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Facile synthesis and electrochemical performances of binder-free flexible graphene/acetylene black sandwich film

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ABSTRACT

Graphene/acetylene black sandwich film was fabricated by a simple vacuum filtration procedure using a stable complex suspension of graphene oxide (GO) and acetylene black followed by a hydroiodic acid (HI) immersion process to fully reduce the GO to graphene sheets. The self-restacking of individual graphene sheets were greatly alleviated and electric conductivity was obviously improved using the acetylene black nanoparticles as both effective spacers to expand the inter-layer interval of the individual graphene sheets during the film assembly course and highly conducting bridges to facilitate the electron/ion transfer between the upper and lower graphene sheets. The flexible graphene/acetylene black film was utilized as supercapacitor electrode without additional conductive additives, binders and current collectors, which achieved an obviously higher specific capacitance (ca. 136.6 $F g^{-1}$ at 0.5 $A g^{-1}$) and much better specific capacitance retention at high current densities than that of the pure graphene film electrode, indicating that such a novel sandwich film structure allows for a higher charge storage capability. More importantly, the assembled symmetric supercapacitor device displayed a satisfactory specific capacitance of 59.2 $F g^{-1}$ at 0.1 $A g^{-1}$, 47.6 $F g^{-1}$ at 0.5 $A g^{-1}$ and 42.8 $F g^{-1}$ at 1 $A g^{-1}$, and only negligible 4.05% capacitance degradation have been found after 1000 continuous charge-discharge cycles at 0.5 $A g^{-1}$, revealing outstanding rate capability, excellent electrochemical reversibility and long-term cyclability. These results proved that such a flexible and highly conductive graphene/acetylene black film can be promising electroactive materials in the development of advanced electrochemical energy storage devices.

1. Introduction

With a rapidly growing demand for portable electronic products (such as folding displays and wearable devices [1,2]), considerable efforts have been made to explore ultrathin and foldable thin film energy storage devices. Among them, flexible supercapacitors with free-standing electrodes present great application promise in future portable electronic devices owing to their high power density and fast charge-discharge rate [3–5].

One key challenge for the development of flexible supercapacitors is to search ultra-light, effective, safe, clean and cheap electrode materials and design special nanostructures. Graphene, the first two-dimensional atomic crystal, emerges as a conceptually new class of carbon material, and its unique planar nanostructure and unusual properties (such as high specific surface area, outstanding electrical conductivity, superior mechanical flexibility, broad electrochemical window and tunable pore structure) promise its potential applications in electrochemical energy storage as the electrode materials for foldable supercapacitors [6]. Furthermore, it was demonstrated that graphene paper or graphene-based film materials showed extraordinary electrochemical performances and were considered as promising candidates for the construction of next-generation flexible storage devices, no matter be directly used or incorporated with other electrode materials [7–10]. However, the specific capacitance calculated from the charge-discharge curves of unmodified graphene-based films as freestanding electrodes is in the range of 51 to 73 $F g^{-1}$ [5,11–13] and definitely needed to be enhanced owing to single graphene sheets can easily restack together because of their van der Waals bonding during the electrode

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fabrication process [14], bringing about the great decrease in effective surface areas and energy densities for electrochemical energy storage.

Recently, carbon nanotubes [15–19], mesoporous carbon [20], porous silica [21], carbon nanofiber [22], carbon black [11], Au metal nanoparticles [23], silver-nanowire [24], nano-sized TiO_2 [25], vanadium oxide nanowire [14], CuO nanosheets [26], sulfur nanoparticles [27], polyaniline [28–30], cellulose nanofiber [31], and cation surfactants [32] have been incorporated into the interlayer of the individual graphene sheets to overcome their self-agglomeration and improve the conductivity as free-standing paper-like graphene electrodes with high performances for practical electrochemical energy storage. These electrochemically active spacers help to maintain the physical separation of the graphene sheets, enhance their effective ionic and electronic transport rate, and give rise to a significant improvement in electrochemical capacitance performances [33]. Moreover, acetylene black has been widely used as conductive additives in the electrode preparation process [34] due to its excellent conductivity, large specific area, good rate capability, low density, negligible cost and high purity, but has not been utilized to act as highly conductive separator for individual graphene sheets yet.

In light of the above considerations, novel binder and current collector-free flexible graphene/acetylene black sandwich films were prepared and instantly used for supercapacitor application via a simple, controllable and efficient vacuum filtration from a stable complex suspension of graphene oxide (GO) and acetylene black followed by a HI immersion process to reduce the GO to graphene sheets. Traditionally, for supercapacitor, conductive additives and polymer binders need to be uniformly blended with electroactive materials in the electrode preparation process, and then jointly pressed on current collectors (such as nickel foams and aluminum foils), which results in a low mass loading of electroactive materials, electrochemical columbic efficiency and high cost. Recently, various methods, such as chemical vapor deposition process [35], in-situ polymerization [36] and direct growth [37], have been employed to prepare binder or additive-free electrodes for supercapacitors.

