



Three-dimensional carbon composites as electrode materials for symmetric Li-ion capacitors in organic electrolyte



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HIGHLIGHTS

- Supercapacitor was fabricated using LiClO₄/propylene carbonate as electrolyte.
- Hybrid electrode material consists of graphene sheets and carbon nanotubes.
- The capacitor delivers high capacitance and high Li⁺ diffusion coefficient.
- The energy density of capacitor can reach as high as 18 Wh kg⁻¹ at 3000 W kg⁻¹.
- The hybrid is a promising material due to its low cost and high performance.

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ABSTRACT

Symmetric electrochemical capacitors (ECs) have been fabricated using graphene nanosheets (GNs) modified with carbon nanotubes (CNTs) as electrode materials and LiClO₄/propylene carbonate as organic electrolyte. An efficient homogenizing method is employed to insert CNTs into the GNs, forming three-dimensional CNT/GN framework. The electrochemical properties of as-prepared Li-ion ECs are well characterized by cyclic voltammetry, galvanostatic charge–discharge cycling, and *ac* impedance spectroscopy. The CNT/GN-based EC delivers high specific capacitance of 107 F g⁻¹, low equivalent resistance of 33.0 Ω, and high Li⁺ diffusion coefficient of 1.09 × 10⁻¹³ cm² s⁻¹, showing an obvious enhancement as compared to GN- and CNT-based ones. This improved performance can be attributed to the fact that the presence of CNTs facilitates not only more electro-active sites on the graphene surface but also better Li⁺ diffusion accessibility and electrolyte wetting in the carbon framework. The energy density of CNT/GN-based EC can reach as high as approximately 18 Wh kg⁻¹ at a power density of 3000 W kg⁻¹, analyzed by the Ragone plot. Accordingly, the CNT/GN hybrid can be a promising electrode material for Li-ion ECs owing to its low cost, high performance, and easy fabrication.

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1. Introduction

Electrochemical capacitors (ECs) as promising electrochemical energy storage devices are applied in a variety of commercial applications due to their long cycle life, low maintenance cost and extraordinary high power density [1,2]. Theoretically, the ECs are capable of storing electrical energy through an electrostatic interaction of charges at electrode/electrolyte interface [3,4]. The electrodes of ECs are commonly made of porous carbons, which provide a large number of active sites available for forming electric double layer in liquid or gel phase. The carbon-based electrodes also

exhibit an excellent combination of properties including good electrical conductivity and lightweight, thus imparting a great potential for high-performance ECs [5–7]. Recently, carbon nanotubes (CNTs) and graphene nanosheets (GNs) gradually emerged as promising candidates, showing superior electrochemical performance and great feasibility for commercialization. For instance, past literature reported the electrochemical performance of CNT- and GN-based [8–10] capacitors, based on the aqueous electrolytes such as sulfuric acid or alkali media. Especially, GNs have received lots of attention for its application in ECs and Li-ion batteries because of their two-dimensional structure and unique properties such as high theoretical surface area, superior mechanical strength, and good electrical conductivity [11–13]. However, GNs tend to easily aggregate and thus form multilayered agglomerate, because of the van der Waals force interaction [14]. This unwanted

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phenomenon seriously decreases the site accessibility of ions in the GN aggregates.

To resolve the above drawback, one strategy is to utilize these carbon structures as conductive carbon scaffold to attain high surface area available for the formation of electric double layer. More recently, one-dimensional CNTs have been inserted into the graphene oxide (GO) sheets, creating a three-dimensional carbon framework. The hierarchically three-dimensional hybrid has been confirmed to enhance the performance of electrochemical capacitors in aqueous electrolyte [15,16]. To the best of our knowledge, there are few reports examining how the carbon framework as electrode material affecting the electrochemical performance of ECs in organic electrolyte. Generally, the energy density (E) of an EC is calculated using the equation $E = 1/2 CV^2$, where C is the specific capacitance of ECs and V is the cell voltage [17–19]. Herein the E value of ECs can be raised by either increasing the specific capacitance of electrode materials such as novel CNTs and GNs, or enlarging the cell voltage, which can be attained by using organic electrolytes because of their wider potential window [17]. Accordingly, the selection of organic electrolyte can significantly enhance the energy density of ECs due to its large V value.

On the basis of the above deduction, this present work aims at the fabrication of symmetric ECs using novel three-dimensional CNT/GN framework and LiClO_4 salt as electrode material and electrolyte, respectively. The key point is to fabricate the CNT/GN framework as electrode materials for the symmetric ECs. Herein the symmetric ECs that employ the CNT/GN composites as both negative and positive electrode (so-called “Dual-Carbon” cells [20]) are systematically characterized by cyclic voltammetry (CV), galvanostatic charge–discharge cycling, and *ac* impedance spectroscopy. As a result, the symmetric ECs based on the CNT/GN hybrid electrodes in LiClO_4 electrolyte exhibit a high energy density (approximately 18 Wh kg^{-1}) with a power density of 3000 W kg^{-1} . This satisfactory performance reveals that the fabrication of CNT/GN framework delivers a great feasibility for commercializing EC's future applications.

