Silver nanowires as the current collector for a flexible in-plane micro-supercapacitor via a one-step, mask-free patterning strategy

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Abstract

The fabrication of a current collector-contained in-plane micro-supercapacitor (MSC) usually requires the patterning of the current collector first and then subsequent patterning of the active material with the assistance of a photoresist and mask. However, this two-step patterning process is too complicated and the photoresist used is harmful to the properties of nanomaterials. Here, we demonstrate a one-step, mask-free strategy to pattern the current collector and the active material at the same time, for the fabrication of an all-solid-state flexible in-plane MSC. Silver nanowires (AgNWs) are used as the current collector. An atmospheric pressure pulsed cold micro-plasma-jet is used to realize the one-step, mask-free production of interdigitated multi-walled carbon nanotube (MWCNT)/AgNW electrodes. Remarkably, the fabricated MWCNT/AgNW-based MSC shows good flexibility and excellent rate capability. Moreover, the performance of properties including cyclic stability, equivalent series resistance, relaxation time and energy/power densities of the MWCNT/AgNW-based MSC are significantly enhanced by the presence of the AgNW current collector.

Supplementary material for this article is available online

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(Some figures may appear in colour only in the online journal)

1. Introduction

Supercapacitors (also called electrochemical capacitors) have been widely applied in energy storage because of their unique features such as high power densities, long cycling lifetimes, and fast charge/discharge capabilities [1, 2]. Among supercapacitors, all-solid-state flexible micro-supercapacitors (MSCs) have attracted significant attention owing to extensive demand for portable and wearable microelectronic devices [3–6]. In general, MSCs are fabricated either through the configuration of sandwich-like electrodes, or in-plane interdigital electrodes. Due to the improved electrochemical performance, reduced device volume, and easier integration into microelectronic devices, the in-plane interdigital design is preferred over the conventional sandwich-like design [3, 7–9].

Most research into all-solid-state flexible MSCs focuses on the development of active materials [10–13] and solid-state electrolytes [14–16]. However, research into current collectors is still limited. Up to now, materials including silver nanowire (AgNW) [17–19], graphene [20], nickel layer [21], and titanium-gold [22–25] have been employed as current collectors.
collectors in the design and fabrication of MSCs. AgNW has the advantages of excellent conductance, low-cost fabrication, solution-processability and excellent flexibility [26–28]. On the basis of these properties, AgNW is used as the conducting bridge in the active material of in-plane MSCs [29]. However, when employed as a current collector, AgNW is mainly suitable for the fabrication of conventional sandwich-like MSCs, but is inapplicable for the fabrication of in-plane MSCs due to the lack of patterning strategies. Besides, current collectors such as graphene can only slightly enhance the performance of MSCs, and current collectors such as nickel layer suffer from poor flexibility. So both these kinds of current collector are not good choices. Titanium-gold is widely used as the current collector for in-plane MSCs. Unfortunately, the fabrication process of titanium-gold-based in-plane MSCs—which requires the patterning of the current collector first and the subsequent patterning of the active material with the assistance of a photoresist and mask [29–35]—are high-cost and especially complicated. Moreover, the photoresist used in the fabrication process affects properties such as the active surface and porous structure of the active materials [36]. Therefore, more effort must be devoted to developing novel patterning strategies for current collector-contained in-plane MSC fabrication.

In this work, we use AgNWs as the current collector to fabricate all-solid-state flexible in-plane MSCs through one-step, mask-free patterning of both the active material and the current collector. Multi-walled carbon nanotubes (MWCNTs) are used as the active material, for their unique structure, high surface area and outstanding chemical stability [37–39]. An atmospheric pressure pulsed cold micro-plasma-jet is used to realize the one-step production of interdigitated MWCNT/AgNW electrodes. The micro-plasma-jet, which is formed by discrete plasma bullets [40], is able to etch MWCNTs [41] as well as AgNWs [42]. Once the plasma bullets come into contact with the MWCNT/AgNW film, the electrical charges in the bullets instantly flow in the samples and thus strong joule heating is induced, resulting in the etching of MWCNTs and AgNWs. Meanwhile, the plasma-jet contains a high concentration of 

