

In-situ synthesis of carbon nanotube/graphene composite sponge and its application as compressible supercapacitor electrode



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ABSTRACT

Carbon nanotube/graphene (CNT/G) composite sponge is prepared by *in-situ* partially unzipping of CNT sponge. Polypyrrole is then electro-polymerized onto the sponge to form CNT/graphene/polypyrrole (CNT/G/PPy) ternary composite sponge. The capacitive behavior of the composite is investigated by using cyclic voltammetry, galvanostatic charge/discharge and electrochemical impedance spectroscopy. The results show that the degree of unzipping of CNT can be controlled by regulating the period of reaction. The specific capacitance of CNT/G sponge shows a significant improvement compared to that of the original CNT sponge (from 4 to 103 F/g). With PPy coating, the CNT/G/PPy displays a high specific capacitance of 225 F/g and excellent capacitance retention of 90.6% after 1000 cycles. In addition, the CNT/G/PPy sponge shows a high capacitance performance under compression. This work indicates that it is possible to build high performance compressive electrodes using CNT/G core networks coated with conductive polymer.

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1. Introduction

Supercapacitor, also called electrochemical capacitor, is a capacitor which store charges using either ion adsorption at the interface of electrode and electrolyte (electrochemical double-layer capacitor, EDLC) or fast surface redox reactions [1,2]. Supercapacitor has been continuously studied for years due to its promising performance of storing energy such as high energy density, high power density, and fast rate of charge/discharge [3,4]. Among different shapes of electrodes, three-dimensional (3D) compressive bulk has great potentials in applications of home furnishing, wearable devices, and automobile, etc. Many works have been conducted to develop materials for three-dimensional porous electrode [5–7]. Carbon materials are one of these materials [8].

Carbon nanotube (CNT) and graphene have been identified to possess great potentials in supercapacitors, because of their high

electrical conductivity and large specific surface area [9–10]. By changing the microstructure of CNT and graphene [11–15], or introducing pseudocapacitive materials, such as polypyrrole (PPy) [16], polyaniline [17], and MnO₂ [18,19], capacitance of supercapacitors have been continuously promoted with improvements in energy density, power density, and cycling stability. Besides the capacitors in film and fiber shapes, 3D porous capacitor based on CNTs or graphene has also been studied extensively [20–22]. 3D porous CNT and graphene materials are suitable to serve as compressive electrode since the porous structure enables them to deform while have a large specific surface area [23,24] at the same time. However, many graphene-based 3D materials are hydrogel or aquogel, which cannot construct uniform internal conductive networks due to the large number of defects. Besides, the length of the third dimension of cavities is typically limited to the length of few CNTs [6,22,25,26].

Herein, we demonstrate one effective, simple, *in-situ* method to fabricate CNT/graphene (CNT/G) composite sponge based on original CNT sponge. Unzipping CNTs to fabricate Graphene nanoribbons (GNRs) have been studied previously [27,28] that similar method in Ref. [27] was used in this work. By regulating the reaction period, we controlled the degree of unzipping CNTs to keep the CNT framework as well as the conductive networks. We

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tested the capacitive behavior of as-prepared CNT/G sponge electrode in a three-electrode system. The results demonstrated that the specific capacitance of CNT/G sponge was 103 F/g at a scan rate of 2 mV/s, which is very high compared to that of clean CNT sponge of 4 F/g. To enhance the mechanical strength, as well as the supercapacitor performance of CNT/G sponge, we introduced a pseudomaterial, PPy. In fact, CNTs and graphene coated with PPy have been studied by several team before [16,23], but only very few research tried depositing pyrrole onto CNTs and graphene simultaneously to get CNT/G composite sponge. By regulating the period of electro-polymerization, we obtained compressible CNT/G/PPy sponge with various mass fractions of PPy. Performance of supercapacitors made of as-prepared composite sponge was subsequently tested. The results indicated that the specific capacitance was up to 225 F/g. In addition, cycling tests indicated that capacitance of CNT/G/PPy composite sponge retained 90.6% after 1000 cycles at 20 mV/s. Furthermore, compression tests indicated that capacitance retained 92% at the compressed state ($\epsilon \approx 50\%$).

2. Experimental

2.1. Synthesis of CNT sponge

CNT sponges were synthesized by using CVD method as previously reported [23,29]. A solution of ferrocene dissolving in 1,2-dichlorobenzene with a concentration of 0.06 g/mL was injected into the quartz tube of CVD furnace with a flow of 0.13 mL/min by using peristaltic pump, where ferrocene and 1,2-dichlorobenzene were used as catalyst and carbon source, respectively. The reaction temperature in the CVD furnace was 860 °C, while the temperature at the entrance of carbon source was 250 °C to make the ferrocene and 1,2-dichlorobenzene evaporate.

To collect CNTs, we put a quartz boat in the deposition area, where the CNT sponge was peeled off after reaction.

