercapacitor processed by a dc-pulse nitrogen atmospheric-pressure plasma jet

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ABSTRACT

This study investigates flexible quasi-solid-state SnO_2/CNT nanocomposite supercapacitors fabricated using a dc-pulse nitrogen atmospheric-pressure plasma jet (APPJ). The optimal APPJ processing time is merely 15 s. Cyclic voltammetry (potential scan rate = 2 mV/s) shows an areal capacitance of 3.86 mF/cm^2 when flat and 4.42 mF/cm^2 under bending (bending radius R = 0.55 cm), indicating good functionality under flexing. The capacitance retention rate is 98.3% as evaluated after a 1000-cycle cyclic voltammetry test under bending (R = 0.55 cm), suggesting good operational stability.

1. Introduction

An atmospheric-pressure plasma jet (APPJ) has high energy density and contains highly reactive species, thus affording rapid material processing capability. APPJ operations can be performed at regular pressure without using vacuum pumps and a chamber that are costly and require routine maintenance. Therefore, APPJ is considered suitable for cost-effective rapid material processing. Recent developments in APPJs have overcome previous problems including high breakdown voltage, continuous arcing, and instability, making this technology ready for industrial use [1–8]. Practical APPJ materials processes such as rapid etching on polymer substrates [9,10] and carbonaceous materials [11], selective surface patterning [12] and surface modification [13], and rapid processing of nanoporous metal oxides [14–17] and nanocomposites [18,19], have been implemented successfully. The application of atmospheric-pressure plasma technology for bacterial inactivation [2,20,21] and biomedicine [6] has also attracted much research attention. Atmospheric-pressure plasma has been found to react vigorously with carbonaceous materials [9–11,14–19,22–25]. Reactive oxygen atoms in the APPJ are considered responsible for the rapid etching of polyimide foils [9,10]. Rapid mask-free patterning (etching) of carbon nanotube (CNT) micro-supercapacitors has also been realized [11]; in this case, ozone generated by the APPJ is considered as the main oxidation reactants. Screen-printed pastes containing ethyl cellulose and CNT (or reduced graphene oxides) were also found to be completely removed (or oxidized) within 1 min when processed using a dc-pulse nitrogen APPJ [22,23]. In this scenario, the ultrafast processing capability is attributed to the synergetic effect of the reactive plasma species and heat.

Supercapacitors are passive energy storage devices with charge/energy storage mechanisms of pseudocapacitance and/or electrical double layer capacitance (EDLC) [26,27]. Pseudocapacitance typically originates from Faradaic reactions at the material surfaces and EDLC is based on ion adsorption and charge separation at the electrode/electrolyte interface [28,29]. Supercapacitors have attracted interest owing to their excellent power density, cycle efficiency, and fast charging–discharging rate compared to batteries [30,31]. Flexible solid-state or quasi-solid-state supercapacitors are of great interest for integration into flexible wearable electronic devices [11,26,30–33]. Many electrodes of supercapacitors are made using wet chemical processes that allow direct synthesis routes of the supercapacitor electrode materials [34,35]. In regard to the advantage of APPJ processes, it can be scaled up using a scanning APPJ roll-to-roll process [36]. In our previous studies, we have fabricated liquid-electrolyte Fe_2O_3/CNT [37] and SnO_2/CNT [18,36] nanocomposite supercapacitors using a dc-pulse nitrogen APPJ. In the current study, we use a dc-pulse nitrogen APPJ to process SnO_2/CNT

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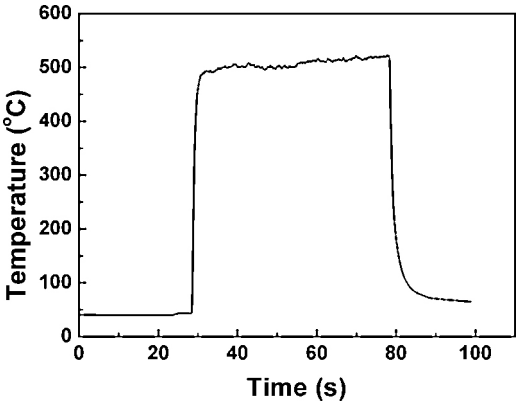

Fig. 1. Representative temperature evolution profile of substrate under APPJ operation.

nanocomposite electrodes for flexible quasi-solid-state supercapacitors. Owing to the vigorous reaction between the APPJ and the printed electrode materials, the optimal processing time is merely 15 s. The characteristics of flat and bended flexible quasi-solid-state SnO_2/CNT nanocomposite supercapacitors processed by APPJ are evaluated and reported.

