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Reduced graphene oxide/carbon nanotube hybrid film as high performance negative electrode for supercapacitor

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ABSTRACT

Interconnecting different carbon building blocks, such as 1-dimensional (1D) carbon nanotubes (CNTs) and 2-dimensional (2D) graphene sheets, is an effective way to build hybrid carbon architectures with fascinating new properties. Here we report the synthesis of a binder-free reduced graphene oxide/carbon nanotube (rGO/CNT) hybrid film and its capacitive behaviour in both positive and negative potential window with 1 M Na_2SO_4 aqueous electrolyte. It is found that intercalating small amount of CNTs into rGO sheets result in excellent specific capacitance of 272 F g^{-1} at a scan rate of 5 mV s^{-1} in negative potential window of −0.8 to 0 V. In contrast, moderate specific capacitance of 132 F g^{-1} at the same scan rate is obtained in positive potential window of 0 to 0.8 V. The reason of the enhanced capacitance in negative potential window is discussed. We propose that the remarkable improvement of capacitance in negative potential window is mainly due to the strong cation adsorption at the oxidized surface of rGO sheets. The addition of CNTs can significantly improve the rate capability and cyclic stability of the electrode compared to that of pure rGO electrode. As-synthesized rGO/CNT hybrid film shows great potential in neutral aqueous electrolyte based asymmetric supercapacitors as high performance negative electrode, and other applications such as flexible batteries, seawater desalination, and biomedical applications.

1. Introduction

Supercapacitors have attracted considerable attention for decades owing to their high power density, fast charging/discharging rate and long cycle life [1]. However, the energy density of supercapacitors is still inferior to that of lithium-ion batteries (LIBs). Therefore, developing supercapacitor with high energy density while maintaining their intrinsic advantages is pivotal to meet future energy demands, but still remains a great challenge [2,3]. The enhancement of energy density could be achieved by combining electrochemical double layer capacitors (EDLCs) with pseudo-capacitors (faradaic) to improve capacitance, as well as by broadening the operating voltage window [4–6]. Aqueous electrolyte based asymmetric supercapacitors (ASCs) could extend the operating voltage window up to 2 V beyond the thermodynamic limit of water decomposition [7]. This could be achieved by making full use of EDL capacitance and pseudo-capacitance in their suitable potential windows [8–10]. Recently, Salunkhe et al. [11] reported the fabrication of ASC with coaxial CNT/$Ni(OH)_2$ composites as positive electrode and reduced graphene oxide as negative electrode. The ACS device with operation voltage of 1.8 V attained energy density of 35 W h kg^{-1} and power density of 1.8 kW kg^{-1}. Although the operating voltage window of aqueous electrolyte based ASCs is smaller than that of non-aqueous electrolyte based supercapacitors [12,13], aqueous electrolyte based ASCs is still promising due to its environmental friendliness and cost-effective assembly process. The materials for positive electrode of ASCs have been extensively studied and exciting results has been achieved [14–18]. However, the development of high performance negative electrode for ASCs was urgently important to improve the overall performance of ASCs.

In carbon family, few-layer graphene is a promising candidate as negative electrode in ASCs in comparison to active carbon, mesoporous carbon and carbon nanotubes, since it provides open channels between the 2-dimensional (2D) nanosheets, leading to ultrahigh ion-accessible surface area [19,20]. Reduced graphene oxide (rGO) was widely used in supercapacitor applications

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because of its potential for large-scale production [21,22]. However, rGO sheets tend to restack together in the reduction process due to strong van der Waals interaction [23]. As a result, the surface area of rGO cannot be fully utilized, and the specific capacitance might thus be largely decreased. To address this issue, one strategy is introducing spacers in between graphene sheets to prevent their restacking [24]. Carbon nanotubes and metal/metal oxide nanostructure were reported as effective spacers between graphene layers to improve capacitance [25–29]. Shao et al. [30] synthesized graphene/Ag hybrid thin film as negative electrode for ASCs and found specific capacitance around 180 F g^{-1} at 5 mV s^{-1}. Chang et al. [31] reported graphene/MoO_3 nanosheets composite as negative electrode for ACs in 1 M Na_2SO_4 electrolyte and achieved a specific capacitance of 198 F g^{-1} at 5 mV s^{-1}. Deng et al. [32] prepared graphene/multiwall carbon nanotubes (GR/MCNT) as negative electrode. The specific capacitance of GR/MCNT was from 64 to 91 F g^{-1} in 1 M Na_2SO_4 solution, which was higher than the specific capacitance of GR or MCNT. Despite the progress on graphene/CNT hybrid and their supercapacitive performance, few work has been reported on the investigation of rGO/CNT hybrid film in both positive and negative potential windows with neutral aqueous electrolyte. In-depth investigation could provide better understanding of the electrochemical properties of the hybrid system and pave the way for its potential application in high-performance energy device.

