



Electrochemical properties of carbon nanotube/graphene oxide hybrid electrodes fabricated via layer-by-layer self-assembly



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ABSTRACT

Carbon nanotube/graphene oxide (CNT/GO) hybrid electrodes were synthesized via layer-by-layer (LBL) self-assembly. Transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM), atomic force microscopy (AFM) and scanning electron microscopy (SEM) were carried out to characterize their microstructures, while Raman and Fourier transform infrared (FTIR) spectroscopy were used to investigate surface characteristics of the as-prepared samples. A 4-point probe was used to measure the electrical conductivities of the samples. Electrochemical properties of the CNT/GO hybrid electrodes were measured by cyclic voltammetry (CV), charge–discharge tests and electrochemical impedance spectroscopy (EIS). It was found that LBL self-assembled technique could directly synthesize CNT/GO hybrid materials on copper foils without any additives and the energy stored in these hybrid electrodes could be controlled by the electrode thickness. The electrode with a thickness of only 917.0 nm delivered a reversible capacity of 0.265 mAh cm⁻² at a current density of 0.01 mA cm⁻². Even at a higher current density of 0.4 mA cm⁻², it still exhibited a reversible capacity of 0.030 mAh cm⁻². These CNT/GO hybrid electrodes with thicknesses of less than one micron might be promising candidates for energy storage in micro devices.

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1. Introduction

Lithium ion batteries (LIBs) have been widely accepted as a promising device for energy storage due to their high energy capacity and long cycle life [1]. The advancement of the human society, especially the prosperity of the electric vehicle industry, requires a new device that can store more energy with small volume. However, the commercial traditional anode, graphite, evidently cannot meet this demand due to its low specific capacity (372 mAh g⁻¹) [2]. Therefore, it is necessary to upgrade the traditional LIBs so as to improve their specific capacity. In a LIB, energy specific capacity strongly depends on the properties of the electrode materials. Therefore, it is critical to find out suitable electrode materials that can provide high specific capacities. Among all the available electrode materials, graphene seems to be a promising anode material for high-performance LIBs [3,4]. Theoretically, graphene can exhibit extremely large specific capacity (794–1054 mAh g⁻¹) due to its large specific surface area for lithium ion storage [5,6]. In practical applications, graphene tends

to agglomerate, resulting in low reversible capacity when used as an anode material for LIBs [7,8]. In order to solve this problem, one effective approach is to design and develop hybrid materials based on graphene sheets such as inserting metal nanoparticles, in situ growing CNTs and combining with other carbon materials [9–12]. CNTs, as a one-dimensional carbon material, are considered to be a good candidate for incorporating with graphene [13–15]. Not only can CNTs separate graphene sheets, but they also enhance the conductivity between graphene sheets. In addition, the synergic effect between CNTs and graphene augments the energy specific capacity of the hybrid material. Thus, CNT–graphene hybrid materials are expected to solve the agglomerated issue of graphene, providing novel electrodes with high specific capacity and good cyclability for LIBs.

There are various methods to prepare CNT–graphene hybrid materials such as solution processing [16,17], layer-by-layer (LBL) self-assembly [18–20], vacuum filtration [21,22], and chemical vapor deposition (CVD) [23,24]. LBL self-assembly is an effective method to synthesize multicomponent thin films with microstructures that can be finely controlled at nanometer scales. Thus, it provides an ideal approach to design and synthesize homogeneous nanocomposites.

In this paper, we exploited LBL self assembled technique to fabricate CNT/GO hybrid electrodes for LIBs. TEM, FESEM, AFM, SEM,

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Raman and FTIR spectroscopy, and a 4-point probe were carried out to characterize the morphologies and surface characteristics of the hybrid electrodes. Their electrochemical properties were measured via CV, charge–discharge tests and EIS.

2. Experimental

2.1. Preparation of amino functionalized CNT solution

Multi-wall CNTs purchased from XFNANO (95% purity, length 1–5 μm , outer diameter 15–5 nm) were added into concentrated $\text{H}_2\text{SO}_4/\text{HNO}_3$ (3/1 v/v, 96% and 70%, respectively). After stirring at 70 $^\circ\text{C}$ for 4 h, the slurry was washed with deionized water until pH = 7 using a nylon membrane filter (0.22 μm) and then dried at 80 $^\circ\text{C}$ for 24 h. Subsequently, the acid-treated CNTs were chlorinated by reacting with SOCl_2 (Henan Kaifeng Chemical Co., Ltd.) at 70 $^\circ\text{C}$ for 24 h. $\text{NH}_2(\text{CH}_2)_2\text{NH}_2$ (Nanjing Jinyue Chemical Co., Ltd.) was then added with dehydrated toluene (Wanxing Chemical Co., Ltd.) as the solvent when the redundant SOCl_2 was evaporated. The reaction was carried on for 24 h at 70 $^\circ\text{C}$. After washing with ethanol and deionized water, amino functionalized CNT (CNT-NH₂) powder was obtained from drying the as-received filter cake at 80 $^\circ\text{C}$ in vacuum for 24 h. A certain amount of as-prepared CNT-NH₂ powder was dispersed in deionized water by ultrasonication for 1 h and uniform CNT-NH₂ solution was obtained.

