



Porous nitrogen-doped graphene/carbon nanotubes composite with an enhanced supercapacitor performance



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ABSTRACT

A facile, time-saving and one-step process to prepare graphene-based materials with excellent comprehensive capacitive performance is very promising for practical applications. Here, porous nitrogen-doped graphene/carbon nanotubes composite (PNGC) with loosened structure was prepared by pyrolysis method and the porous structure of PNGC was controlled by combined action of urea and low-cost lignosulfonate. PNGC is equipped with porous structure and thin graphene nanosheets, and meanwhile possess numerous active sites and high surface areas. Importantly, PNGC exhibits a high specific capacitance of 246.6 F g^{-1} at a current density of 0.5 A g^{-1} and high stability of 96.5% capacitance retention ratio after 2000 cycles at 100 mV s^{-1} , indicating an excellent performance of PNGC. Furthermore, the corresponding mechanism of pore formation in PNGC is hence proposed. This work of obtaining PNGC is of paramount importance for the future practical application of electrode materials for supercapacitor application.

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1. Introduction

Supercapacitors are divided into three types, electrical double layer capacitors (EDLCs), faradic pseudocapacitors, and hybrid supercapacitors [1]. The EDLCs, which are also called electrochemical capacitors, have attracted remarkable attention due to their superior properties, higher power density and longer cycle life than secondary batteries [2–4]. It is well known that EDLCs show very excellent stabilities but small specific capacitances; while for faradic pseudocapacitors, they usually have high specific capacitance but poor stability [1]. In this regard, many attempts have been devoted to improve the energy density of EDLCs by combining EDLCs with faradic pseudocapacitance to form hybrid electrochemical supercapacitors [5–8], which possess both high specific capacitance and excellent stability.

As we all know, the capacitance of EDLCs depends on the area of interface between electrodes and electrolyte [9]. Therefore, many porous carbon materials with high surface area, such as carbon nanofiber [10], activated carbon [11], carbon aerogels [5], etc., have been widely used as electrodes for the fabrication of EDLCs. However, the conductivities of most traditional porous carbon materials will decrease when their surface areas are increased [12].

However, carbon nanotubes (CNTs) with both high conductivity and high surface area possess very low capacitance due to the high contact resistance between electrodes and current collector [13]. On the contrast, the conductivity of graphene can not only be improved with the increase of its surface area, but also the contact resistance is very low [1].

Graphene shows a very high theoretical surface area of $2630 \text{ m}^2 \text{ g}^{-1}$ and excellent electronic conductivity of 10^7 S m^{-1} [14], which is a brilliant candidate as an electrode material of supercapacitor. However, due to the aggregation of graphene sheets and deficiency of effective channel for electrolyte ions to reach, the performances of graphene-based materials are greatly limited [1]. Accordingly, substantial efforts have been dedicated to solve the above problems. The easiest way to think of is to introduce spacers, such as carbon spheres [15], carbon nanotubes [6,16] and carbon nanofibers [17], into graphene sheets. Theoretically, CNTs are considered as ideal spacers to separate graphene sheets and enhance the conductivities of graphene/CNTs composites [6,16,18], because of a high conductivity of CNTs. However, the graphene/CNTs composites still tend to stack tightly during drying. In terms of morphology, materials with higher surface area are considered to perform better for more fully contacting between electrolyte and electrodes surface and faster electrolyte ions transfer [19,20]. To improve surface area of graphene-based composites, templates such as ZnO [21] and MgO [22], are introduced to prepare high surface area graphene-based

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composites, whereas the residual templates tend to influence the performances of materials. In order to achieve high performance, another method frequently exploited is to dope heteroatoms including N [6], S [23] and B [24] into graphitic structure for enhancing electrical property of grapheme [6,7]. Up to now, nitrogen-doped graphene has been fabricated by chemical vapor deposition (CVD) [25,26] nitrogen plasma [27], supercritical reaction [28] and arc discharge [29]. However, these processes have some deficiencies, including considerable precise equipment, high maintenance cost and limited yield.

