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Alkylated graphene nanosheets for supercapacitor electrodes: High performance and chain length effect

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ABSTRACT

Single electrode materials capable of both electric double-layer and Faradic redox-based pseudo capacitance can be used for fabrication of high performance supercapacitors in an easy way and thus are highly desirable in the energy storage field. This contribution reports a new kind of such materials based on alkylated graphene materials (**C_nrGO**, *n* is the carbon number of their alkyl side chains) having different alkyl side chains (*n* = 4, 8, and 16). These materials were prepared via esterification of KOH-treated **GO** with the corresponding alkyl bromides in the presence of a phase transfer catalyst. More importantly, water was used as the reaction medium, and thus endowing the preparation method an eco-friend feature. The so-prepared graphene materials displayed chain length-dependent specific surface area and the population of residue C—O functionalities, and thus affording vast differences in their supercapacitor behaviors. **C_4rGO**, the product having butyl side chains, showed the best supercapacitor performance with a capacitance up to 242.2 F g^{-1} at a scan rate of 100 mV s^{-1} and a good cycling stability.

1. Introduction

Owing to their merits of high instant power density, quick charge and discharge processes, and excellent long-term stability, supercapacitors are one of promising electrical energy storage devices attracting significant attention in both scientific and industrial communities [1–5]. According to their operating mechanisms, supercapacitors can be divided into two types, the electric double-layer (EDL) and the pseudo-ones. In the former devices, electrodes absorb charged species (ions) on their surfaces during the charge process and reversibly desorb them during the discharge process. While in the latter ones, certain additional electrochemical oxidation and reduction processes are involved. Since they can achieve a higher capacitance than EDL type, pseudocapacitors are welcomed in the field. To realize such devices, two general strategies have been reported to date [1–5]. One is to utilize a composition at least made of an electrically conductive material and a redox-active substance. The other is the use of a single material capable of both electrical conductance and Faradic redox activity. Obviously, the latter approach is much simple and easy for device fabrication. However, the developed such materials with high performance are still rare, remaining as one of big challenges in the field.

Soon after its discovery in 2004 [6], graphene has rapidly emerged as one of star materials for supercapacitors due to its excellent electrical conductivity and extraordinarily large specific surface area [7–9]. In the early stage, graphene was mostly used as conducting material for the construction of EDL-type supercapacitors [10–12] and for combination with other redox-active materials, such as polyanilines [13–17], RuO_2 [18], and MnO_2 [19], for pseudocapacitors. The specific capacitances for the former devices were reported mostly in the range of 100–200 F g^{-1}, while for the latter up to 1000 F g^{-1} [3]. More recently, modified graphene materials possessing both EDL and Faradic redox activities have been reported [20–23]. For example, the integration of certain heteroatoms, like N and B, into graphene frameworks, greatly improved their capacitive performances [20–23]. Zhi and coworkers demonstrated acid-assisted ultra-rapid thermal treatment on graphene oxide (**GO**) can reserve certain oxygen-containing functionalities on the surface of carbon nanosheets and thus make Faradic redox active [23]. In this contribution, we report a new kind of graphene derivatives (**C_nrGO**, *n* is the number of carbon for the alkyl chains) capable of both EDL and Faradic redox capacitor mechanisms, which are based on alkylation of reduced graphene oxide (**rGO**) with different alkyl chains (Fig. 1). Their specific capacitance was found to highly depend on their chain

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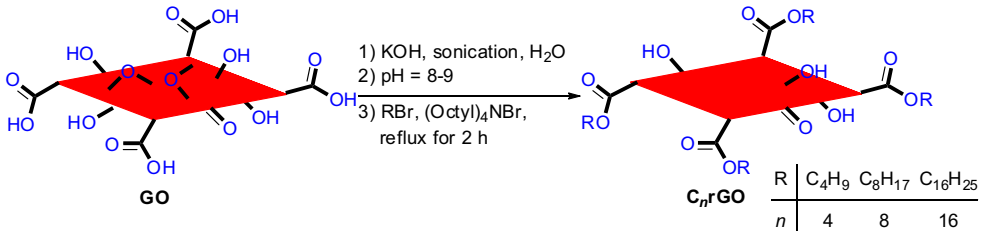

Fig. 1. Schematic illustration for preparation of alkylated graphene nanosheets. (A colour version of this figure can be viewed online.)

lengths and achieve a value as high as 242.2 F g^{-1} at a current density of 100 mV s^{-1}. Furthermore, all these alkylated graphene materials exhibited good cycling stabilities. More importantly, water was applied as the reaction medium, which endows their preparation method a simple and environmentally benign feature.

