Applied Surface Science 435 (2018) 699–707

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Flexible graphene/carbon nanotube hybrid papers chemical-reduction-tailored by gallic acid for high-performance electrochemical capacitive energy storages

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ARTICLE INFO

Article history:
Received 9 September 2017
Received in revised form
20 November 2017
Accepted 20 November 2017
Available online 21 November 2017

Keywords:
Gallic acid
Graphene
Mechanically-robust
Hybrid papers
Flexible supercapacitors

ABSTRACT

Mechanically robust graphene papers with both high gravimetric and volumetric capacitances are desired for high-performance energy storages. However, it's still a challenge to tailor the structure of graphene papers in order to meet this requirement. In this work, a kind of chemical-reduction-tailored mechanically-robust reduced graphene oxide/carbon nanotube hybrid paper has been reported for high-performance electrochemical capacitive energy storages. Gallic acid (GA), as an excellent reducing agent, was used to reduce graphene oxide. Through vacuum filtration of gallic acid reduced graphene oxide (GA-rGO) and carboxylic multiwalled carbon nanotubes (MWCNTs) aqueous suspensions, mechanically robust GA-rGO/MWCNTs hybrid papers were obtained. The resultant hybrid papers showed high gravimetric capacitance of 337.6 F g^{-1} (0.5 A g^{-1}) and volumetric capacitance of 151.2 F cm^{-3} (0.25 A cm^{-3}). In addition, the assembled symmetric device based on the hybrid papers exhibited high gravimetric capacitance of 291.6 F g^{-1} (0.5 A g^{-1}) and volumetric capacitance of 136.6 F cm^{-3} (0.25 A cm^{-3}). Meanwhile, it exhibited excellent rate capability and cycling stability. Above all, this chemical reduction tailoring technique and the resultant high-performance GA-rGO/MWCNTs hybrid papers give an insight for designing high-performance electrodes and hold a great potential in the field of energy storages.

1. Introduction

The tremendous growth of portable devices for a variety of applications stimulates the urgent demand for high electrical power to provide quick pulse power [1]. Supercapacitors, as one of remarkable high-performance energy storage devices, have attracted much attention due to their ultra-long cycling life, high power capability, and relative low price [2,3]. There are mainly two types of supercapacitors: (1) electrochemical double-layer capacitors (EDLC), which store energy by adsorbing anions and cations to form a double-layer on the surface of electrode/electrolyte interface, such as graphene [4], carbon nanotubes [5], bio-inspired carbon [6] et al; (2) pseudo-capacitors, which store energy by surface redox reactions, such as RuO_2 [7], MnO_2 [8], Co_3O_4 [9] and electrically conducting polymers [10] et al. Pseudo-capacitors exhibit much higher specific capacitance than EDLC. However, pseudo-capacitors suffer from rapid capacitance decay and poor cycle stabilities, which restrict its potential application for energy storage devices [11].

Graphene, a single layer of sp^2 bonded carbon atoms in a honeycomb arrangement, has recently attracted much attention due to its huge theoretical specific surface area, excellent in-plane electrical conductivity, and remarkable mechanical strength [12]. At present, there are mainly several methods to fabricate graphene, such as micromechanical exfoliation of graphite [13], chemical vapor deposition [14], and reduction of graphene oxide (GO) [15]. Amongst, the reduction of GO by chemical methods has many merits compared with other methods, such as low-cost, scalable-fabrication and excellent performance. Many reducing reagents, including hydrazine [15], hydroquinone [16], and $NaBH_4$ [17] etc., have been used to reduce GO. However, these reducing agents are usually pollutive, highly poisonous and explosive, which impede the ways to fabricate high-quality graphene. So, it's desirable to develop a low-cost, high-efficient, environmental-friendly method that is able to balance graphene quality and production efficiency well.

To enhance the electrochemical capacitance of graphene-based supercapacitors, a typical strategy was to utilize the electrodes

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https://doi.org/10.1016/j.apsusc.2017.11.163
0169-4332/

with large surface areas, high electrical conductivity and functionalized groups [18]. As we know, rGO possesses a unique two-dimensional structure, which endow graphene with potentials as an ideal candidate material for energy storage and conversion, and the capacitance value up to 550 F g^{-1} based on the entire specific surface area (2630 m^2 g^{-1}) is fully utilized in theory [19,20]. However, graphene-based supercapacitors usually suffered from compact structures which arose from restacking of graphene layers via Van der Waals interactions during reduction process and finally caused rapid decay of the specific capacitance. Great efforts have been applied to enhance the high specific capacitance with high power density utilizing graphene/CNTs-based materials, such as 3D graphene networks [19], graphene/polyaniline nanofiber [21], polypyrrole/graphene nanosheets [22], mesoporous carbon spheres/reduced graphene oxide [23] and so on. Although great advancements have been made for graphene-based energy storage electrodes, it's still a challenge to develop high-performance electrochemical capacitive electrodes through tailoring the structures of graphene papers for high-performance energy storages.