\[
O_3
\]

which can etch MWCNTs directly [43]. Therefore, the interdigitated MWCNT/AgNW electrodes can be easily produced through micro-plasma-jet etching. The fabricated MWCNT/AgNW-based MSC presents good flexibility under cyclic bending as well as excellent rate capability. What’s more, the electrochemical performance—including cyclic stability, equivalent series resistance (ESR), relaxation time and energy/power densities—of the MWCNT/AgNW-based MSC is significantly enhanced by the presence of a AgNW current collector.

2. Experimental

2.1. Materials and characterization

MWCNTs with an average length of 10 μm (purity > 95%) were provided by Nanjing XFNANO Materials Tech Co., Ltd. AgNWs with an average length of 20 μm (purity > 99.5%) were provided by Guangdong Nanhai ETEB Technology Co., Ltd. A scanning electron microscope (SEM, Nova NanoSEM 450) and a transmission electron microscope (TEM, Tecnai G2 20) were employed to study the morphology of the samples. Electrochemical measurements including cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS) were carried out in a two-electrode system using a workstation (CorrTest, CS310) at room temperature.

2.2. Preparation of the MWCNT/AgNW composite film

Figure 1(a) shows a schematic diagram of the preparation of the MWCNT/AgNW composite film. A MWCNT solution with a concentration of 0.1 mg ml⁻¹ in de-ionized water, and a AgNW solution with a concentration of 0.01 mg ml⁻¹ in ethyl alcohol were prepared for use. MWCNTs were dispersed into de-ionized water with the help of sodium dodecyl sulphate (SDS, 0.5 mg ml⁻¹). Firstly, 60 ml of MWCNT solution was taken out and vacuum filtered with the assistance of a membrane (mixed cellulose ester). The pore size of the membrane was 220 nm. After this filtration process, a MWCNT layer was formed on the membrane. Secondly, 50 ml of AgNW solution was put into the same filtration cap for a second filtration process. Thus a MWCNT/AgNW composite film was obtained on the membrane. Then, a piece of polyethylene terephthalate (PET) was put on the membrane followed by continuous vacuum filtering for 10 min to enhance the adhesion between the MWCNT/AgNW composite film and the PET. At last, the membrane and PET were put into an acetone bath. As the membrane dissolved, a uniform MWCNT/AgNW film with a total thickness of 1.2 μm adhered on PET was obtained.

2.3. Generation of the micro-plasma-jet

Figure 1(b) shows a schematic illustration of the experimental setup for micro-plasma-jet generation. A glass tube, which had a nozzle outlet at the lower side and a steel needle inside it, was used to produce the plasma-jet. The diameters of the glass tube, the nozzle outlet, and the tip of the steel needle were 1 mm, 50 μm, and 30 μm respectively. He gas with a flow rate of 98 sccm and O₂ gas with a flow rate of 2 sccm were used as the mixed working gas. A pulsed direct current signal (voltage amplitude: 7 kV, pulse frequency: 6 kHz, pulse width: 800 ns) was connected to the steel needle, serving as the power supply. The inset of figure 1(b) shows a photographic image of the micro-plasma-jet, which was produced around the tip of the steel needle and shot out from the nozzle outlet.

2.4. Fabrication of the in-plane MSC

Figure 1(c) shows a schematic diagram of the fabrication of the all-solid-state flexible in-plane MSC. The MWCNT/AgNW film on PET was fixed on a computer-controlled XY motorized stage. The micro-plasma-jet produced interdigitated electrodes on the film by scanning with a velocity of 1 mm s⁻¹. After this, two pieces of copper foil were adhered
on the edge of the two interdigitated electrodes with the assistance of conductive silver ink for better measurement. PVA–H₃PO₄ was then drop-coated as the gel electrolyte. The PVA–H₃PO₄ electrolyte was synthesized by dissolving 4 g of PVA (Mₐ ≈ 95 000 g mol⁻¹, Acros) and 3.2 g of H₃PO₄ (85 wt% aqueous solution, Aldrich) in 60 ml of deionized water. One of the fabricated flexible in-plane MSCs with interdigitated MWCNT/AgNW electrodes is shown in figure 1(d).

