Highly-curved carbon nanotubes supported graphene porous layer structure with high gravimetric density as an electrode material for high-performance supercapacitors

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ABSTRACT

Graphene aerogel is one of the most promising candidates for supercapacitors electrode material because of its high specific surface area and good electronic conductivity. However, the extremely low gravimetric density seriously limits its further practical applications. In this paper, a compression strategy was utilized to increase the gravimetric density by forming a unique highly-curved carbon nanotubes supported graphene porous 3D layer structure. The structure and morphology were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), Raman spectrum and N_2 adsorption/desorption measurement. Results demonstrate that the highly-curved carbon nanotubes between the graphene layers can prevent the restacking of the graphene layers. The newly formed structure retains the merits of graphene aerogel such as high specific surface area, good electronic conductivity, and porous structure. The electrochemical performance was investigated by a galvanostatic charge-discharge test (GDC) and a specific capacitance of $246.3 \, F \, g^{-1}$ was achieved, endowing it with great application potential as an supercapacitors electrode material.

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1. Introduction

Developing renewable and clean energy such as wind power and solar energy is an attractive method to deal with the urgent issues of environmental pollution and energy exhaustion [1—4]. The storage and conversion devices are of great importance to realize the application of these green powers [5—9]. Supercapacitors have been attracting lots of attention because of their high power density, long cycle life and low requirements for working condition [10—13]. These advantages make supercapacitors wildly used by small electronic equipment and large electric devices.

The electrochemical performance of supercapacitors is mainly determined by electrode materials [14—16]. Graphene, composed of one layer of sp^2-bonded carbon atoms, has a unique two-dimensional structure, endowing it with many advantages such as high specific surface area, good electronic conductivity and excellent thermal conductivity [17—21]. However, graphene sheets have a strong tendency to agglomerate and restack during preparation process, which result in a worsening electrochemical performance [22—24]. Until now, many efforts have been made to reduce the undesirable restacking such as self-assemble and spacer addition [25—32].

The graphene aerogel, prepared by a self-assemble method, is an attractive electrode material for supercapacitors due to its high SSA, high conductivity and three dimensional (3D) interconnected porous structure [33—35]. Shi et al. [36] reported that the 3D graphene aerogel, prepared by hydrothermal inducing method, possessed copious hierarchical pores and performed a very high specific capacitance of $175 \, F \, g^{-1}$ in an aqueous electrolyte. Moreover, continuous work has been done to further enhance the specific surface area of graphene based aerogel [37—42]. Recently, Zhang et al. [43] prepared graphene-based aerogel with sandwich-like porous carbon/graphene sheets, delivering an extremely high SSA of $2650 \, m^2 \, g^{-1}$. The significantly improved SSA makes the graphene aerogel an ideal candidate for supercapacitors electrode material. However, the as-prepared high SSA graphene aerogel is widely known as superlight material with low gravimetric density,

which even could stand on tumbleweeds due to its high pore volume and thin constructed walls. The low gravimetric density seriously limits its further applications in energy storage devices, owing to its related low specific volumetric capacitance.

Based on our previous research [44], high pressure treatment can dramatically transform the 3D graphene aerogel structure to 2D layer structure. In this paper, graphene/highly-curved carbon nanotubes layer structure (GCCL) was prepared by a facile method, including chemical vapour deposition and the subsequent high-pressure treatment. The compression step significantly improves the gravimetric density and the highly-curved CNTs between the graphene layers greatly alleviate the destruction of the structure. Consequently, a novel 3D layer material with high gravimetric density and retained advantages from the graphene aerogel including high SSA and porous structure was obtained. Moreover, the deposited CNTs leads to the formation of 3D conductive network and consequently enhanced electronic conductivity.

2. Experimental

2.1. Preparation of GCCL

All chemicals used are analytical grade without any further purification. The synthesis strategy of the GCCL is shown in Scheme 1.

Graphene/catalyst precursor was prepared using a facile immersion method. Firstly, graphene oxide aqueous colloid (GO) was prepared by an oxidation process. The stable graphene oxide dispersion ($2 \, mg \, mL^{-1}$) was obtained by adding suitable amount of water, and Resol-resin (RF) solution was fabricated with a literature procedure [45]. Subsequently, RF solution was added into GO aqueous colloid drop by drop with a mass ratio of 4:1. Then the mixture was transferred to a Teflon-lined reactor and a hydrothermal treatment was used at $180 \, ^\circ C$ for 24 h. After being filtered to remove the residual water, the obtained graphene hydrogel was immersed in $NiAc_2 \cdot 4H_2O$ solution ($2 \, mg \, mL^{-1}$) for 12 h. The Graphene/catalyst precursor was obtained after a further freeze-dry process.

