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Binder-free activated graphene compact films for all-solid-state micro-supercapacitors with high areal and volumetric capacitances

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ABSTRACT

Micro-supercapacitors (MSCs) hold great promise as highly competitive miniaturized power sources satisfying the increased demand in microelectronics; however, simultaneously achieving high areal and volumetric capacitances is still a great challenge. Here we demonstrated the designed construction of binder-free, electrically conductive, nanoporous activated graphene (AG) compact films for high-performance MSCs. The binder-free AG films are fabricated by alternating deposition of electrochemically exfoliated graphene (EG) and nanoporous AG with a high specific surface area of 2920 m^2/g, and then dry transferring onto the target substrates with a high-pressure mechanical densification process. Remarkably, the resulting compressed AG films showed uniform morphology in lateral dimensions, high conductivity (60 S/cm), nanoporous feature (<10 nm), and high packing density (0.8 g/cm^3). The all-solid-state MSCs (AG-MSCs) based on these AG films simultaneously delivered an unprecedented areal capacitance of 89.5 mF/cm^2 and volumetric capacitance of 147 F/cm^3 for MSCs at 10 mV/s. Moreover, the fabricated AG-MSCs could be operated at a large scan rate of 10,000 mV/s, and showed outstanding cycling stability (capacitance retention of $>99.6\%$ after 10,000 cycles). Our results suggested that AG-MSCs are competitive for prospective applications of miniaturized energy storage devices.

1. Introduction

Micro-supercapacitors (MSCs) hold promise as highly competitive miniaturized power sources satisfying the increased demand in portable, wearable and implantable microelectronics, since they potentially integrate the unprecedented advantages of high power density of electrolytic capacitor (10^2–10^3 W cm^{-3}) and energy delivery of lithium thin-film battery (10 mW h cm^{-3}) [1–4]. The pseudocapacitive MSCs utilizing Faradaic reactions of metal oxides, e.g., RuO_2 [5], MnO_2 [6], VS_2 [7], and conducting polymers, e.g., polypyrrole [8], and polyaniline [9,10], have been intensively explored, but suffer from low power density, short cycle life, and slow frequency response [11]. To overcome these drawbacks, carbon-based MSCs store electric energy in a double layer at electrochemically stable, high specific surface area electrodes have gained increased attentions, including activated carbon [12,13], carbide-derived carbon [14,15], onion-like carbon [16], carbon nanotubes (CNTs) [17,18], nanoporous carbon (NPC) [19], and graphene [2,3,20–23]. In particular, high surface area of nanocarbons for MSCs can provide an extensively accessible interface between the electrode and electrolyte, and allow the large storage of gravimetric capacitance, power and energy density. Unfortunately, the volumetric metrics in both capacitance and energy density (per volume of the active material) are not impressive due to their low packing densities [24,25].

Simultaneously achieving high areal and volumetric capacitances of MSCs remains a great challenge [1,26], because both of them tend to vary oppositely with the increased thickness of electrode films, in particular, composed of high surface area nanocarbon materials. For instance, electrochemically deposited films of onion-like carbon (OLC), with a specific surface area of 500 m^2/g, for MSCs was able to cycle at a high scan rate of 200 V/s,

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but showed a low volumetric capacitance of 1.3 F/cm^3 [16]. Recently, a 7.6 μm-thick film of laser-scribed graphene, with exceptionally high surface area of over 1500 m^2/g, for MSCs demonstrated a high power density of 200 W/cm^3; however, the volumetric capacitance reported was only 3.05 F/cm^3 [27]. Similarly, other nanocarbon films consisting of high surface area NPC [19], reduced graphene oxide/CNTs (rGO/CNT) [28], vertically aligned CNTs (VACNT) [29] exhibited impressive areal capacitance of >5 mF/cm^2, but in most cases presented relatively low volumetric capacitance of <28 F/cm^3 due to their low packing densities (typically <0.5 g/cm^3). Undoubtedly, the low volumetric capacitance of these nanocarbon-based films for MSCs is attributed to the lack of advanced manufacture technologies that efficiently process high surface area activated materials into high packing density films. Currently, great efforts have been devoted to introducing new nanocarbon materials for MSCs, however, the reasonable design and manufacture of electrically conductive, highly porous, densely compact, binder- and additive- free films composed of high surface area nanocarbons have not been reported for high areal and volumetric capacitance MSCs.

In this work, we demonstrated the construction of binder-free, electrically conductive, highly porous, activated graphene (AG) compact films with remarkable areal capacitance and volumetric capacitance for high-performance MSCs. The binder-free AG compact films were fabricated by alternating deposition of two different graphene materials, e.g., electrochemically exfoliated graphene (EG) and nanoporous AG with a high specific surface area of 2920 m^2/g (Fig. 1a–e), and then dry transferring onto the target substrates (e.g., Si wafer) with a high-pressure mechanical densification process (Fig. 1f and g). Afterwards, the resulting compressed AG films exhibited uniform morphology in lateral dimensions, high conductivity (60 S/cm), nanoporous feature (<10 nm), and high packing density (0.65–0.8 g/cm^3). The all-solid-state planar MSCs (AG-MSCs) manufactured by lithographical micropatterns of the as-produced AG films on silicon wafers (Fig. 1h and i), delivered an unprecedented areal capacitance of 89.5 mF/cm^2 and volumetric capacitance of 147 F/cm^3 for MSCs. Moreover, the fabricated AG-MSCs could be operated at a large scan rate of 10,000 mV/s with a significant capacitance of 19.4 F/cm^3, and showed excellent long-life cycling stability (99.6% after 10,000 cycles).