2.5. Calculation of the volumetric capacitances, energy and power densities

The capacitance (C_{device}) of the flexible in-plane MSC was calculated using the formula

\[ C_{device} = \frac{1}{2v (V_f - V_i)} \int_{V_i}^{V_f} I(V) \, dV. \]  

(1)

The volumetric capacitance (C_v) was calculated according to the formula

\[ C_v = \frac{C_{device}}{V} \]  

(2)

where v is the scan rate, V_i and V_f are the potential limits of the CV curves, and I(V) is the discharge current. V refers to the whole volume of the MSC device, including the volumes of the active materials, the interspaces between electrodes, and the AgNW current collectors.

The volumetric energy density E (Wh cm⁻³) and power density P (W cm⁻³) were estimated from the CV curves by:

\[ E = \frac{C_v \times (\Delta V)^2}{2 \times 3600} \]  

(3)

\[ P = \frac{E \times 3600}{\Delta t} \]  

(4)

where \( \Delta V \) is the operating voltage window of the discharging process and \( \Delta t \) is the discharge time.

3. Results and discussion

Figures 2(a)–(d) show the digital photographs and SEM images of both the MWCNT side and the AgNW side of the fabricated MWCNT/AgNW composite film. The digital photographs (figures 2(a), (b)) of the two sides of the film present completely different colours. The top-view SEM images (figures 2(c), (d)) show the random network morphology of MWCNTs and AgNWs in the composite film. Figure S1 is available online at stacks.iop.org/NANO/29/055401/mmedia, and shows the TEM images of the MWCNTs and AgNWs, whose diameters are 15 nm and 30 nm respectively. Figure 2(e) shows the cross-sectional SEM image of the MWCNT/AgNW film, which consists of a MWCNT layer with a thickness of 1 μm and a AgNW layer with a thickness of 200 nm. Figure 2(f) shows the top-view SEM image of one finger electrode of the fabricated MWCNT/AgNW-based in-plane MSC. The width of the finger electrode is 800 μm and the width of the interspace between electrodes is 200 μm. More details about the dimensions of the MSC are shown in figure S2. The total area of the MSC is calculated to be 0.72 cm². Figure S3 shows the top-view and cross-sectional SEM images of the interspace between finger electrodes. After the micro-plasma-jet etching, the MWCNTs in the interspace are removed and the AgNWs are broken into
pieces, proving that the interspaces are good separators between interdigitated electrodes and the micro-plasma-jet is suitable for MWCNT-AgNW-based MSC fabrication.

To demonstrate the advantages of AgNWs as a current collector, the electrochemical performance of the MWCNT/AgNW-based MSC (C-A-MSC) is compared with that of the MWCNT-based MSC (C-MSC). The MSC based on bare interdigitated AgNWs (A-MSC) is also electrochemically tested to observe the contribution of a AgNW layer to the capacitance. Figure 3(a) shows the CV curves of the C-A-MSC, C-MSC and A-MSC at a scan rate of 10 mV s⁻¹. The stack capacitances of the C-A-MSC, C-MSC and A-MSC at this scan rate are calculated to be 2.29 F cm⁻³, 2.17 F cm⁻³ and 0.08 F cm⁻³ respectively. The capacitance of the C-A-MSC is a little higher than that of the C-MSC, which is due to a slight contribution of the AgNW layer to the capacitance,
Figure 4. Electrochemical performance of the C-MSC and C-A-MSC. (a) Cyclic stability of the C-MSC and C-A-MSC after 10 000 cycle tests at a scan rate of 200 mV s$^{-1}$. The inset presents the CV curves of the C-A-MSC in the first and last of the 10 000 cycles. (b) Complex plane plots of the impedance spectra. The inset presents the focused high-frequency region. (c) Plots of normalized $C''$ ($C'' = Z' / |Z|^2$) versus frequency derived from the impedance spectra. (d) Ragone plots of energy density versus power density for the C-MSC and C-A-MSC compared to reference data from other carbon-based in-plane MSCs.