2.2. Preparation of GO solution

Natural graphite (Nanjing, China) was used for the preparation of GO via a modified Hummers' method [25]. Graphite powder was first oxidized by reacting with concentrated H_2SO_4 with the existence of NaNO_3 . The reaction vessel was immersed in an ice bath, and potassium permanganate was added slowly. During this reaction, the temperature was kept at around 0 $^\circ\text{C}$. After 24 h, the graphite powder was oxidized into graphite oxide. The mixture was then diluted with 50 ml deionized water before adding 10 ml H_2O_2 into the solution to remove the redundant potassium permanganate. The graphite oxide was thoroughly rinsed and filtered by diluted HCl and deionized water until pH = 7. GO solution was then obtained by exfoliated graphite oxide suspension through ultrasonication for 1 h.

2.3. LBL assembly of CNT/GO electrodes

Copper foils were exposed to a 7:3 (volume) mixture of H_2SO_4 and H_2O_2 for 30 s and carefully washed with deionized water prior to use. For self-assembly the pretreated copper foils were immersed into a CNT-NH₂ solution for 30 min (self-assembled a CNT layer), followed by thorough rinsing with deionized water and drying under a nitrogen flow. Next, the CNT-NH₂-coated copper foil was immersed into a GO solution for 30 min (self-assembled a GO layer), rinsed, and dried. This procedure produced a layer of CNT-NH₂ and GO, respectively. As illustrated in Fig. 1, electrodes with 20, 40, and 80 layers (the coating densities were 0.10 mg/cm^2 , 0.18 mg/cm^2 , and 0.35 mg/cm^2 , respectively) could be fabricated by repeating this procedure for proper times and the samples were denoted as 20L, 40L and 80L, respectively.

2.4. Microstructure and morphology characterization

Microstructures of the CNT-NH₂ and GO samples were determined by transmission electron microscopy (TEM, JEM-2100F). Surface morphologies of the samples were characterized by field emission scanning electron microscopy (FESEM, JASM-6200) and atomic force microscopy (AFM). Scanning electron microscopy

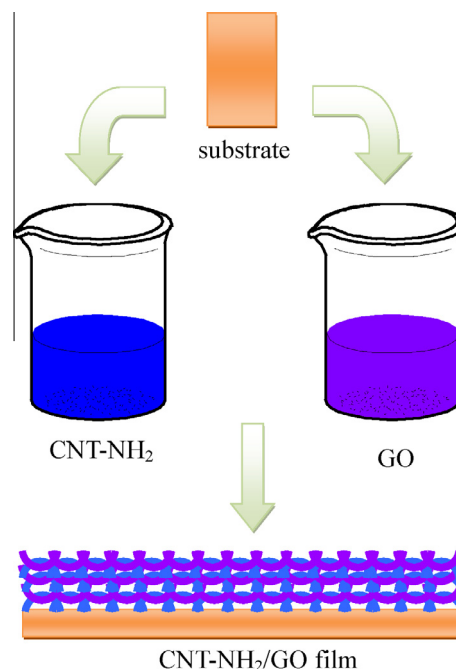


Fig. 1. A schematic illustration of the formation process of CNT/GO hybrid electrodes.

(SEM, JSM-6360LV) was carried out to determine the cross-sections of the samples. Surface characteristics of the samples were studied by Raman spectroscopy (Lab-RAM Hr800) and Fourier transform infrared spectroscopy (FTIR, Nicolet 6700). Electrical conductivities of the samples were measured by a 4-point probe (KDY-4).

2.5. Electrochemical measurements

Button cells were assembled in an Ar-filled glove box with metallic lithium plates as both reference and counter electrodes, and the as-prepared CNT/GO hybrid electrodes as working electrodes. Polypropylene membrane (Celgard-2400) was used as a separator. 1 M LiPF_6 solution in a 1:1 (volume) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) was used as electrolyte. The cells were charged and discharged at different current densities from 0.01 to 0.4 mA cm^{-2} between 0.01 and 3 V versus Li/Li^+ . For obtaining CV curves, the button cells were tested on an electrochemical analyzer (PAR 2273A, PerkinElmer Inc.) with a scanning rate of 1 mA s^{-1} at a voltage window of 3–0.01 V. EIS measurements were performed with an impedance analyzer in a frequency range of 100,000–0.1 Hz in an automatic sweep mode from high to low frequency. Charge always referred to lithiation, while discharge presented delithiation.

3. Results and discussions

Fig. 2 is a digital image of the CNT/GO hybrid electrodes with different layers, which visually reveals that CNT/GO hybrid

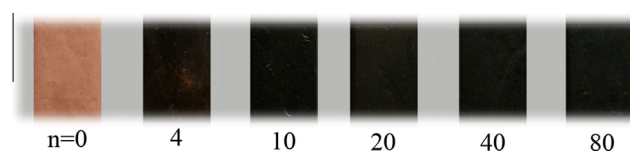


Fig. 2. Digital image of CNT/GO hybrid electrodes with different layers.

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