



Short Communication

Cross-linked graphene/carbon nanotube networks with polydopamine “glue” for flexible supercapacitors

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ABSTRACT

Three-dimensional (3D) graphene-based composites can possess exceptional electrochemical performance owing to their unique structure and properties. Herein, a 3D cross-linked hierarchical porous polydopamine (PDA) modified reduced graphene oxide (rGO)/amino functionalized carbon nanotube (CNT-NH₂) composites were synthesized via hydrothermal method. The hierarchical electrode incorporates the advantages of 1D nanotube for effective charge transport, 2D graphene nanosheet for fast ion transport and 3D cross-linked hierarchical porous substrate for mechanical stability and flexibility. Attributing to these characters, the obtained rGO/CNT-NH₂/PDA (GCP) electrode presents a high capacitance (176.2 F g⁻¹ at 0.5 A g⁻¹) in aqueous 6.0 M KOH electrolyte. Symmetric supercapacitor based on GCP-50 electrodes exhibits a high energy density of 4.22 Wh kg⁻¹ and excellent cycling stability with 98.9% capacitance retention after 10,000 cycles. Furthermore, the supercapacitors show superior flexibility and stability. The facile synthesis, promising electrochemical results and 3D hierarchical porous nanostructure of GCPs present potential for supercapacitor and other energy storage applications.

1. Introduction

Supercapacitor has been widely regarded as one important class of energy-storage devices, attributing to its excellent power density (10 kW kg⁻¹), extremely long cycle life (> 10⁵ cycles) and fast charge-discharge rate [1]. Supercapacitors are divided into electric double layer capacitance (EDLC) and pseudocapacitance on the capacitive mechanisms. EDLC physically stores charges through reversible electrostatic attraction at the electrode-electrolyte surface. This type supercapacitor owns the specialty of low cost, long cycle life, high electron transport of the electrode material but low capacitance of electrode. Carbon materials are the main source of EDLC electrode [2]. Pseudocapacitance chemically stores charges and boosts the energy density through the fast Faradaic reactions at the electrode surface. The pseudocapacitor possesses the character of high capacitance, low electron transport of electrode and relative poor life cycle due to the volume transformation during the Faradaic reaction process [3]. Electrode materials for pseudocapacitor are conductive polymers and transition metal oxides/hydroxides/sulfides [4–6].

Among various electrochemical electrode materials [7–10], graphene with unique high conductivity, large specific surface area (2600 m² g⁻¹) and advanced theoretical specific capacitance (550 F g⁻¹),

is regarded as one kind of perfect EDLC electrode material [11]. The most effective approach to produce the graphene in mass for industrial application is the oxidation and reduction of graphite [12–14]. Graphene oxide (GO) attached with –OH and epoxy groups is reduced through disposing their oxygen-containing groups [15,16]. However, reduced graphene oxide (rGO) suffers from the small surface area due to the irreversible agglomeration and the loss of electrical conductivity. Therefore, it is necessary to develop an effective and feasible way to dissolve the aforementioned drawbacks to obtain graphene-based electrodes with relatively high capacitance.

Substantial attempts have been brought out to reduce the aggregation of GO [17] and improve the capacitance of the graphene-based electrodes, such as incorporating carbon nanotube (CNTs) [12,18], conductive polymers [8,19], transition metal compounds between graphene layers [20,21], or designing three-dimensional (3D) interpenetrating structures [22]. CNT with high conductivity, large surface area, electrochemically active property and excellent softness, has drawn widely attention in energy storage area [23,24]. Efforts to combine graphene and CNTs have been made to synthesize electrode materials for supercapacitor and other applications [12,18,22,25–28]. Wei et al. prepare 3D sandwich structures CNT/graphene through chemical vapor deposition (CVD) approach. The unique structure

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boosts the transportation of electrons and electrolyte ions throughout the electrodes, facilitating the electrochemical performances of the composites [12].

Moreover, the wettability of the electrode materials is a very important element in charge storage through reversible ion adsorption. Superior surface wettability accelerates the facile infiltration of the electrolyte into the porous electrode materials. It has been proved that the doped nitrogen boosts the wettability of the material [29,30]. Dopamine (DA), full of the functional catechol and amine groups, is a mimic of the specialized mussel adhesive protein. Therefore, the nitrogen in polydopamine (PDA) can enhance the wettability of the material, which is benefit on the electrolyte ion diffusion across the electrode material [31]. Additionally, the doped nitrogen introduced the pseudocapacitance, resulting in improved capacitive performance of electrode materials. In addition, DA can self-polymerize into PDA along with the reaction with GO sheets, further strengthen the building of 3D structure [32].

Herein, a series of 3D cross-linked structure rGO/CNT-NH₂/PDA (GCP) composites are fabricated through an efficient and facile self-assembly route. The nanostructure of the composites can tailor by varying the amounts of polydopamine. Moreover, the N doping from PDA and CNT-NH₂ could bring in pseudocapacitance. Benefiting from these features, the GCP electrode presents a high capacitance of 176.2 F g⁻¹ at 0.5 A g⁻¹. Remarkably, the symmetric supercapacitor assembled with GCP electrodes use 6 M KOH as electrolyte delivers a capacitance of 47 F g⁻¹, energy density of 4.22 Wh kg⁻¹ and retention rate of 98.9% after 10,000 cycles at 2 A g⁻¹. Furthermore, the supercapacitor possesses excellent flexibility and mechanical stability.

