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Carbon-based flexible micro-supercapacitor fabrication via mask-free ambient micro-plasma-jet etching

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ABSTRACT

We demonstrate a general and facile method to fabricate all-solid-state flexible micro-supercapacitors (MSCs) with micropatterned multi-walled carbon nanotube (MWNT) electrodes via mask-free micro-plasma-jet etching in ambient conditions. Localized pulsed plasma jet etches the MWNTs rapidly and produces the interdigitated electrode patterns by scanning. This mask-free patterning technique is easy operated, cost-effective, readily scalable, free from photoresist contamination and applicable to various kinds of carbon-based materials. A solid-state polyvinyl alcohol-H_3PO_4 gel electrolyte is introduced to realize an all-solid-state flexible MSC assembly. Cyclic voltammetry measurements exhibit the expected electrical double layer behavior. The fabricated MSC with twelve interdigitated electrodes exhibits a stack capacitance of 2.02 F cm^{-3} at a scan rate of 10 mV s^{-1}. Moreover, the MSC shows stable performance under repeated bending, with retention of 98.2% of capacitance after 600 bending cycles. Furthermore, both the output voltage and the total capacitance of the MSC could be controlled via the serial or parallel connection.

1. Introduction

The increasing demand for wearable and portable devices has accelerated the development of energy storage devices. Among the presently available energy storage devices, supercapacitors (SCs), also known as ultra-capacitors, are attracting significant interest owing to the advantages of high power densities, fast charging and discharging rates, long cycling lifetimes, high round trip efficiency, low cost, and intrinsic safety [1,2]. Recent advances in SCs have been motivated by the requirement to reduce total device volume and be easily integrated into circuits of micro devices, and the fabrication of all-solid-state micro-supercapacitors (MSCs) has proved to be a particularly promising approach to achieve these goals [3–5].

Due to the characteristics of good electric conductivity and high specific surface area, carbon-based materials have been widely explored as electrode materials for MSCs, such as graphene [6–9], carbon nanotubes (CNTs) [10–14], graphene/CNT composites [15–21], diamond foam [22], activated carbon [23,24], onion-like carbon [25] and carbide-derived carbon [26]. To prepare interdigitated electrodes with carbon-based materials for MSCs, a lot of patterning techniques have been developed, including photolithography with subsequent etching [15,27–35], laser scribing [6,7,36–41], selective wetting [10], and printing [9,42,43]. However, the technique of laser scribing is mainly employed in the case of graphene and some polymers, and the technique of selective wetting is only suitable for patterning materials that can be dispersed in a hydrophilic solvent. So these two methods are both limited when facing other carbon-based materials. As to the technique of printing, the fabrication processes are complex and the patterning resolutions are usually low.

Photolithography with subsequent etching is the most widely used patterning technique for MSC fabrication. However, this technique involves conventional lithographic techniques and employs masks for the definition of patterns on substrates. As a result, this technique is awkward for simply building cost-effective devices for commercial applications [7]. What is more, the photoresist (PR) used in this technique is impossible to be completely removed and carbon-based films are susceptible to PR residue contamination due to their unique characteristics such as active surface

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properties and a microscopic porous network structure. Such PR contamination consequently degrades the electrical properties of carbon-based films [44]. Therefore, it remains a challenge to develop a general and facile technique that does not require PR, masks or complicated operation while producing carbon-based high-performance MSCs.

Herein, we demonstrate a novel mask-free plasma-scanning method to fabricate all-solid-state flexible MSCs via the application of an atmospheric pulsed micro-plasma-jet (APMPJ) [45,46]. Unlike other fabrication methods, this direct scanning technique does not require PR, masks, post-processing, vacuum system, high temperature treatment or clean room operations. Moreover, this technique is readily scalable and cost-effective. Furthermore, our etching method is suitable for not only CNTs but also many other carbon-based materials, making this plasma patterning strategy a promising candidate for the fabrication of carbon-based flexible electronic devices.

2. Experimental

2.1. Fabrication of CNT films

Multi-walled CNT (MWNT) powders were purchased from Nanjing XFNANO Materials Tech Co.,Ltd. The CNT films were prepared using a method similar to that developed by Wu et al. [47]. Sodium dodecyl sulfate (SDS) was used to disperse CNTs into deionized water. CNTs with a concentration of 0.3 mg ml^{-1} and SDS of 3 mg ml^{-1} were dissolved in deionized water and sonicated for 10 h. Following sonication, the CNT solution was centrifuged at 10,000 g for 10 min to remove CNT aggregates in bundles and other impurities. The upper 50% of the supernatant solution was carefully decanted for use. Then 20 ml of the solution was got and vacuum filtered through mixed cellulose ester (MCE) membranes with a pore size of 220 nm. The MCE membrane was then transferred to a piece of polyethylene terephthalate (PET) where the membrane was dissolved in acetone bath, leaving behind the CNT film with a thickness of 1 μm (Fig. S1). At last, the CNT film was immersed into deionized water for 10 min to remove the surfactant and dried in a dry oven at 60 °C for 30 min. This process was repeated twice to further remove surfactants and enhance adhesion between CNTs and the substrate.

