



Highly flexible and shape-persistent graphene microtube and its application in supercapacitor



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ABSTRACT

Graphene microtube has a robust potential application in gas separation, catalysis, water treatment and electronics. At present it remains two big challenges: high persistence of the tubular structure and high quality of the microtube. Here, a novel electrochemical technique was proposed, in which graphene oxides can be simultaneously deposited and reduced on a template wire at room temperature. After removing the template, the tubular structure was formed and complied well with the shape of the template. Moreover, the tube wall is composed of highly aligned graphene sheets. These combined characters bring about excellent flexibility and electrochemical properties, e.g., the specific capacitance of the graphene microtube is 2.5 times the value of the graphene fiber with the same sectional area.

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1. Introduction

Graphene, a two-dimensional carbon nanomaterial, has attracted much attention due to its extraordinary properties in mechanical, thermal, electrical and optical fields [1–3]. A single-layer graphene sheet with a thickness of 0.34 nm and a length or width of several to dozens of microns finds an application after assembled into a macro structure. To this end, various structures have been developed, e.g., film, sponge, ribbon, fiber and microtube [4–7]. Among them, graphene microtube is an emerging member. Since carbon tube has shown a great potential in gas separation, catalysis, water treatment and electronics, graphene microtube, an analogue of carbon tube, will prevail in these fields [8–12].

So far several methods have been developed to generate the graphene microtube, e.g., chemical vapor deposition (CVD) [13,14], hydrothermal synthesis [15] and wet-spinning [11]. However, these methods feature some disadvantages. In a typical CVD protocol, graphene was grown on a Cu wire under a super-high temperature of 1000 °C. When removing the Cu wire, the resulting tubular structure collapsed and it therefore failed to maintain its shape [14]. For the other two methods, graphene oxides (GO) were used as the

starting material and the microtubes were reported to be shape-persistent, however with a low quality. They require long heat treatment time, for instance 2.5 h at 230 °C, or hazardous reducing agents to improve the quality [11,15]. The disadvantages of the available methods arouse a pressing need for an efficient and facile method towards shape-persistent and high-quality graphene microtube.

As for the use of the graphene microtube, a great potential is to construct exquisite fiber-shaped supercapacitors, which have been deemed as a promising energy storage device for the thriving flexible and wearable electronics [16–19]. They prevail over film-shaped and bulk supercapacitors in flexibility, wearability and scalable connection [20,21]. However, to the best of our knowledge the energy storage performance of the graphene microtube has not been unveiled to date. The main reason may be the poor quality of the existing graphene microtubes.

Herein, a novel electrochemical technique was proposed. GO could be simultaneously deposited and reduced on a Cu wire. After etching the Cu wire the tubular structure was retained, resulting in the graphene microtube. The method has several merits: short preparation time (e.g., 20 min), low temperatures (e.g., at room temperature) and environmental benignity. Moreover, the achieved graphene microtube is shape-persistent and possesses a high quality derived from the highly aligned graphene sheets in the tube wall. Consequently, it presents excellent flexibility and electrochemical performance. The graphene microtube maintains stable

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under bending with an angle of 50° and has a large gravimetric specific capacitance of 135.5 F g⁻¹, which is 2.5 times the value of the graphene fiber with the same sectional area.

2. Experimental section

2.1. Preparation of graphene microtube (ERGO)

Graphene oxides (GO) were synthesized by a modified Hummers' method [22]. 1.0 wt% GO suspension of 85 ml was prepared by ultrasonic treatment for 20 min, afterwards adding 85 ml of 0.2 M lithium perchlorate aqueous solution under stirring, resulting in the plating solution. Cu wires with a diameter of 0.1 mm were washed by 1 M HCl solution, deionized water and ethanol successively, and then dried in the air. A three-electrode system was carried out to electrochemically grow the graphene microtube. The Cu wire, Pt wire served as the working and counter electrodes, respectively, together with the Ag/AgCl reference electrode. A constant potential mode was applied, i.e., the potential was kept at -1 V. The growth time was varied from 5 min to 60 min. The plating solution was kept at room temperature (25 °C) and stirred smoothly. When the growth ended, the graphene-coated Cu wire was immersed into 2 M FeCl₃ aqueous solution to etch the Cu wire, then washed with deionized water and dried in the air resulting in the graphene microtube.

2.2. Preparation of GO fiber and chemical reduced GO (CRGO) fiber

GO suspension with a concentration of 10 mg ml⁻¹ was made by ultrasonic treatment for 20 min. Then the dispersion was heated to evaporate the water to achieve a high concentration of 40 mg ml⁻¹ in 60 °C water bath. Continuous wet-spinning was carried out with a homemade spinning machine [23]. The GO dispersion was loaded into a plastic syringe and then injected into a rotating coagulation bath resulting in a gel fiber, which was rolled onto a drum and dried at 60 °C in vacuum leading to a GO fiber. Finally, the GO fiber was reduced by hydriodic acid (45%, Sinopharm) at 95 °C for 8 h followed by washing with deionized water thoroughly and drying at 80 °C for 12 h in vacuum.