2. Experimental details

2.1. Preparation of SnO_2/CNT pastes for screen-printing

0.04 g SnO_2 nanoparticles (purity: 99.97%, diameter: 35–55 nm), 0.04 g CNTs (purity: 98%, diameter: 5–20 nm, length: >1 μm, Golden Innovation Business Co., Ltd), 1.8 g ethanolic solution containing 10 wt% ethyl cellulose (30–50 mPa s, #46080, Fluka), 1.4 g ethanolic solution containing 10 wt% ethyl cellulose (5–15 mPa s, #46070, Fluka), 2.596 g terpineol (anhydrous, #86480, Fluka), and 0.4698 g ethanol were mixed and stirred for 24 h using a magnetic stirrer. 4 ml of the mixture was condensed at 55 °C for 5 min using a rotovap.

2.2. Preparation of SnO_2/CNT electrode on carbon cloth

The resultant pastes were screen-printed on carbon cloth; the printing area was 2 cm × 1.5 cm. Then, a nitrogen APPJ was used for calcination. A K-type thermocouple was used for measuring the substrate temperature during APPJ operation. Fig. 1 shows the evolution of the substrate temperature measured at the center of the APPJ processing area. The temperature rapidly increased to 480 °C in 2 s and reached 500 °C in 7 s after the APPJ was ignited. The temperature also decreased rapidly after turning off the APPJ. This suggests that the dc-pulse nitrogen APPJ is very suitable for rapid calcination.

2.3. Fabrication of quasi-solid-state supercapacitor

After APPJ-calcination, a gel-electrolyte containing a mixture of polyvinyl alcohol (PVA) and H_2SO_4 was spread on each SnO_2/CNT electrode and dried naturally for 24 h. This procedure was repeated three times. The two pieces of PVA/H_2SO_4 coated SnO_2/CNT electrodes were mechanically pressed on the PVA/H_2SO_4 sides. The flexible quasi-solid-state supercapacitor was then completed. The gel electrolyte was prepared by mixing 15 ml 1-M H_2SO_4 into 1.5 g PVA and stirring at 80 °C for 4 h using a magnetic stirrer. After natural cooling, the gel electrolyte was completed.

2.4. Characterization of materials and supercapacitors

The APPJ-sintered SnO_2/CNT on carbon cloth was examined by scanning electron microscopy (SEM, Nova NanoSEM 230, FEI). For characterizing the supercapacitor, an electrochemical workstation (Zahner Zennium) was used for cyclic voltammetry (CV), galvanostatic charging/discharging (GCD), and cycling stability measurements. CV was performed between 0 and 0.8 V at 2, 20, and 200 mV/s. GCD was performed from 0 to 0.8 V at 100, 250, and 500 μA. The cycling stability was evaluated by CV at a scan rate of 200 mV/s for 1000 cycles. The supercapacitor was evaluated under both flat and bending conditions.

3. Results and discussion

Fig. 2 shows the representative 15-s APPJ-sintered SnO_2/CNT nanocomposite on the carbon cloth substrate. The SnO_2/CNT nanocomposites were deposited on and/or between the carbon fibers. Organic binders (ethyl cellulose, terpineol) were removed and the synthesized material revealed a nanoporous structure. This nanoporous composite significantly increased the surface area for energy storage.

Fig. 3(a) shows the representative cyclic voltammogram when the supercapacitor is flat and is under bending. A two-electrode configuration was used for the measurement with potential scan rates of 2, 20, and 200 mV/s. The areal capacitance can be

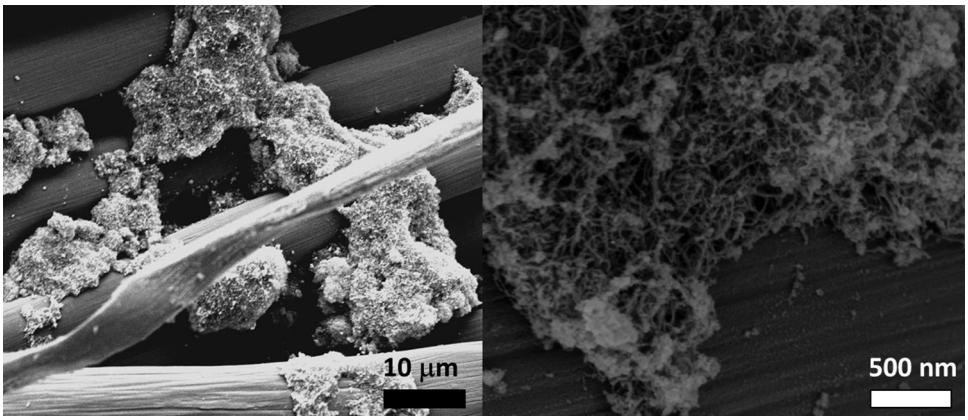

Fig. 2. SEM images of SnO_2/CNT nanocomposite on carbon cloth (left: 5000×; right: 100,000×).