2. Experimental

The preparation of GNs consisted of the following two steps. First, the GO sheets were chemically exfoliated from natural graphite using a modified Hummers' method [9,21]. Second, the GNs were thermally reduced from the GO sheets through a thermal reduction at $350 \text{ }^\circ\text{C}$ under H_2 -containing atmosphere. The GN powder was then stored and dispersed in ethanol solution after an ultrasonic bath. The multi-layered CNTs (commercial product, prepared by chemical vapor deposition method) were also homogeneously dispersed in ethanol. After mixing the GN and CNT suspensions, the CNT/GN slurry was placed into a high-performance homogenizer (IKA, Model T25, Germany), equipped with a rotor-stator generator. The homogenizing process was performed at room temperature with a high rotation speed of 24,000 rpm for 1 h, forming the well-dispersed CNT/GN hybrid. The schematic illustration of the formation of CNT/GN ($=2/8$ in w/w) hybrid is depicted in Fig. 1.

The crystallization degree of carbon composites were characterized by Raman spectroscopy (Renishaw Micro-Raman spectrometer). The crystalline structure of carbon composites was studied by X-ray diffraction (XRD) with $\text{Cu-K}\alpha$ radiation, using an automated X-ray diffractometer (Shimadzu Labx XRD-6000). The distance of interlayer spacing (d_{002}) in the carbon composites was determined by using the XRD patterns according to the Bragg's equation. An automated adsorption apparatus (Micromeritics, ASAP 2020) was adopted to examine the porous characteristics of carbon composites, using N_2 physisorption at $-196 \text{ }^\circ\text{C}$. The full pore

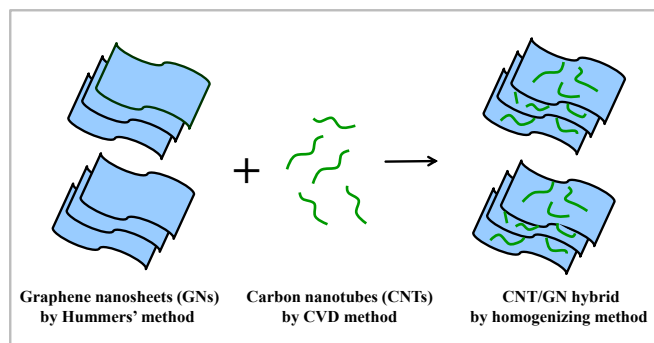


Fig. 1. Schematic illustrating for the fabrication of three-dimensional CNT/GN framework through an efficient homogenizing method.

size distributions of composites were analyzed by density functional theory (DFT) model. The nano-structural observation of as-prepared composites was investigated using field-emission scanning electron microscope (FE-SEM, JEOL JSM-6701F) and transmission electron microscope (TEM, JEOL JEM-2100).

To prepare the electrode for the electrochemical capacitive performance, the CNT/GN composites were first mixed with one binder (poly-vinylidene fluoride) and one conducting media (acetylene black, KS-6) with the weight ratio of 85:10:5 in *N*-methyl pyrrolidinone (NMP) solvent to form the electrode slurry. The mixture was blended with a three-dimensional mixer using zirconium balls for 3 h to ensure the uniformity of carbon slurry. The resultant slurry was then uniformly coated on a stainless foil substrate with a doctor blade, followed by evaporating the solvent, NMP, with a blow dryer. The prepared electrode sheets were dried at $135 \text{ }^\circ\text{C}$ in a vacuum oven for 12 h and pressed under a pressure of $\sim 200 \text{ kg cm}^{-2}$. The electrode layers were adjusted to control a thickness of approximately $100 \text{ }\mu\text{m}$. Afterward, the symmetric ECs (CR2032-type) were assembled in a glove box for electrochemical characterization. In the ECs, the porous polypropylene film served as the separator, and 1.0 M LiClO_4 in propylene carbonate was used as the electrolyte solution. The ECs were charged and discharged using a conventional protocol within the voltage range of $0\text{--}2.0 \text{ V}$ with different current densities at ambient temperature. An *ac* impedance spectroscopy measurement was carried out in the frequency range of 100 kHz to 0.01 Hz at open circuit potential with an alternating current perturbation of 5 mV . The impedance analysis of ECs was performed using an impedance analyzer (CH Instrument, Inc., CHI 608), and the equivalent circuit was analyzed using a computer software (Z-view).

3. Results and discussion

3.1. Characterization of CNT/GN hybrid

Raman spectroscopy is a powerful technique to analyze the graphite degree of carbon materials, as shown in Fig. 2. The Raman *G* band at $\sim 1580 \text{ cm}^{-1}$ is basically ascribed to the stacking of hexagonal graphite network plane, while the *D* band at $\sim 1350 \text{ cm}^{-1}$ corresponds to the amorphous carbon or deformation vibrations of a hexagonal ring [22–24]. The intensity ratios of I_D/I_G are 0.93 and 0.24 for fresh GN and CNT samples, respectively. This result reflects that the CNT sample possesses a highly crystalline structure, whereas some imperfect defects or surface oxides exist in the basal plane or edge of GNs. The CNT/GN hybrid is found to have the I_D/I_G ratio of ~ 0.95 . This can be attributed to the fact that the CNTs are entirely covered with GNs, thus exhibiting the Raman characteristics of graphene. Such high magnitude of I_D/I_G ratios reveals a small

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