2.3. Characterization

The structure and morphology of graphene microtubes were characterized by scanning electron microscope (SEM, Hitachi, SU8010). The composition and bonds were studied by Raman spectroscopy (Renishaw microRaman, 514.5 nm laser) and X-ray photoelectron spectroscopy (XPS, Thermo, Escalab 250). The weight of microtubes was measured by an ultra-microbalance (Mettler Toledo, XP6). The sheet resistance of graphene microtubes was tested by four-point probe (SX1944) and their conductivity was investigated by electrometer (Keithley, 6517B). The specific surface area and the pore diameter distribution were measured using the Brenauer-Emmett-Teller (BET) method by a surface area and porosity system (Micromeritics, ASAP2460) at 77 K.

2.4. Fabrication of all-solid-state supercapacitors and electrochemical measurements

Electrochemical workstation (Chenhua, CHI 660E) was used to investigate the electrochemical properties. A gel electrolyte was prepared. First, deionized water (10 ml) was mixed with phosphoric acid (10 mL) and stirred for 30 min. Second, PVA powder (1788, 10 g) was dissolved in 90 mL deionized water at 90 °C and then added to the above solution under stirring for 1 h, followed by

cooling to the room temperature. A symmetrical two-electrode system was utilized. Two graphene microtubes were placed in parallel and separated by the gel electrolyte leading to a fiber-shaped supercapacitor. The current density was varied from 0.1 to 10 A g⁻¹. The voltage window was in a range of 0–0.8 V. The capacitance of the graphene microtubes was calculated from the galvanostatic charge/discharge curves, using the following equation:

$$C = (2 \times I \times \Delta t) / \Delta U$$

where I , Δt and ΔU correspond to the discharge current, discharge time and voltage window, respectively. The gravimetric specific capacitance (C_m) was computed from dividing C by the mass, which here is based on one graphene microtube, i.e., single electrode. To test the flexible performance, the fiber-shaped supercapacitor was fixed on a PET substrate and the electrochemical property was monitored when bending the substrate.

3. Results and discussion

Fig. 1 represents the preparation scheme of the electrochemically grown graphene microtube. GO was simultaneously deposited and reduced on the Cu wire driven by a protonation process under an electric field. After etching the Cu wire the graphene microtube was finally obtained. From the cyclic voltammograms (Fig. S1a) in a potential range from -0.4 to -1.5 V (vs. Ag/AgCl), a large cathodic current peak occurs at -1.2 V with a starting potential of -0.8 V. This large reduction current is ascribed to the reduction of the surface oxygen groups of GO since the reduction of water to hydrogen occurs at more negative potentials (e.g., nearly -1.5 V) [24]. Also from the Amperometric i - t curve at a constant potential of -1 V (Fig. S1b), the cathodic current decreased when extending the growth time, which indicates an increasingly inefficient reduction. Thus the growth time will affect the wall thickness of the microtube. From optical images (Fig. S2), the color of Cu wire was changed from golden yellow to dark after a short growth time, which verifies the graphene coating.

The architecture of graphene microtubes can be helical (Fig. 2a) or straight (Fig. 2b) corresponding to the shape of Cu wire. A characterized wavy surface was found for the graphene microtubes (Fig. 2c–e), which was caused by the wrinkling of the graphene sheets. The cross-sectional morphologies of the graphene microtubes with different growth time are shown in Fig. 2f–m. A hollow tubular structure is evident for all cases. And the inner diameters are complied with that of the Cu wire. More interestingly, a distinct layer-by-layer structure of the graphene sheets in the tube wall was formed (Fig. 2j, k, 2l and 2m), which indicates a high alignment of the graphene sheets. This could be beneficial for the properties of the graphene microtubes.

The wall thickness of the microtubes decreased after an initial increase when increasing the growth time and a maximum value was reached at the growth time of 20 min. Specifically, they are 1.2 μ m, 1.9 μ m, 1.3 μ m and 1.0 μ m according to the growth time of 10 min, 20 min, 30 min and 60 min, respectively. This trend was proofed by the mass of graphene microtubes (Fig. S3). Specifically, the dependence of the mass of graphene microtubes on the growth time was investigated. A maximum mass of 26 μ g cm⁻¹ was achieved at the growth time of 20 min. To have a deep probe, XPS tests were carried out for the reduced graphene oxides (rGO) on the Cu wire with different growth time, which were free of the following processes, e.g., etching the Cu wire and water washing (Fig. S4). And the concentrations of O element were listed in Table S1, i.e., 21.5%, 19.8%, 37.6% and 44.2% for the growth time of 10 min, 20 min, 30min and 60 min, respectively. The result is consistent with the

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