Figure 5. (a) Bending test of the C-A-MSC. (b) CV curves for the C-A-MSC under different bend radii. (c) CV curves of the C-A-MSC during cyclic bending with a bend radius of 4 mm. (d) Capacitance retention of the C-A-MSC during cyclic bending.
and the enhancement of ESR through the introduction of a AgNW current collector. Figures 3(b) and (c) show the CV curves at scan rates of 100 mV s\(^{-1}\) and 1000 mV s\(^{-1}\) respectively. Interestingly, when the scan rate increases, the CV curves of the C-A-MSC maintain a quasi-rectangular shape while the curves of the C-MSC do not. Figure 3(d) shows the variations in the stack capacitances of these MSCs with scan rate. The stack capacitances of the A-MSC are much smaller than those of the C-A-MSC and C-MSC at each scan rate, suggesting a slight contribution of the pure and bare AgNW thin film to the capacitance. At a scan rate of 2 V s\(^{-1}\), the stack capacitance of the C-A-MSC is about three times larger than that of the C-MSC. Remarkably, the stack capacitance of the C-A-MSC decreases much more slowly than that of the C-MSC during the increasing of the scan rate, demonstrating a significant improvement in rate capability with the presence of AgNWs as the current collector. Figure 3(e) shows the areal capacitances of these MSCs as a function of scan rate. The areal capacitances of the C-A-MSC, C-MSC and A-MSC at a scan rate of 10 mV s\(^{-1}\) are calculated to be 274.8 \(\mu\)F cm\(^{-2}\), 227.0 \(\mu\)F cm\(^{-2}\) and 1.6 \(\mu\)F cm\(^{-2}\) respectively. The comparisons of areal capacitances at different scan rates reveal the same conclusions as the stack capacitance results. As the C-A-MSC has the best performance, more electrochemical tests are performed on it. Figure 3(f) shows the GCD curves of the C-A-MSC measured at current densities between 0.07 A cm\(^{-3}\) and 0.28 A cm\(^{-3}\), which are all triangular in shape. The Coulombic efficiencies at current densities of 0.28 A cm\(^{-3}\), 0.21 A cm\(^{-3}\), 0.14 A cm\(^{-3}\), and 0.07 A cm\(^{-3}\) are 96.3\%, 94.7\%, 86.6\%, and 73.1\% respectively. GCD comparisons between the C-A-MSC and C-MSC at different current densities are shown in figure S4, which displays the better GCD performance of the C-A-MSC. All the MSCs above were fabricated according to the dimensions shown in figure S2. It is worth noting that these dimensions were selected in advance through performance comparison under different dimensions. Figure S5(a) shows the stack capacitances of the C-A-MSC with four (C-A-MSC(4)), eight (C-A-MSC(8)), and twelve (C-A-MSC(12)) finger electrodes at scan rates from 10 mV s\(^{-1}\) to 2000 mV s\(^{-1}\). Among these three MSCs, C-A-MSC(12) has the best performance, thus this dimension is selected. The effect of the thickness of the AgNW current collector on the capacitance of the MSC was also investigated. It is shown in figure S5(b) that the rate capability of the C-A-MSC is significantly enhanced with the increasing of the thickness of the AgNW layer, until the thickness exceeds 200 nm. As a result, a thickness of 200 nm is selected for the experiment.