2. Experimental

2.1. Materials

Potassium hydroxide (KOH) and natural graphite powder were brought from Sinopharm chemical reagent. Amino modified multi-wall carbon nanotube (CNT-NH₂, the length: 50 μm) was received from Nanjing XFNANO Materials. Dopamine hydrochloride, tris buffer solution, methyl pyrrolidone (NMP) were obtained from Beijing J&K Scientific Co., Ltd. Polyvinylidene fluoride (PVDF), acetylene black were received from Shanxi Li zhi yuan battery material Co., Ltd.

2.2. Materials preparation

2.2.1. Synthesis of GO

GO was prepared from natural graphite powder according to literature procedure [33].

2.2.2. Preparation of GO/CNT-NH₂/PDA

In order to synthesis the three-dimensional cross-linked network composites, 25 mg amino modified multi-wall carbon nanotube was added to 25 mL of 1 mg mL⁻¹ graphene oxide solution. The resulting compound was sonicated until the solution dispersed evenly. Polydopamine modified graphene/ CNT-NH₂ hydrogel (GO/CNT-NH₂/PDA) was prepared by the following procedure using dopamine as the reductant and crosslink agent. Typically, dopamine hydrochloride (2.5 mg mL⁻¹) was added into GO/CNT-NH₂ aqueous dispersions with pH adjusted to about 8.5 by tris buffer solution, and then the mixture was reacted under stirring at 45 °C for 24 h.

2.2.3. Preparation of rGO/CNT-NH₂/PDA (GCP) aerogel

To prepare the reduced rGO/CNT-NH₂/PDA aerogel, the obtained suspension (GO/CNT-NH₂/PDA) was operated hydrothermal reaction at 180 °C for 12 h. After the reaction, the black precipitate was collected via filtering and freeze dried. The obtained hydrogels were denoted as rGO/CNT-NH₂/PDA (GCP-x), where x stands for the mass percentage of dopamine to graphene in the composites. Here, they were 0, 10, 50 and

90, respectively. For comparison, rGO/PDA-50 (GP-50) hybrids were synthesized without CNT-NH₂ under the same condition, and the mass percentage of dopamine to graphene was 50.

2.2.4. Preparation of GCP electrodes and supercapacitors

The electrochemical performance of GCPs hydrogels were investigated in three- electrode system with Pt wire as the counter electrode and HgO/Hg as the reference electrode, respectively. The working electrode was prepared using GCPs on the glass carbon electrode. The mass of the working electrode is 8 × 10⁻⁶ g. The flexible symmetric supercapacitor is assembled with two same GCPs as electrodes, a NKK membrane as separator and 6 M KOH as electrolyte packed in aluminum-plastic membrane. The working electrode was prepared as following: mixing the active materials (80 wt %), polyvinylidene fluoride (PVDF, 10 wt %), acetylene black (10 wt %) in NMP in the ball mill for 6 hours until uniformly dispersed. The obtained slurry being coated on the pretreated nickel foil and at last dried at 80 °C in the vacuum oven overnight. Then the electrode foils were prepared in the size of 2*2 cm² for use. The resulting work electrode has a mass density of ~1.5 mg cm⁻².

2.3. Characterization

The morphology of the synthesized GCP composites were investigated by environmental scanning electron microscope (SEM, FEI, QuanTA-200F) with energy-dispersive X-ray spectrometry (EDS) accessory and transmission electron microscope (TEM, JEOL, JEM-2100F). The pore structure of GCPs were determined by N₂ adsorption-desorption isotherms at Quantachrome Autosorb sorption analyzer by the Nonlocal Density Functional Theory (NLDFT) method. X-ray diffraction (XRD, Bruker D-8) were applied to analyze the crystallite structures of the products. The elemental compositions and the structures of GCPs were measured by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, THERMO SCIENTIFIC Co.) and Raman spectroscopy (Horiba Jobin Yvon; XploRA microraman system) with a 523 nm laser. The contact angles of the GCPs were measured by drop shape analyzer (DSA 100, Kruss, Germany).

2.4. Electrochemical measurement

The specific capacitance C_s (F g⁻¹) value of the GCPs can be calculated from the cyclic voltammetry curves by Eq. (1):

$$C_s = \int_{V_a}^{V_b} IVdV / (vm(V_a - V_b)) \quad (1)$$

The C_s can also be obtained from galvanostatic charge/discharge (GCD) data via Eq. (2):

$$C_s = (I \times \Delta t) / (\Delta V \times m) \quad (2)$$

Specific energy (E, Wh kg⁻¹) and power (P, W kg⁻¹) density were calculated by Eqs. (2) and (3), respectively:

$$E = 1 / (2C_s \Delta V^2) \quad (3)$$

$$P = E / \Delta t \quad (4)$$

Where v (V s⁻¹) represents the sweep rate, m (g) represents the weight of electrode material, I (A) is the current, V_a to V_b (V) is the applied voltage operating range, ΔV (V) is the voltage range of discharge after IR drop, Δt (s) is on behalf of the discharge time, C_s (F g⁻¹) is the specific capacitance.

The electrochemical performance was measured on CHI 660E electrochemical working station. The cycle life tests were operated on LAND electrochemical test cabinet.

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