In a typical process, the graphene/catalyst precursor was placed in a horizontal quartz tubular furnace. The temperature was heated to $450 \, ^\circ C$ at $5 \, ^\circ C/min$ and kept at $450 \, ^\circ C$ for 4 h in H_2/Ar (H_2, 5 wt%) atmosphere. Subsequently, the temperature was heated to $550 \, ^\circ C$ and then ethanol ($0.3 \, mL \, min^{-1}$) was added as carbon source for 30 min in Ar atmosphere. After being washed by HCl solution and dry step, the graphene/highly-curved CNTs composite aerogel (GCCA) was obtained. Finally, GCCA was compressed under 3 MPa and a unique 3D layer structure was obtained, denoted as GCCL. For comparison, a sample without catalyst and CNTs deposition was also prepared and named as GAL.

2.2. Electrochemical measurements

The electrochemical performance was evaluated by a two-electrode configuration. Stainless steel sheets (diameter 1.7 cm) and Ni foam (diameter 1.6 cm) were employed as current collectors. KOH ($6.0 \, mol \, L^{-1}$) solution was used as the electrolyte. The active material and polytetrafluoroethylene were mixed at a ratio of 95:5 and subsequently pressed onto a piece of nickel foam dish under 10 MPa. After that, the dish was transferred into a vacuum oven and dried at $120 \, ^\circ C$ for 12 h. The mass loading of the active material for each dish was 12 ± 0.02 mg. Electrochemical impedance spectroscopy (EIS) was tested at a range from 0.1 Hz to 100 kHz with an alternating-current (AC) amplitude of 5 mV at the open circuit potential. The cyclic voltammograms (CV) curve and galvanostatic charge-discharge performance (GDC) were measured on an Arbin test system. Gravimetric capacitances were calculated from the slope of the fitting straight line of the galvanostatic discharge curves by following equation:

$$C = \frac{4I\Delta t}{m\Delta V}$$

where I is the charge/discharge current density and m refers to the total mass of both anode and cathode materials.

2.3. Material characterization

The morphology was characterized by scanning electron microscope (SEM, NOVA NANOSEM 450). The structure was determined by X-ray Diffraction (XRD, Bruker D8 Advance) with Cu Kα
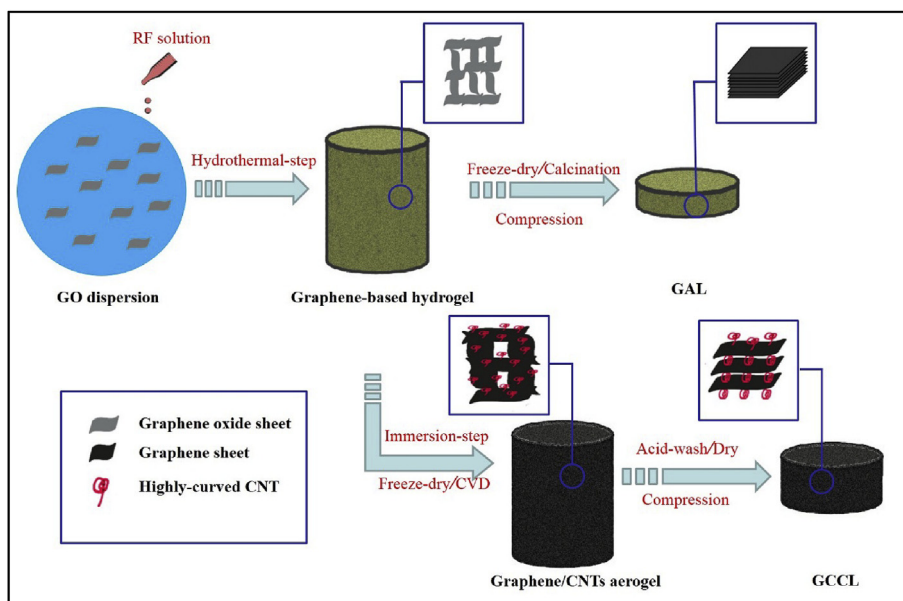
Scheme 1. Synthesis process of GCCL.