2. Experimental

2.1. Synthesis of AG

The AG was fabricated by the KOH activation of graphene oxide (GO) derived from natural graphite flake by a modified Hummers method [30,31]. Typically, 50 mL GO with a high concentration of 7 mg/mL and 2100 mg KOH powder (mass ratio of GO:KOH is 1:6) were first dispersed into 50 mL water and strongly stirred for 1 h at a speed of 300 rpm. Then, the water in the mixed solution was naturally evaporated at 100 °C until black slurry of GO/KOH was formed. Afterward, the mixed slurry was directly transferred into a stainless steel tube and put into a furnace, and kept for 30 min in a N_2 gas flow of 300 ml/min, and heated at 110 °C for 1 h to dry the slurry. Further, the activation of GO was conducted at 700 °C for 1 h with a heating rate of 3 °C/min. After cooling down, the mixture was washed with 1 mol/L HCl to completely remove

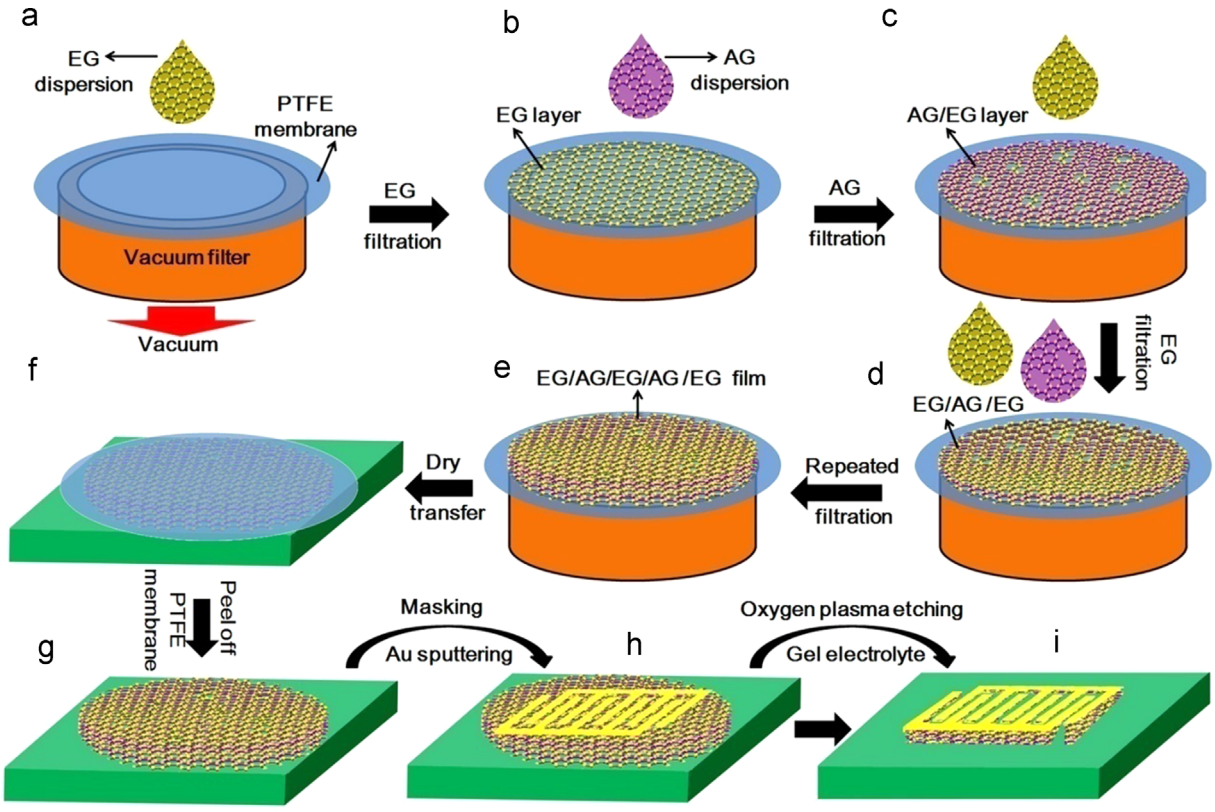

Fig. 1. Schematic illustration of binder-free AG compact films for in-plane MSCs. (a) Vacuum filtration of EG dispersion on a PTFE membrane filter. (b) Vacuum filtration of AG dispersion on the top of EG film. (c) Vacuum filtration of EG dispersion on the top of an AG/EG film. (d) Repeated filtration of the AG layer and EG layer on the EG/AG/EG film. (e) Dry transfer of the alternating deposited AG film (EG/AG/EG/AG/EG) on the surface of SiO_2/Si wafer under high pressure. (f) A compressed AG film on SiO_2/Si wafer after peeling off the PTFE membrane. (g) Thermally evaporation of gold micropatterns as current collector. (h) Oxygen plasma etching and drop-casting of gel electrolyte on interdigital electrodes. (i) An all-solid-state AG-MSC achieved.