Herein, we report an effective route to obtain flexible graphene/acetylene black film via a facile vacuum filtration-chemical reduction approach, which can be directly utilized as supercapacitor electrode without additional conductive additives, binders and current collectors. Furthermore, acetylene black nanoparticles that were intercalated between graphene sheets can act as both high conductive spacers to effectively prevent restacking of the graphene sheets and excellent electrode materials for electric double layer capacitors (EDLCs).

2. Experimental Section

2.1. Reagents and Materials

Commercial natural graphite (99.9995 wt.% purity, Alfa Aesar), $NaNO_3$ (99% purity, Sinopharm Chemical Reagent Co. Ltd), H_2SO_4 (96% purity, Sinopharm Chemical Reagent Co. Ltd), $KMnO_4$ (99% purity, Sinopharm Chemical Reagent Co. Ltd), HCl (Sinopharm Chemical Reagent Co. Ltd), H_2O_2 (30 wt.% aqueous solution, Sinopharm Chemical Reagent Co. Ltd), anodic aluminum oxide (AAO) membrane (Whatman Anodisc TM 47), hydroiodic acid (HI, 55 wt.%, Aladdin-reagent Inc.) and acetylene black (Chevron Chemical Company, TX, USA) were used as received.

2.2. Preparation of Graphite Oxide Suspension

As described in literatures [38,39], graphite oxide used in present study was made by a complete oxidation process. In brief, 1 g natural graphite powders (Sigma–Aldrich, ca. 20 μm) and 1 g $NaNO_3$ were placed in a reaction vessel that was preliminarily immersed in an ice bath, followed by slowly adding 35 ml H_2SO_4 under violent stirring. After 5 g $KMnO_4$ was gradually added over about 1 h, the mixture was gently stirred at room temperature and allowed to go on for 120 h to fully oxidize graphite powder to graphite oxide (GO). Subsequently, the GO obtained was added to 100 ml of 5 wt.% H_2SO_4 aqueous solutions over about 2 h with gentle stirring, and then 100 ml of 30 wt.% H_2O_2 was added. After centrifugation and washing procedure with an aqueous solution of 5 wt.% HCl, GO suspension was uniformly dispersed in deionized water by ultrasonication. Its concentration was measured by a vacuum freeze drying process and diluted with deionized water to 0.375 mg mL^{-1}.

2.3. Synthesis of graphene/acetylene black sandwich films

1.875 g acetylene black was added into the above as-prepared 50 mL GO suspension and homogeneously mixed together using ultrasound. Afterwards, the obtained well-dispersed aqueous solution was filtrated using anodic aluminum oxide (AAO) membrane and then dried in a vacuum oven at 60 °C for 0.5 h. After been peeled off from the AAO membrane, the GO/acetylene black film was fully immersed into 10 mL 55 wt.% HI solution and kept at 100 °C for 1 h to completely reduce the GO film to graphene film [40]. Finally, the obtained graphene/acetylene black film was cooled to room temperature, washed with DI water and vacuum-dried.

In comparison, pure graphene film without acetylene black was also synthesized in the same way.

2.4. Structure and morphology characterization

The structural and morphological analysis of the samples was performed by field-emission scanning electron microscope (FESEM, S4800, Hitachi). The specific surface area of the pure graphene film and graphene/acetylene black film were determined by Brunaur–Emmett–Teller (BET) surface analyzer (ASAP 2010, Micromeritics, USA).

2.5. Electrochemical characterization

The electrochemical behaviors of the graphene/acetylene black film electrode were evaluated using cyclic voltammetry (CV), galvanostatic charge-discharge and electrochemical impedance spectroscopy (EIS) and cycle-life tests at VersaSTAT3 electrochemical workstation (Princeton Applied Research, USA). CV curves were conducted in a potential range between −0.5 and 0.3 V versus Hg/HgO at scan rates of 2–200 mV s^{-1}. Galvanostatic charge-discharge tests were carried out in the potential range of −0.9 to 0.1 V (vs. Hg/HgO) at different current densities of 0.5, 1, 2, 3 and 4 A g^{-1}, and the cycling behavior was characterized up to 1000 cycles. Electrochemical impedance spectroscopy was carried out to prove the capacitive performance at open circuit potential with a frequency range of 0.01–10^5 Hz. These electrochemical measurements were carried out at room temperature in a 6 mol L^{-1} KOH solution using a three-electrode system consisting of the graphene/acetylene black film electrode directly as working electrode, a Hg/HgO electrode as reference electrode and platinum plate (1 cm × 1 cm) as counter electrode.

For further accurate evaluation of the graphene/acetylene black film electrode, a symmetric electrochemical capacitor was assembled using two same graphene/acetylene black films (1 × 1 cm^2) as the positive electrode and negative electrode, a