Herein, we proposed the synthesis of a graphene oxide/carbon nanotube (GO/CNT) hybrid film by a simple solution coating method followed by thermal annealing at 200 °C to obtain rGO/CNT hybrid film electrode. The electrochemical performance of the hybrid film in both positive and negative potential windows in 1 M Na_2SO_4 neutral aqueous electrolyte was systematically investigated. The specific capacitance of rGO/CNT hybrid film was about two times larger in negative potential window (−0.8 to 0 V) than in positive potential window (0 to 0.8 V). Such distinct capacitive behavior might be attributed to the effect of oxygen-containing functional groups on the capacitance of the hybrid film. Compared to pure rGO film, the rGO/CNT hybrid film demonstrated much higher specific capacitance, higher rate capability and better cyclic performance in Na_2SO_4 aqueous solution, suggesting its promising application in ASCs as negative electrode.

2. Experimental

2.1. Preparation of rGO/CNT electrode

Graphene oxide (GO) colloid (thickness: 0.6∼1.2 nm, lateral size: 2∼5 μm, purity > 99%) was purchased from Timesnano, Chengdu Organic Chemicals Co. Ltd. Multi-walled carbon nanotubes (length: 20 ∼ 50 μm, outer diameter: 8∼25 nm, purity > 98%) was synthesized by using chemical vapor deposition (CVD) method (Tsinghua Nanfeng). The GO colloid was dispersed in ethanol followed by one-hour sonication to form a 1 mg ml^{-1} suspension. Certain amount of CNT was added to the GO suspension followed by sonication (30 min for 6 times). The weight ratio of GO to CNT was 10:1, 10:2 and 10:4, denoted as GC01, GC02 and GC03, respectively. Pure GO was also treated under the same conditions as a control sample. Typically, 0.3 ml of the GO and GO/CNT suspension after sonication was coated onto titanium foil (2 × 2 cm). The samples were dried in an oven at 40 °C for three hours, then annealed in a tube furnace at 200 °C for two hours in argon gas. In this low treating temperature, GO was partially reduced. Finally, rGO and rGO/CNT thin film electrodes were obtained.

2.2. Sample characterization

Scanning electron microscope (SEM, JSM-7001F) was used for morphology analysis. The structure of the samples was investigated under a transmission electron microscope (Technai G20). X-ray diffraction patterns of the samples were obtained using Rigaku D/max 2500 with Cu Kα irradiation (λ = 1.5406 Å). Raman spectra were acquired by a HR800 micro-Raman spectrometer (Horiba Jobin Yvon) using a 633 nm He-Ne laser. Chemical composition was explored by using X-ray photoelectron spectroscopy (ESCALAB 250 Xi) with monochromatic Al Kα X-ray source and resolution of 0.05 eV. Fourier transform infrared attenuated total reflectance (FTIR-ATR) spectra were recorded on a Bruker Vertex 70 v spectrophotometer.

2.3. Electrochemical measurements

Electrochemical measurements were carried out in a three-electrode setup with a CHI 660D workstation operating at room temperature. The working electrode was titanium foil coated with active material. Ag/AgCl electrode and Pt wire served as reference electrode and counter electrode, respectively. 1 M Na_2SO_4 aqueous solution was used as electrolyte. The cyclic voltammetry (CV) curves were acquired at scan rates of 5, 10 and 50 mV s^{-1} in positive and negative potential windows. Galvanostatic charge/discharge tests were made at current densities of 0.4, 1, 2, 4 A g^{-1} and electrochemical impedance spectroscopy (EIS) in the frequency range from 100 kHz to 0.01 Hz. The modelling of the EIS results was performed with Z-view software. The specific capacitance C_p was calculated from the CV curves using the following equation

$$C_p = \frac{\int IdV}{mv\Delta V} \quad (1)$$

where I is the applied current, m is the mass of active electrode material, v is the potential scan rate, and ΔV is the potential range. The specific capacitance calculated from the discharge line was based on the following equation

$$C_p = \frac{I}{m(dV/dt)} \quad (2)$$

where I is the applied current, m is the mass of active electrode material, and dV/dt is the slope of the discharge curve.

3. Results and discussion

The crystalline nature of GO was confirmed through selected area electron diffraction pattern (SAED) as shown in inset of Fig. S1 (see supporting information). The non-circular dots in SAED were due to the stacking of GO sheets with good interlayered coherence. The GO/CNT coated on Titanium foils was annealed in a tube furnace at 200 °C for 2 hours in argon gas to obtain rGO/CNT thin film electrodes. Fig. 1a illustrated the structure of rGO/CNT hybrid film with CNTs intercalated between rGO sheets. XRD patterns of GO, rGO and rGO/CNT (as shown in Fig. 1b) were obtained to elucidate the phase structure of the films. A distinct peak at 10.9° was observed for the GO film, corresponding to d-spacing of 8.11 Å between the GO sheets. After thermal annealing, the peak at 10.9° vanished and two broad peaks centered at 20.6° (d-spacing: 4.31 Å) and 24.3° (d-spacing: 3.66 Å) emerged. The decrease of interlayer distance indicated de-oxygenation of GO. Both the XRD peaks of the rGO and rGO/CNT samples were weak and broad, revealing high stacking disorder through the in-plane direction of the electrode film. It also implied that the addition of CNTs hardly