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Flexible supercapacitors on chips with interdigital carbon nanotube fiber electrodes

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ABSTRACT

In this study, a new type of all-solid-state flexible supercapacitor on chips is fabricated by directly arranging carbon nanotube fibers as interdigital electrodes on polymer substrates. The as-fabricated supercapacitors exhibited excellent electrochemical performance with high specific capacitance of 11.23 F/g at a current density of 0.075 A/g and superior charge/discharge rate performance of up to 20 V/s. The supercapacitors on-chips also showed outstanding flexibility with stable electrochemical functions. The flexible supercapacitor on chips provides real possibilities to the applications of supercapacitors as energy storage units in portable, flexible and wearable electronic devices.

1. Introduction

The current trend of portable electronic devices has urgent requirement to develop the miniaturized, integratable and implantable component units [1–4]. However, the integration of energy-storage units with appropriate size and electrode geometries is key and challenging [2]. Supercapacitors (SCs) are considered as one important class of energy storage devices because of their excellent properties of high powder density, long cycling life and high discharge efficiency. Thus, the development of supercapacitors on chips has attracted significant attention in recent years.

Recent works have reported that SCs can be fabricated onto a chip with a planar interdigital architecture [1–9]. Some active film materials, such as onion-like carbon (OLCs) [2,9], carbide derived carbon (AC) [1], porous carbon [10], graphene [4,5], metal oxide [6], and conductive polymers [7], were used in previous on-chip SCs due to their outstanding properties [11,12]. Owing to the remarkable physical and chemical properties, carbon nanotubes (CNT) have been widely researched for electrode materials in supercapacitors [13,14]. CNT fibers consisting by millions of carbon nanotubes possess better operability and softness, and they have become an ideal material for flexible and wearable supercapacitor applications [15–18].

Here, a new type of all-solid-state flexible supercapacitor on chips is fabricated by interdigital arrangement of carbon nanotube fibers as microelectrodes on flexible polymer films. The as-fabricated SCs exhibit high specific capacitance, excellent charge/discharge rate performance and outstanding flexibility with stable functions. More importantly, the device can be steadily connected in series or parallel to obtain higher output voltage or current. The facile and low-cost strategy of device fabrication is convenient for designing arbitrary architecture of electrode circuits, facilitating their integration applications in portable and flexible electronic devices.

2. Experiment

CNT fibers were synthesized by the chemical vapor deposition (CVD) method by injecting the mixture of ethanol (24.0 g), ferrocene (0.45 g), thiophene (0.16 g) and deionized water (1.4 g) into the reactor with hydrogen flow of 1800 sccm at 1150 °C [19,20]. The gel electrolyte of H_2SO_4/PVA (Polyvinyl Alcohol) was prepared by mixing concentrated H_2SO_4 (5 g, 98%) into deionized water (50 g), then adding PVA powder (5 g, molecular weight 140, 000–180, 000, Sigma Aldrich), followed by heating to 85–90 °C and magnetic stirring until the mixture became clear. PDMS (Polydimethylsiloxane, Sylgard184, Dowcorning) sheet pre-prepared with 0.5 mm thickness was used as the flexible substrates.

Fabrication of SCs: Firstly, The PDMS substrate (2.5 cm × 3 cm) was coated with one layer gel electrolyte by dropping two drops of

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the gel on the surface and paving using a glass slide. Then, 20 CNT fibers were carefully arranged onto the PDMS substrate using tweezers, forming into an interdigital architecture. Thus each pole contains 10 fiber electrodes and the orientation of the electrodes parallel to the wide sides of the substrate. Afterwards, dropping the gel electrolyte onto the electrode surfaces, making sure all the fibers are completely packaged. Finally, the ends of electrodes were attached with copper foils by silver-paste liquid (SPI Co. of America), in order to connect external circuit for testing.

The structure of CNT fibers was characterized by scanning electron microscopy (SEM, S-4800, Hatchi, Japan) and transmission electron microscopy (TEM, Tecnai-G2 F20, Philips, Holland). All the electrochemical performance of the SCs was measured by cyclic voltammetry (CV), galvanostatic charge/discharge (CD) and electrochemical impedance spectroscopy (EIS) using electrochemical workstation (CHI660C, Chenhua, Shanghai, China).

The mass specific capacitance (C_{mass}) of the supercapacitor was calculated according to the following Eq. (1):

$$C_{mass} = \frac{I \cdot \triangle t}{m \cdot \triangle V} \quad (1)$$

where I is the current applied (A), Δt is discharge time (s), m is mass of fiber electrodes (g) and ΔV is potential window (V).

3. Results and discussion

Fig. 1(a) illustrates the simplified schematic images of the fabrication process of all-solid-state SCs on flexible chips with CNT fibers as interdigital electrodes. This fabrication method for planar SCs is facile and high efficiency because it only involves arranging CNT fibers on substrate chips directly and coating with H_2SO_4/PVA gel electrolyte. More importantly, CNT fibers resembling an electric wire with superior flexibility, light-weight and conductivity, not only can be prepared into interdigital architecture, but also be designed with arbitrary configurations as close as to the integrated circuit.