Further electrochemical properties of the C-A-MSC and C-MSC are compared and analysed. As depicted in figure 4(a), the stack capacitance of the C-A-MSC retains 92.3\% of its initial value after 10 000 cycles of CV testing at a scan rate of 200 mV s\(^{-1}\). By contrast, the C-MSC retains only 90.2\% of its initial capacitance after the cyclic test with the same experimental conditions. The CV curves of the C-A-MSC for the first and last of the 10 000 cycles are shown in the inset of figure 4(a). Figure 4(b) shows the EIS results for the MSCs, and the equivalent circuit is shown in figure S6.

The low-frequency segments of the plots show nearly vertical lines, displaying the typical features of electric double-layer supercapacitors. The mid-frequency segment with a slope of 45° is called the Warburg resistance. Compared with the C-MSC, the C-A-MSC presents a much shorter Warburg region, suggesting a lower charge-transfer resistance and a more efficient ion diffusion process. Moreover, a high-frequency semicircle is observed in the inset of figure 4(b), which is possibly caused by the porous nature of the active materials [44]. The ESR values of the C-A-MSC and C-MSC are 269 Ω and 962 Ω respectively. The smaller ESR of the C-A-MSC also confirms the improvement in electrochemical performance with the presence of AgNWs as the current collector. Figure 4(c) shows plots of normalized capacitance (\(C'\)) versus frequency. The relaxation time constant (\(\tau_0\)) is related not only to the point where the behaviour of the supercapacitor transfers from capacitive to resistive, but also to the point of maximum energy dissipation [9, 41]. Here, \(\tau_0\) of the MSC can be calculated according to the equation \(\tau_0 = 1/f_0\), where \(f_0\) is the frequency at the peak in the plot. The value of \(\tau_0\) for the C-A-MSC is calculated to be 0.182 s, which is much smaller than that for the C-MSC (0.738 s). The Ragone plot in figure 4(d) presents the stack energy and power densities of the MSCs. The C-A-MSC delivers an energy density of 0.17 mWh cm\(^{-3}\) at power density 1.2 W cm\(^{-3}\), which is comparable to, or higher than, those of recently reported all-solid-state flexible in-plane MSCs [8, 13, 45]. Moreover, the power/energy performance of the C-A-MSC is superior to that of the C-MSC, which demonstrates the advantages of a AgNW current collector and is in agreement with the CV results.

The good mechanical strength of MWCNTs and AgNWs endows the C-A-MSC with excellent mechanical flexibility. The flexibility of the C-A-MSC is investigated by fixing one side of the MSC, and convexly bending the other side repeatedly, as displayed in figure 5(a). Figure 5(b) shows the CV curves of the bent C-A-MSC under different bend radii at a scan rate of 100 mV s\(^{-1}\). The nearly identical quasi-rectangular shapes of these CV curves suggest that bending has almost no effect on the electrochemical properties of the C-A-MSC. Moreover, the C-A-MSC also presents excellent stability under cyclic bending. Figure 5(c) shows CV curves of the C-A-MSC during cyclic bending, with a bend radius of 4 mm. A fatigue test reveals that after 800 bending–stretching cycles, 94.9\% of the initial capacitance of the device is retained (figure 5(d)). These results demonstrate that the flexible C-A-MSC has outstanding mechanical and electrochemical stability under cyclic bending, ensuring great potential for portable energy devices and microelectronic devices.

4. Conclusion
We successfully use AgNWs as the current collector for all-solid-state flexible in-plane MSC fabrication via a one-step mask-free patterning strategy. The atmospheric pressure pulsed cold micro-plasma-jet applied can easily realize the
one-step mask-free patterning of the current collector and the active material at the same time. This one-step patterning strategy is more facile than the traditional two-step patterning method. Compared with the MSC without AgNW current collector, the fabricated MSC with AgNW current collector shows much better rate capability. Moreover, the AgNW current collector brings significant improvements to the MSC’s performance, including in cyclic stability, ESR, relaxation time, and energy/power densities. Furthermore, the MSC with AgNW current collector presents good flexibility, with retention of 94.9% of the device’s initial capacitance after 800 stretching–bending cycles. This work provides a facile route for the fabrication of current collector-contained high-performance flexible in-plane MSCs.

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