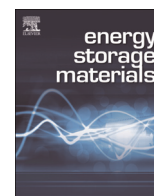




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Densely stacked bubble-pillared graphene blocks for high volumetric performance supercapacitors

Qian Wang^a, Jun Yan^{a,*}, Zelin Dong^b, Liangti Qu^b, Zhuangjun Fan^{a,*}^a Key Laboratory of Superlight Materials and Surface Technology, Ministry of Education, College of Material Science and Chemical Engineering, Harbin Engineering University, Harbin 150001, China^b Key Laboratory of Cluster Science, Ministry of Education of China, Department of Chemistry, School of Science, Beijing Institute of Technology, Beijing 100081, China

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ABSTRACT

We report here the template-free synthesis of densely stacked bubble-pillared graphene blocks (DSBG) with abundant stable oxygen-containing functional groups as the electrode materials for supercapacitors through thermal treatment of graphene oxide. Owing to its dense, bubble-pillared structure and ultra-high pseudocapacitance from oxygen-containing functional groups, the resultant DSBG electrode possesses remarkable gravimetric and volumetric capacitance (352 F g^{-1} and 739 F cm^{-3}) in an aqueous electrolyte. More importantly, the assembled symmetric supercapacitor based on free-standing DSBG film exhibits superior energy density (23.4 W h kg^{-1} and 37.4 W h L^{-1}) in an aqueous electrolyte, well competitive with those of the previously reported carbon materials in aqueous electrolytes. The outstanding electrochemical performances may render such DSBG material a highly promising candidate for miniaturized and compact energy storage devices in the near future.

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1. Introduction

Supercapacitors are considered to be the state-of-the-art energy-storage devices potentially bridging the gap between batteries and conventional capacitors because of their high power density, fast charge/discharge capability and ultralong cycling life [1–5]. Recently, considerable research efforts have been devoted to enhancing the energy densities of supercapacitors, and the reached energy densities are close to and even exceed those of batteries without compromising the power delivery and cycling life by virtue of hybridizing various carbon nanomaterials with pseudocapacitive materials or optimizing the structure of carbon nanomaterials [5–8]. Unfortunately, only the gravimetric performance has been the focus of research in most cases and the volumetric performance has been usually overlooked. Volumetric performances are of significant importance for energy storage devices especially in a limited space due to the requirement of the design and fabrication of miniaturized and compact energy storage devices from a technological point of view [2,7,9,10].

As a two-dimensional (2D) carbon material, graphene has been widely regarded as a promising electrode material due to its ultrahigh theoretical specific surface area (SSA), excellent electrical conductivity and high mechanical stability as well as outstanding

chemical stability [2,4,10,11]. However, the pore volume of graphene is usually relatively large, resulting in low packing density and consequently poor volumetric performance, which severely limits its future practical applications [12–15]. Currently, considerable efforts have been made in order to improve the volumetric performance of graphene based materials. More recently, our group demonstrated that oxygen-functionalized graphene nanosheets (FGN-300) with high SSA but low pore volume exhibited both high gravimetric and high volumetric capacitance (456 F g^{-1} and 470 F cm^{-3}) that came from the combination of electrical double-layer capacitance (EDLC) and pseudocapacitance [16]. Alternatively, Li and co-workers [4] reported that a novel liquid-mediated dense graphene film showed a volumetric energy density as high as 59.9 W h L^{-1} in an organic electrolyte. Although the increased packing density of graphene materials by some promising approaches, such as mechanical densification [17], vacuum-assisted self-assembly [9], fabrication of highly dense and vertically aligned graphene [18] and evaporation-induced drying [19], is beneficial for the enhanced volumetric performances for supercapacitors, it still remains challenging to achieve high capacitance due to poor utilization of surface area of sheets.

More interestingly, several groups have demonstrated the formation of graphene bubbles in recent years [20–23]. In these works, graphene should be firstly grown on the surface of specific substrates (SiO_2 , Pt, Ru, etc.) and then be strain-engineered to form nanoscale bubbles or templates are usually required during the formation process of bubbles. In sharp contrast, in this work, we

* Corresponding authors.

E-mail addresses: yanjun198201@163.com (J. Yan), fanzhj666@163.com (Z. Fan).

report novel densely stacked bubble-pillared graphene blocks (DSBG) as energy storage units for supercapacitors through thermal treatment of graphene oxide (GO). Owing to its dense, bubble-pillared structure and high pseudocapacitance from stable oxygen-containing functional groups, the resultant DSBG electrode possesses remarkable gravimetric and volumetric specific capacitance (352 F g^{-1} and 739 F cm^{-3}) in an aqueous electrolyte, much higher than those of chemical reduced graphene oxide (RGO) and thermal reduced graphene oxide (TRG). Moreover, the assembled symmetric supercapacitor based on free-standing DSBG film exhibits superior energy density (23.4 W h kg^{-1} and 37.4 W h L^{-1}) in $1 \text{ M Na}_2\text{SO}_4$ aqueous electrolyte, which is highly comparable to the so far reported carbon materials including activated carbon, carbon nanotubes (CNTs) and new-emerging graphene in aqueous electrolytes.