2. Experimental

2.1. Synthesis of C_nrGO

The starting material, **GO**, was prepared from graphite flakes (+100 mesh, Aldrich) following a modified Hummer's method [24]. In a general procedure, **GO** (0.2 g) was added into a KOH aqueous solution (6 M, 100 mL). After the mixture was subjected to ultrasonication for 2 h, the medium pH was adjusted to 8–9 with dilute hydrochloric acid. Then, alkyl bromide (0.01 mol) and tetraoctylammonium bromide (0.1 mmol) were added. The resulted reaction mixture was stirred at 100 °C for 2 h, and then cooled to room temperature and filtered with a nylon membrane having a pore size of 0.45 μm. The filtrate cake was subsequently washed with water and methanol, and then dried under vacuum, affording the final alkylated graphene product in yield of 264 mg for **C_4rGO**, 246 mg for **C_8rGO**, while 242 mg for **C_{16}rGO**.

In order to understand chemical structure change during the preparation procedure and to further check the specific effect of alkylation on material capacitor performance, the KOH-treated **GO** without further reacting with alkyl bromide was used as reference. Such material was prepared by following the same procedure as that for **C_nrGO** until the pH adjustment step. Afterward, the suspension was filtrated over a nylon membrane having a pore size of 0.45 μm. The cake was washed with water and methanol, and dried under vacuum overnight, giving the product of 205 mg. Since most of oxygen-containing functionalities were eliminated during the KOH treatment, this product was named as **rGO-K**.

2.2. Material characterization

Elemental analysis was carried out with an Elementar vario EL III elemental analyzer. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet AVATAR-360 Fourier transform infrared spectrophotometer. UV–vis spectroscopy was performed on a Varian Cary 100 spectrometer. Raman spectra were measured on a Renishaw inVia Reflex micro-Raman spectrometer using a 100-fold objective lens and a crystal laser excitation of 514.5 nm. Atomic force microscopy (AFM) was performed under ambient conditions on a Veeco instrument Nanoscope IIIa Multimode apparatus operating in a non-contact mode with a silicon tip and cantilever operating at a frequency of 325 kHz and a scanning speed of 1.5 Hz. Sample was prepared by placing a drop of very dilute DMF dispersion on a mica substrate and dried in vacuum at room temperature. X-ray photoelectron spectra (XPS) were recorded on a PHI-5000 VersaProbe spectrometer under 10^{-7} Pa using monochromatic Al K_α X-ray source operating at 100 W. The morphology of alkylated graphenes was investigated by a Hitachi S-4800 field emission scanning electron microscope (FE SEM) operating at 3 kV. Sample was prepared by freeze-dried and immobilized on a conductive tape. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were performed on a JEOL JEM-2010 microscope operating at 120 kV. Sample was prepared by placing a drop of very dilute acetonitrile dispersion on a holey-carbon-coated copper grid and dried at ambient conditions. Thermogravimetric analysis (TGA) was carried out on a Q500 TGA instrument under a N_2 flow at a heating rate of 10 °C min^{-1}.

2.3. Electrochemical measurements

Electrochemical measurements were performed on a Princeton PARSTAT 2273 and Land CT2001A with a three-electrode system using aqueous KOH solution (6 M) as the electrolyte at room temperature. The working electrode was prepared by mixing an active material with carbon black and polytetrafluoroethylene in a weight ratio of 85:15:5 in ethanol. The slurry was painted at the one side surface of nickel foam with an area of 1 cm^2 and folded, pressed under a pressure of 7.5 MPa. By means of weight difference, the mass loading of the active material on Ni foam electrode was estimated to be 4, 5.75, 5.24 and 5.03 mg for **C_4rGO**, **C_8rGO**, **C_{16}rGO**, and **rGO-K**, respectively. A Pt plate and Ag/AgCl electrode were used as the counter and reference electrodes, respectively. The specific capacitance of the electrode was calculated from the cyclic voltammetry (CV) curves according to the following formula:

$$C = \frac{1}{2m\Delta V}\int_{V_{initial}}^{V_{final}} \frac{I}{dV/dt}dV$$

where C (F g^{-1}) is the specific capacitance, m (g) is the mass of the active material in the electrodes, ΔV (V) is the potential window, $V_{initial}$ (V) and V_{final} (V) are the starting and end potential in one cycle, I (A) is the instantaneous current at a given potential, and dV/dt is the potential scanning rate. The discharge specific capacitance is calculated from the discharge curve using the following formula:

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

where I (A), Δt (s), m (g), and ΔV (V) are the discharge current, discharge time consumed in the potential range of ΔV, mass of the active material, and the potential window, respectively.

2.4. Specific surface area measurement

In this work, material specific surface area (SSA) was measured by means of two methods: a usual Brunauer–Emmett–Teller (BET) way performed on solid state and a dye-absorption way carried out in solution using methylene blue (MB) dye as a probe [25]. In BET method, nitrogen adsorption was performed on a Micromeritics accelerated surface area porosimetry (ASAP 2020, USA) autoadsorption analyzer. Prior to gas adsorption, all the samples were outgassed in a vacuum at 120 °C for 24 h. After N_2 adsorption