2.2. Synthesis of polyvinyl alcohol (PVA)–H_3PO_4 gel electrolyte

In order to synthesize PVA-H_3PO_4 gel electrolyte, 5 g of PVA (M_w ~ 95 000 g mol^{-1}, Acros) and 4 g of H_3PO_4 (85 wt% aqueous solution, Aldrich) were dissolved in 75 ml of deionized water at 85 °C with vigorous stirring until the solution became transparent.

2.3. Fabrication of all-solid-state flexible MSCs

The APMPJ scanned CNT films into interdigitated electrodes with a relative moving speed of 500 μm s^{-1}. For better electric contact with probes of the measurement analyzer, the electrode edges of the MSCs were extended using an adhesive copper tape with help of silver paint. At last, PVA–H_3PO_4 solution was drop-coated onto the surface of the CNT film.

2.4. Characterization of all-solid-state MSCs

Scanning electron microscopy (SEM, FEI Sirion 200) was used to estimate the thickness of CNT films and investigate the morphology of CNT finger electrodes. The electrochemical performance of the all-solid-state MSC was measured with cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS) using an electrochemical analyzer (CorrTest, CS310).

3. Results and discussion

Fig. 1a shows the schematic illustration of etching a CNT film into interdigitated electrodes via the APMPJ scanning without use of PR or masks. A mixture of He and O_2 gas at the volume ratio of $He:O_2 = 49:1$ with a total flow rate of 100 sccm was used as the working gas. A glass tube with an inner diameter of 1 mm was used to guide the working gas flowing. There was a nozzle outlet at the end of the glass tube with an inner diameter of 100 μm. A CNT film on PET was placed on a computer-controlled sample stage which was 2 mm below the nozzle of the glass tube. There was a steel needle in the center of the glass tube. The steel needle, which served as a high-voltage (HV) electrode with a tip diameter of 50 μm, was connected directly to a pulsed direct current (DC) power supply. When HV pulsed DC voltage (voltage amplitude of 7 kV, pulse frequency of 6 kHz, and pulse width of 800 ns) was applied to the HV electrode, a plasma jet was generated at the end of the needle. Fig. 1b shows the photographic image of the generated APMPJ. The plasma jet etched the CNT film into micro patterns with a scanning speed of 500 μm s^{-1}. As shown in Fig. 1c, many interdigitated electrodes with different sizes were produced by the programmed plasma scanning on a piece of CNT film on PET. The effects of plasma parameters on the width of etched lines on CNT film were systematically investigated, as shown in Fig. S2. The etching of CNTs is realized due to the oxidation by O_3 [48,49], which is generated in this type of plasma jet with a high concentration of 2.5×10^{15} cm^{-3} [50]. In addition, a large emission current is generated in plasma-contacted CNTs and brings about strong joule heating [51,52], which promotes the oxidation of CNTs.

Various kinds of CNT patterns on PET were produced by using this etching technique. The transmission electron microscope (TEM) images of MWNTs are shown in Fig. S3. Fig. 2a shows a series of etching dots with diameter from 100 to 200 μm. Fig. 2b shows a CNT array with a space width of 60 μm and Fig. 2c shows a pattern of “HUST” with a space width of 160 μm. This etching technique is also applicable to many other kinds of carbon-based films. Fig. 2d and e shows the micro patterns based on single layer graphene and thin film of reduced graphene oxide, respectively. Therefore, this plasma patterning strategy is a promising candidate for the fabrication of different kinds of carbon-based devices.

The mask-free fabrication processes of CNT-based all-solid-state flexible MSCs are shown in Fig. S4. The structure of the MSCs is demonstrated by the typical SEM image of one finger electrode in Fig. 3a. The width of the finger electrode and the interspace are 900 and 300 μm respectively. Fig. 3b and c shows the top view SEM images of the finger electrode and the interspace respectively. There are very few CNTs which are in pieces in the interspace, meaning that the etched lines can serve as good separators between the positive and negative interdigitated electrodes. To further investigate the morphology of the finger electrode, the edge of the finger electrode is shown by the sectional SEM image in Fig. 3d. The sectional SEM images of the finger electrode and the space are shown in Fig. 3e and f, which also prove the high etching efficiency of our technique.

To investigate the effect of the micro-scale structure of the MSC on its electrochemical properties, different configurations were fabricated and tested. Fig. 4a shows MSCs with 4 (MSC4), 8 (MSC8), and 12 (MSC12) interdigitated electrodes. The electrode widths of these kinds of MSCs are 900, 1500, and 3300 μm respectively and the interspace widths are all 300 μm, as shown in Fig. S5. The electrochemical characterization of MSCs was performed by two-electrode cyclic voltammetry (CV) and galvanostatic charge-