2. Experimental section

2.1. Material synthesis

Firstly, GO was synthesized through the modified Hummers method from natural graphite (Qingdao Graphite Company) [24]. Typically, the obtained GO dispersion (60 mL , 1 mg mL^{-1}) was transferred into a Petri dish (diameter: 10 cm) and dried at 40°C in an oven for 48 h . Subsequently, the dried GO (thickness: $4\text{--}5 \mu\text{m}$) was thermally treated at 300°C for 2 h under the N_2 atmosphere with a heating rate of $3^\circ \text{C min}^{-1}$ and the obtained film was denoted as DSBG film. The prepared DSBG films were also broken into powders (named as DSBG powder) with size of $\sim 10\text{--}40 \mu\text{m}$ using scissors for characterizations. For comparison, the GO film was also heated at 300°C for 2 h with a rapid heating rate of $10^\circ \text{C min}^{-1}$, and the as-obtained exfoliated graphene powder was named as (EG). The RGO powder was prepared by chemical reduction of GO suspension with hydrazine at 100°C and the RGO film was obtained through vacuum-assisted filtration of the obtained RGO suspension after sonication for 2 h . TRG was synthesized through rapid thermal treatment of GO film at 900°C [13].

2.2. Material characterization

X-ray diffraction (XRD) measurements were used to investigate the crystallographic structures of the samples with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$). The microstructure and morphology were characterized by scanning electron microscopy (SEM, Hitachi S-4800). The surface characteristic of the samples were determined on an X-ray photoelectron spectroscopy (XPS) system (ESCALab MKII). Raman spectra were also recorded to analyze the defective nature of the samples with a Jobin-Yvon HR800 Raman spectrometer with 457.9 nm wavelength incident laser light. The N_2 adsorption–desorption isotherms were carried out on Autosorb iQ2 (Quantachrome, USA) at 77 K and the SSA was calculated from the Brunauer–Emmett–Teller (BET) plot of the adsorption isotherm and the pore size distribution were obtained from the non-local density functional theory (NLDFT) method. The particle density of the DSBG powder was calculated through the following equation:

$$\rho = \{V_{\text{total}} + 1/\rho_{\text{carbon}}\}^{-1} \quad (1)$$

where ρ is the particle density of the material and ρ_{carbon} is the true density of carbon (2.26 g cm^{-3}), and V_{total} is the total pore volume estimated from N_2 isotherm at 77 K . Thermogravimetric analysis (TGA) was conducted on a Perkin-Elmer Diamond thermal analyzer. Mechanical property tests were conducted with an Instron material testing system (Instron 3342). The electrical

conductivity of the DSBG film was measured by a two-probe method. The packing density of the DSBG film was measured under a pressure of 2 MPa .

2.3. Electrochemical measurements

The electrochemical performances of both DSBG powder and film were investigated. The working electrode was prepared by mixing the as-prepared DSBG powder, carbon black and poly(tetrafluoroethylene) with a mass ratio of $75:20:5$ in ethanol to form a slurry. Then the slurry was coated onto the nickel foam current collector with coating area of $1 \times 1 \text{ cm}^2$, pressed under a pressure of 10 MPa and dried at 100°C for 12 h in a vacuum oven. The weight of electrochemical active materials in each electrode is about 2.5 mg . With regard to the binder-free film electrode, the free-standing DSBG film with a area of $1 \times 1 \text{ cm}^2$ was cut and pressed between two pieces of nickel foam under a pressure of 2 MPa . The electrochemical measurements were firstly carried out on a CHI 660C electrochemical station using a three-electrode system in 6 M KOH aqueous electrolyte, in which the prepared electrodes, Hg/HgO and Pt foil were used as the working, reference and counter electrodes, respectively. Cyclic voltammogram (CV) and galvanostatic charge/discharge measurements were performed between -1 and 0 V (vs. Hg/HgO) and the specific capacitances of the electrode at various scan rates were calculated based on the following equation:

$$C = \int IdV/m\nu V \quad (2)$$

where I is the current density applied, ν is the scan rate, V is the potential and m is the mass of the electroactive material in the electrode. The electrochemical impedance spectroscopy measurements were performed in the frequency range from 100 kHz to 0.01 Hz at open potential with an ac perturbation of 5 mV . In order to further determine the electrochemical performance of the material, a two-electrode system was also employed in $1 \text{ M Na}_2\text{SO}_4$ aqueous electrolyte to calculate the energy density of the prepared samples. Energy density and power density of the assembled supercapacitor were calculated based on the following equations:

$$E = 0.5CV^2 \quad (3)$$

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

where C is the capacitance of the symmetric supercapacitor and t is the discharge time. The volumetric performances of the materials were calculated according to the following equation:

$$C_v = C_g\rho \quad (5)$$

where C_v presents the volumetric capacitance, C_g presents the gravimetric capacitance, ρ is the particle density of the material.

Real part capacitance $C'(\omega)$ and the imaginary part $C''(\omega)$ are defined as follows:

$$C = C'(\omega) - jC''(\omega) \quad (6)$$

$$C'(\omega) = \frac{-Z''(\omega)}{\omega|Z(\omega)|^2} \quad (7)$$

$$C''(\omega) = \frac{Z'(\omega)}{\omega|Z(\omega)|^2} \quad (8)$$

where $Z'(\omega)$ and $Z''(\omega)$ are the respective real and imaginary parts of the complex impedance $Z(\omega)$. ω is the angular frequency which is given by $\omega = 2\pi f$.

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