Herein, we report a facile and effective chemical-reduction-tailored approach to design mechanically-robust GA-rGO/MWCNTs hybrid papers with ultrahigh gravimetric capacitance and volumetric capacitance, as well as exceptional cyclic stability for electrochemical capacitive energy storage. The resultant film electrodes, with a characteristic of sandwich-like, free-standing and binder-free hybrid architectures, can be constructed by GA-reduction-tailored GA-rGO combined with carbon nanotube. There were several advantages for this kind of novel structure: (1) the mechanical properties of hybrid paper can be enhanced, which facilitates the combination between GO and MWCNTs through hydrogen bonds; (2) the thin films are more inclined to be soaked by electrolytes due to its improvement of infiltration; (3) stacked sheets are able to be avoided resulting in the increase of contact area between carbon materials and electrolytes which is conducive to accumulation of numbers of charges; (4) partial pseudocapacitance are provided which might be ascribed to the existence of oxygen-containing functional groups. Through exploiting this chemical-reduction-tailored approach, the as-fabricated hybrid papers showed ultrahigh gravimetric capacitance of 337.6 F g^{-1} and high volumetric capacitance of 151.2 F cm^{-3}. In addition, symmetric devices were assembled, providing high gravimetric capacitance of 291.6 F g^{-1} and volumetric capacitance of 136.6 F cm^{-3}. Moreover, the device showed an excellent cycling life with 97.7% capacity retention at 10 A g^{-1} after 10,000 cycles.

2. Experimental

2.1. Materials

Graphite powder (500 meshes) was purchased from Qingdao Tianyuan Graphite Co. Ltd (China). Multi-walled CNTs (5–15 μm in length and 40–60 nm in diameter) and GA (purity ≥ 99%) was purchased from Shenzhen Nanotech Port Co. Ltd. All of other chemicals were purchased from Shanghai Chemical Reagents Co. Ltd (China) and used without further purification.

2.2. Reduction of GO via GA

GO was prepared by a modified Hummers' method[24]. The method to reduce GO via GA was similar as previous studies[25]. Briefly, 600 ml of GO aqueous suspensions (0.1 mg ml^{-1}) were firstly treated by ultrasonic (40 kHz, 600 W) for 30 min. Subsequently, 480 mg GA was added, followed by keeping the mixture at 80 °C for 24 h. The resultant black suspensions were cooled down to room temperature and processed by another 30 min of ultrasonication. Finally, the stable graphene aqueous suspensions was obtained.

2.3. Fabrication of GA-rGO/MWCNTs hybrid papers

Carboxylic MWCNTs were obtained by ultrasonicating MWCNTs in a mixture of concentrated HNO_3 and H_2SO_4 (V : V = 1:3) for 8 h according to the method reported by J. Justin Gooding[26]. A certain ratio of MWCNTs was added into the graphene aqueous suspensions and kept stirring for 1 h. The mixture was filtered through cellulose membranes (0.22 μm pore size, 50 mm diameter) and washed with deionized water several times to form hydrogel films. The films was further dried at room temperature for 12 h and peeled off from the cellulose films to form GA-rGO/MWCNTs hybrid papers. GA-rGO/MWCNTs hybrid papers with weight ratios of MWCNTs (5%, 10%, 20%, and 30%) were denoted as GA-rGO/MWCNTs-5%, GA-rGO/MWCNTs-10%, GA-rGO/MWCNTs-20% and GA-rGO/MWCNTs-30%, respectively.

2.4. Characterization

The morphologies of the samples were observed by field-emission scanning electron microscope (FE-SEM, Carl Zeiss Ultra55), transmission electron microscopy (TEM, JEM-2010HT, JEOL, Japan) and atomic force microscopy (AFM, Veeco MultiMode/NanoScope IIIa, operating in the tapping mode). Ultraviolet-visible (UV–Vis) absorption spectrum studies were carried out on a UV–Vis-NIR spectrophotometer (Lambda 950, Perkin-Elmer, USA). Raman spectra were obtained on a Renishaw in Via Reflex Raman spectrometer using a 514 nm laser source. Fourier transform infrared spectroscopy (FTIR) was recorded on a Bruker (Germany) VERTEX 70 spectrometer (KBr pellets). X-ray photoelectron spectroscopy (XPS) spectra were obtained with a Kratos Axis Ultra DLD using monochromated Al Ka X-ray beams as the excitation source (1486.6 eV). X-ray diffraction (XRD) was carried out based on a Rigaku 18 kW D/max-2550 using Cu Kα radiation using 40 kV voltage. Thermal gravity analysis (TGA, PerkinElmer Pyris 1) was executed by heating the samples from 30–800 °C at a heating rate of 5 °C min^{-1} in air atmosphere. For evaluation of mechanical properties of samples, dynamic mechanical analysis (DMA, TAQ800, TA Instruments-Waters LLC) was used to test strips with a dimension of 0.3 cm × 2 cm.

2.5. Electrochemical measurements

Electrochemical performances of electrode materials, including cyclic voltammetry (CV), galvanostatic charge/discharge measurement (GCD), and the electrochemical impedance spectroscopy (EIS) were tested on an electrochemical workstation (CHI 760E) at room temperature. The potential window from 0–1 V was applied. 1 M H_2SO_4 aqueous solution was used as the electrolyte for both three-electrode and two-electrode cells. The electrochemical impedance spectroscopy (EIS) measurements were performed over a frequency range from 10^{-2} to 10^5 Hz at the open circuit potential with 5 mV amplitude. For three-electrode tests, the as-prepared film electrodes were directly used as the working electrode with platinum plate and saturated calomel electrode (SCE) acted as counter electrode and reference electrode, respectively. Gravimetric specific capacitance (C_g) and volumetric specific capacitance (C_v) were calculated as $C_g = (I\Delta t)/(m\Delta U)$ and $C_v = C_m \cdot \rho (\rho = m\,v^{-1})$. Symmetric devices based on GA-rGO/MWCNTs hybrid papers were assembled in a two electrode configuration. Typically, two pieces of GA-rGO/MWCNTs hybrid papers were pressed on two carbon papers as current collector, a filter paper containing 1 M H_2SO_4 was sandwiched between them. The gravimetric specific capacitance (C_{sg}) and volumetric specific capacitance (C_{sv}) of single electrode