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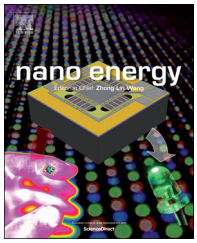

RAPID COMMUNICATION

Freestanding functionalized carbon nanotube-based electrode for solid-state asymmetric supercapacitors

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Abstract
Recently, many attempts have been made to increase the specific capacitance of carbon nanotubes (CNTs). Chemical enhancement by adding redox active functional groups on CNTs increases the specific capacitance, while excessive oxidation decreases conductivity and leads to poor cycle life. Here we report the electrochemical enhancement methods followed by annealing at different temperatures in air to add and adjust the redox active functional groups on freestanding CNT films. Functionalized freestanding CNT films were used as positive electrodes, assembled with freestanding CNT/MoO_{3-x} negative electrodes to fabricate carbon nanotube-based solid-state asymmetric supercapacitors (ASCs). The whole device showed a high volumetric capacitance of 3.0 F cm^{-3}, energy and power density of 1.5 mWh cm^{-3} and 4.2 W cm^{-3}, respectively. We also fabricated a SCs pack to drive a homemade wireless transport system successfully, demonstrating the potential applications of this solid-state system for portable/wearable electronics.

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Introduction

Nowadays, the proliferation of portable/wearable electronics such as wearable displays and flexible sensor networks leads to increasing energy consumption and requires sustainable and portable energy storage devices [1-4]. Green energy from intermittent sources such as solar and wind also requires energy storage systems [5,6]. Supercapacitors (SCs) and batteries are the most common energy storage devices which have been researched for decades [7-11]. Benefiting from the high power density, fast charge/discharge rates and long cycle life, SCs would be favored in various applications, including but not limited to backup power, hybrid vehicles and pace makers [12]. Replacement of liquid electrolyte with solid-state electrolyte offers a promising way to fabricate flexible, lightweight and safe solid-state SCs, which are desirable for portable/wearable electronics [13-17].

By virtue of high conductivity, high specific area, low specific weight and mechanical integrity, carbon nanotubes (CNTs) have attracted the scientific and commercial interest worldwide in fields such as flexible electronics and energy storage [18,19]. However, the low specific capacitance of CNTs hinders their applications as electrodes for high energy SCs [20]. Although chemical enhancement by adding redox active functional groups on CNTs increases the specific capacitance, excessive oxidation decreases conductivity and leads to poor cycle life [21-24]. In this context, it is necessary to develop a stable CNT electrode with high specific capacitance without sacrificing the high power density and long term stability.

Herein, we adopted the electrochemical enhancement methods followed by annealing at different temperatures in air to add and adjust the redox active functional groups on freestanding CNT films. A systematic study of the influence of different functional groups content on electrochemical performance, conductivity and cycle life was also performed. Furthermore, we used functionalized freestanding CNT films as the positive electrodes, assembled with freestanding CNT/MoO_{3-x} negative electrodes to fabricate high performance carbon nanotube-based solid-state asymmetric SCs (ASCs). The whole device, including the electrodes, electrolyte and separator, showed a high volumetric capacitance of 3.0 F cm^{-3}, high energy and power density of 1.5 mWh cm^{-3} and 4.2 W cm^{-3}, respectively, with a stable operation window between 0 and 1.9 V. We also fabricated a SCs pack to drive a homemade wireless transport system successfully, demonstrating the potential applications of this solid-state system for portable/wearable electronics.

Experimental

Preparation of functionalized freestanding CNT films

We used the vacuum filtration method to fabricate the flexible freestanding CNTs films. 0.1 g SDBS used as surfactant was dissolved in DI water (50 mL) containing CNTs (0.050 g, Blue Nano, China), then probe sonicated for 20 min to form CNT ink. The as-obtained solution was filtered through a membrane (220 nm pore size). The obtained filter cake was dried in vacuum for 0.5 h and then peeled off to obtain a freestanding film. After that, the samples were cut into pieces of 1.4 cm × 0.7 cm and treated by an efficient electrochemical enhancement method. A typical three-electrode configuration with freestanding CNT films as the working electrode, Ag/AgCl electrode as the reference electrode, a graphite rod as the counter electrode and 1 M H_2SO_4 aqueous solution as the electrolyte was tested at 2.2 V for 20 min. After that we got the functionalized freestanding CNT films.

Assembly of the solid-state symmetric and asymmetric SCs

A functionalized freestanding positive electrode was assembled with CNT/MoO_{3-x} as negative electrode to fabricate a solid-state ASC. PVA/LiCl gel was prepared by mixing LiCl (12 g) and

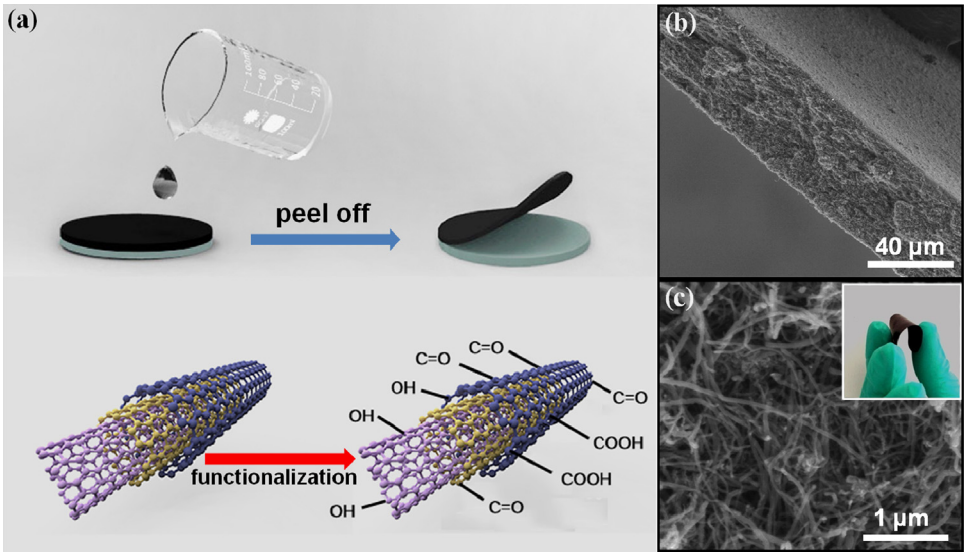

Figure 1 (a) Schematic of the fabrication procedure for functionalized freestanding CNT films. (b) Cross-section SEM image of the functionalized freestanding CNT film. (c) Enlarged cross-section SEM image of the functionalized freestanding CNT films. The inset is digital image of a functionalized freestanding CNT film.