2.2. Preparation of CNT/G Sponge

Fig. 1 shows the process of fabricating CNT/G sponge. Original CNT sponge samples synthesized by chemical vapor deposition (CVD) method were cut into blocks with edge size of several mm (Fig. 1g). Then CNT sponge blocks were immersed in the $\text{KMnO}_4/\text{H}_2\text{SO}_4$ solution with concentration of 0.03 g/mL at 60 °C for 1, 2, and 3 h, respectively, where H_2SO_4 was concentrated H_2SO_4 of 98 wt% (Fig. 1h). The as-prepared CNT/GO sponge was immersed in the deionized water (DI water) subsequently to dilute the concentrated sulfuric acid. Moreover, MnO_2 , the product of previous reaction, could be partly washed at the same time. After being soaked and cleaned for 3 times, CNT/GO sponge was reduced by using HI (45 wt%). Then remaining HI and products of reaction were diluted and cleaned by DI water as before until the electrical conductivity of leach liquor reached a value lower than $10 \mu\text{S}/\text{cm}$ (electrical conductivity of deionized water in our laboratory is about $1 \mu\text{S}/\text{cm}$) (Fig. 1i). Finally, the as-synthesized CNT/G sponge was dried by freeze-drying to keep the micro-structure. Fig. 1d-f show the micro-morphology of CNTs, CNT/GO, and CNT/G, respectively.

2.3. Preparation of CNT/G/PPy sponge

Electrochemical polymerization in three-electrode system was used to coat PPy onto the surface of CNT/G microstructure. The electrolyte was Pyrrole/ NaClO_4 aqueous with a concentration of 0.1 M Pyrrole and 0.1 M NaClO_4 . Ag/AgCl and Platinum were reference electrode and counter electrode, respectively. To ensure that the electrolyte molecules adequately enter the inside of CNT/G

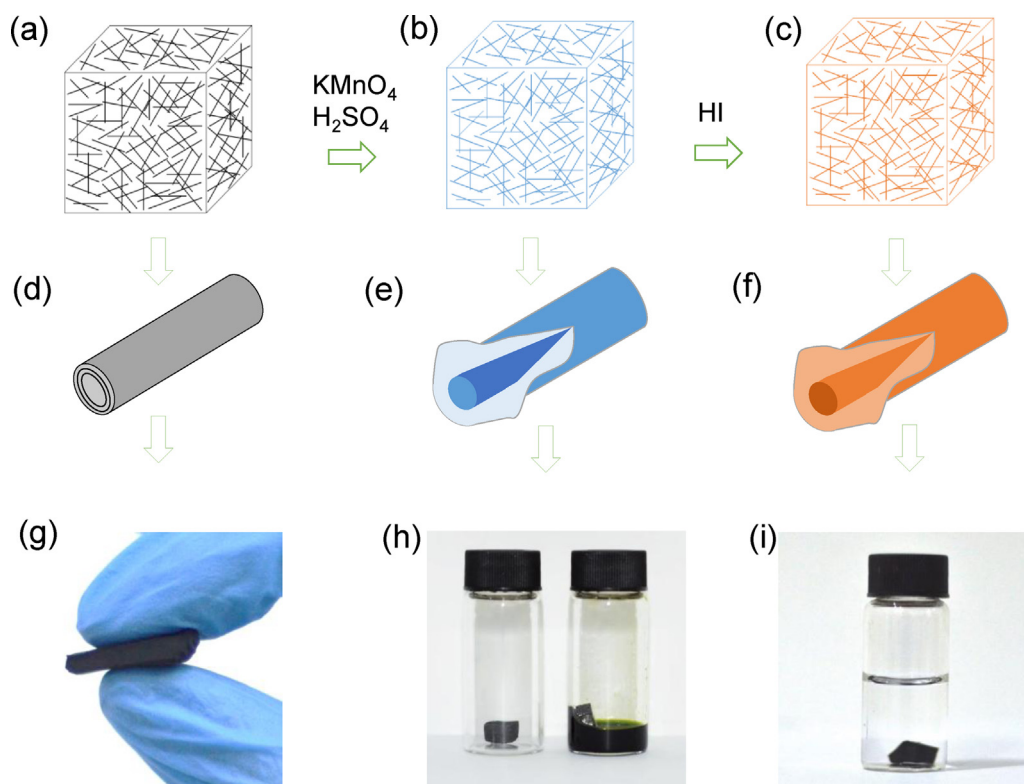


Fig. 1. Illustration of the fabrication process from a CNT sponge to a CNT/G composite sponge. (a,d) Pristine CNT sponge. (b,e) CNT/GO sponge immersed in $\text{KMnO}_4/\text{H}_2\text{SO}_4$. (c,f) CNT/G sponge in deionized water. (g-i) Corresponding photographs.

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