Fig. 1(b) shows an optical picture of an all-solid-state flexible SC as fabricated on PDMS sheet. Each electrode of the device fabricated has ten fingers with equal length of 10 mm and the spacing between the adjacent fingers is kept about 1 mm. The CNT fibers as electrodes were composed of bundled CNTs that interconnect and entangle into networks with high specific surface area and hierarchical pore construction as studied in previous works [19,20], which provides an ideal material as electrodes of supercapacitors. The CNT fiber used has smooth appearance with a diameter of 130 μm (Fig. 1(c)). The linear density of the fiber is 0.4 tex(mg/m) measured by weighting several meters fiber. The bulk density is calculated to be 0.03 g/cm^3. The volume fraction of CNTs is estimated to be 1% according to theoretical density of graphite (2.2 g/cm^3), which means that the porosity of the fiber is up to 99%. TEM image shows that the CNTs have typical double walls with diameters of 5–8 nm which are inter bundled with several individual tubes (Fig. 1(d)).

The electrochemical performance of the interdigital CNT fiber SC on PDMS was analyzed by CV, galvanostatic DC and EIS measurements. The SC showed typical double-layer capacitive behavior as seen from the rectangular shapes of CVs at different scan rates (Fig. 2(a)). The CV curve remained approximately rectangular even at high scan rate of up to 20 V/s, indicating rapid current response of the CNT fiber electrodes to voltage reversal [21]. The mass specific capacitance at different current densities was plotted in Fig. 2(b). The SC showed high capacitance up to 11.23 F/g at a current density of 0.075 A/g. The specific capacitance decreased

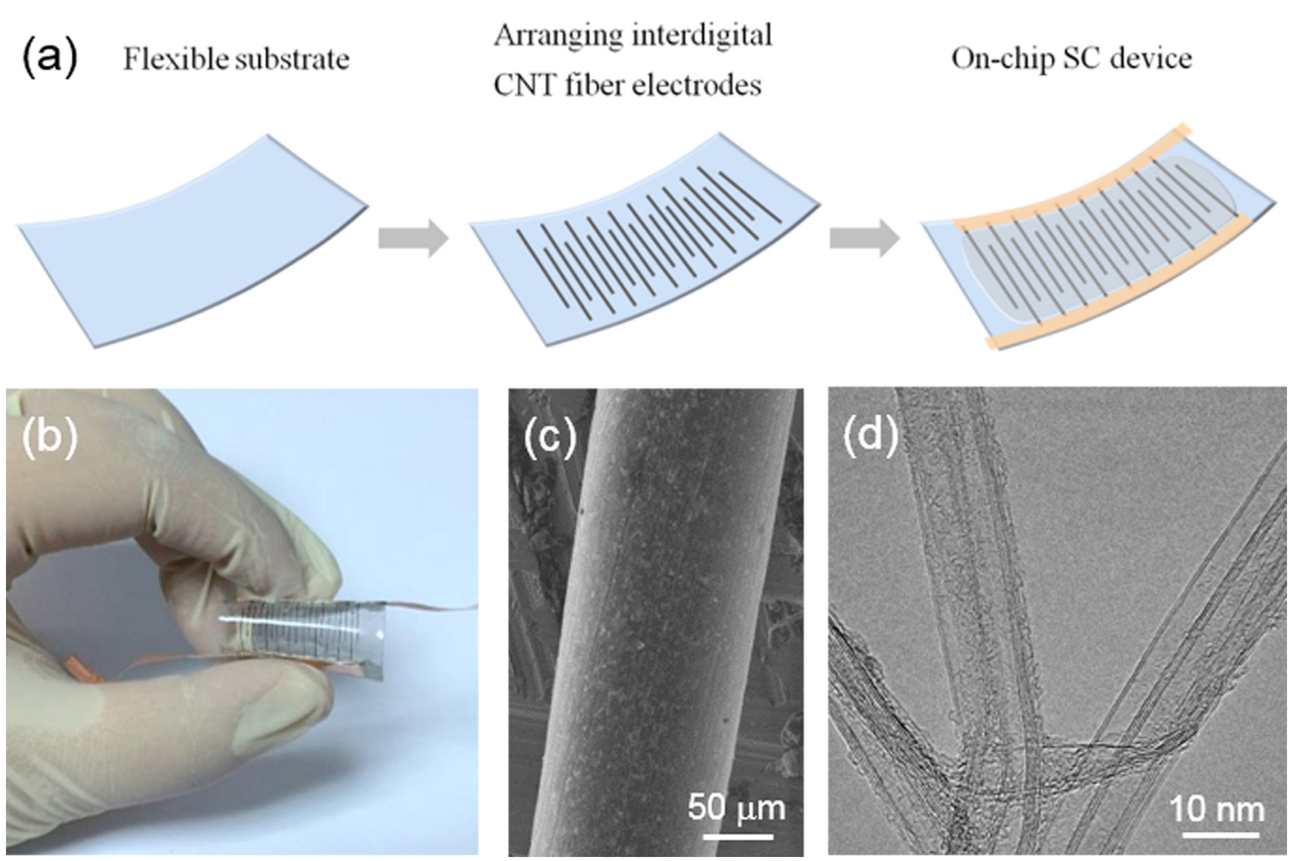

Fig. 1. (a) A schematic of fabrication process of all-solid-state supercapacitors on flexible chips, (b) Optical picture of a supercapacitor, (c) SEM and (d) TEM images of CNT fiber electrodes.