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RAPID COMMUNICATION

Densely packed graphene nanomesh-carbon nanotube hybrid film for ultra-high volumetric performance supercapacitors

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Abstract
For the first time, we report a novel strategy to prepare densely packed graphene nanomesh-carbon nanotube hybrid film (GNCN) through a simple graphene etching process and subsequent vacuum-assisted filtration method. The ion diffusion ability of the GNCN film is greatly enhanced due to the contribution of cross-plane diffusion from graphene nanomesh and in-plane diffusion from CNT-graphene sandwiched structure. In addition, carbon nanotubes can also efficiently improve the overall electrical and mechanical properties of the hybrid film. Based on its high surface area, fast ion diffusion and high film density, the GNCN film electrode exhibits a specific capacitance of 294 F g^{-1} at 5 m V s^{-1}, higher than the RGO film (185 F g^{-1}), as well as excellent rate capability and outstanding cycling performance (93% capacitance retention after 5000 cycles). It is worth noting that the GNCN film electrode shows high energy density of 26 Wh L^{-1}, and ultra-high volumetric capacitance of 331 F cm^{-3}. The strategy provides a facile and effective method to achieve high volumetric performance electrode materials for supercapacitor.
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Introduction

With the rapid development of portable electronic devices, it is important to design and fabricate miniaturized energy storage devices that are required to have both high gravimetric and volumetric performances [1,2]. As an attractive energy storage device, supercapacitor has high power density, fast charge-discharge and long cycle life [3–8]. However, the improvement of the energy density of supercapacitor, especially for volumetric performances, faces an enormous challenge [9–12].

Graphene is considered as a promising candidate electrode material for supercapacitors due to its high surface area, excellent electrical conductivity and remarkable

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mechanical properties [13,14]. Unfortunately, the volumetric capacitances of graphene materials are rather low due to their high pore volume or low bulk density [15]. In order to overcome this question, functionalized dense graphene sheets with a large amount of oxygen-containing groups can provide an ultra-high pseudocapacitance, resulting in high volumetric capacitance [16,17]. Moreover, the other effective strategy is to increase the bulk density such as selecting densely packed graphene sheets, graphene fiber [12,18-20] or graphene film as electrode materials [21-25]. However, ion transport at the electrochemical interfaces is critical for effective energy storage in supercapacitors [26]. Recent advances in designing "spacers" in-between sheets, such as carbon nanotubes, [27-29] water, [30] liquid electrolyte, [15] open up new ways to address this challenge. For example, the packing density of film can be adjusted by controlling "spacers" content trapped in the film, and its high volumetric capacitance is up to 255 F cm^{-3} at 0.1 A g^{-1} in aqueous electrolyte [15]. Although in-plane ion diffusion coefficient of graphene film can be effectively improved, its cross-plane diffusivity is rather low [31]. Therefore, it is still a great challenge to fabricate dense free-standing graphene film that has fast ion diffusion in all direction, ensuring high capacitance and excellent rate performance.

Here, for the first time, we report a novel strategy to prepare densely packed graphene nanomesh-carbon nanotube (CNT) hybrid film (GNCN) through a simple graphene etching process and subsequent vacuum-assisted filtration method. Fast ion diffusion is mainly contributed to cross-plane diffusion from graphene nanomesh and in-plane diffusion from CNT-graphene sandwiched structure. In addition, CNTs can also efficiently improve the overall electrical and mechanical properties of the hybrid film. Based on its high surface area, fast ion diffusion and high film density, the GNCN film electrode displays an ultra-high volumetric capacitance of 331 F cm^{-3} at 5 mV s^{-1} in 6 M KOH, which is among the highest values for graphene film reported in aqueous electrolyte [24,27,28,32-34], as well as excellent rate capability and outstanding cycling performance (93% capacitance retention after 5000 cycles).

Experimental section

Preparation of graphene nanomesh (GN)-carbon nanotube (CNT) hybrid film (GNCN)

Graphene oxide (GO) was synthesized from purified natural graphite (300 μm, Qingdao Graphite Company) by a modified Hummers method [35]. CNTs (multi-walled CNTs, CNano Technology (Beijing) Limited, diameter of ~20 nm, length of 0.5~1μm) were refluxed in 10 wt% nitric acid for 30 min to remove impurities before use. GN was synthesized using a MnO_2 etching method based on our previous work [36]. GNCN film was prepared by a simple vacuum-assisted filtration method [30,32-34]. Briefly, 100 mL of GO suspension (0.5 mg mL^{-1}) and 5 mg CNTs were ultrasonicated for 1 h in an ultrasonic bath (KQ-600KDE, 600 W). Then, $KMnO_4$ was added into the solution, and stirred for 10 min. Subsequently, the resulting suspension was heated using a microwave oven (Haier, 2450 MHz, 700 W) for 5 min. After cooling to room temperature, 50 mL of deionized water, 100 μL hydrazine and 350 μL ammonia were added into the above mixture, stirred for 10 min and kept at 100 °C for 20 min in a water bath. Finally, the product was washed thoroughly with oxalic acid and hydrochloric acid (v/v, 1:1) and deionized water several times. 20 mL of GNCN suspension was vacuum filtrated through a mixed cellulose ester filter membrane (0.45 μm pore size) using Buchner funnel with sand core (40 mm in diameter), the obtained GNCN film was dried in air and then carefully peeled off from the filter membrane. For comparison, GN film and RGO film were prepared using graphene nanomesh and reduced graphene oxide in the absence of CNTs by the same procedure described above, respectively.

Characterization methods

The morphologies and thickness (d) of films were examined by a field emission scanning electron microscopy (SEM, SU70-HSD). The microstructures of the materials were investigated by transition electron microscope (TEM, JEOL JEM2010). The crystallographic structures of the materials were determined by X-ray diffraction (XRD) equipped with Cu Kα radiation (λ =0.15406 nm) at a scanning rate of 10° min^{-1} in the 2θ range from 10° to 80°. Raman spectra were recorded with a Jobin-Yvon HR800 Raman spectrometer with 632.8 nm wavelength incident laser light. Perkin-Elmer PHI-5700 ESCA System multifunctional photoelectron spectrometer was used to examine the surface chemical species of the samples by X-ray photoelectron spectroscope (XPS). The N_2 adsorption-desorption isotherms of the samples were measured at 77 K using NOVA 2000 (Quantachrome, USA) in order to determine the specific surface area which was calculated from the Brunauer-Emmett-Teller (BET) plot of the nitrogen adsorption isotherm. The pore size distribution curves were obtained from adsorption branch isotherms by density functional theory (DFT) method. The adsorbed amount at a relative pressure P/P_0 of 0.99 was used to estimate the total pore volume (V_t), which corresponds to the sum of the mesopore and micropore volumes.

Electrochemical measurements

The as-prepared free-standing films were directly fabricated as additive/binder-free working electrodes by cutting them into square slices with 1 x 1 cm^2 and then pressing the film between two nickel foam current collectors. The loading mass of the electrode was about 0.5 mg cm^{-2}. The electrochemical measurements were done in both three-electrode and two-electrode system. In three-electrode system, two nickel foam coated with film served as the working electrode, a platinum gauze electrode and a Hg/HgO electrode served as counter and reference electrodes respectively. The cyclic voltammetry (CV), the constant current charge/discharge and the electrochemical impedance spectroscopy (EIS) test were carried out on a CHI660C electrochemical workstation in a 6 M KOH aqueous solution at room temperature. CV tests of the three-electrode cell were investigated between −1 and 0 V (vs. Hg/HgO). The constant current charge/discharge was performed in the

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