In this work, porous nitrogen-doped graphene/carbon nanotubes composite (PNGC) was prepared by pyrolysis procedure, and used as an electrode material of supercapacitor. Pyrolysis was adopted as a facile and one-step method for preparation of PNGC, in which graphene oxide (GO) was reduced to enhance the property of supercapacitor and nitrogen atoms were introduced to graphene sheets or CNTs to modify the band structure of the material for faster electron transfer [30]. During the pyrolysis procedure, carbon nanotubes acted as spacers to prevent the aggregation of graphene sheets; urea was used as a nitrogen dopant to contribute pseudocapacitance and worked with low-cost lignosulfonate (LS), a waste from pulp processing industries, to fabricate pores in the graphene nanosheets, providing more “pathways” for ions conduction. All aspects would enhance the performance of supercapacitors ultimately. The electrode material of low-cost PNGC used for supercapacitors expects to achieve high capacity and long cycle life.

2. Experimental section

2.1. Materials

Expanded graphite, sulfuric acid, nitric acid, potassium permanganate, hydrogen peroxide and urea were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used without any further purification. Lignosulfonate was obtained from Liangfeng Chemical Co., Ltd. (Jinan, China) and used as received. Carbon nanotubes were purchased from Nanjing XFNANO Materials TECH Co., Ltd. and purified through mild hydrothermal treatment according to the previous literature [31].

2.2. Preparation of PNGC

Graphene oxide (GO) was fabricated by a modified Hummers' method based on the previous report [26]. The PNGC was prepared by a facile procedure, i.e., mixing and pyrolysis. Firstly, 100 mg GO and 10 mg CNTs were ultrasonic for 2 h, respectively, and then the mixture of GO and CNTs was ultrasonically stirred for 2 h again. Secondly, 10 g urea and 10 mg LS were added into the above mixture; the mixture was dried after 3 hours' magnetically stirring to prepare nitrogen-containing precursor. Finally, PNGC was obtained by pyrolyzing the precursor at 800 °C (with a heating rate of 3 °C min⁻¹ under nitrogen flow) for 2 h and naturally cooled down to room temperature. A schematic representation of PNGC preparation is showed in [Scheme 1](#).

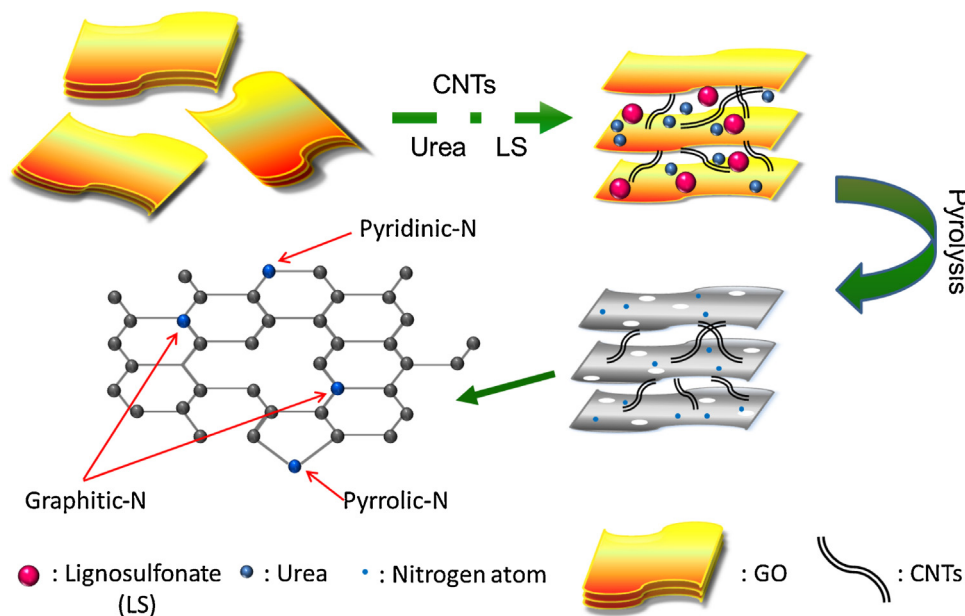
For comparison, reduced oxide graphene (rGO), graphene/carbon nanotubes (GC) LS/graphene/carbon nanotubes (LGC), and N-doped graphene/carbon nanotubes (NGC) were prepared from GO, a mixture of GO and CNTs, a mixture of LS, GO and CNTs, and a mixture of GO, CNTs and urea, respectively, used the identical above-mentioned procedure.

2.3. Characterization of structure and morphology

Morphologies of samples were observed by field emission scanning electron microscopy (SEM, Carl Zeiss ULTRA 55) and transmission electron microscopy (TEM, FEI TECNAI 20). Brunauer-Emmett-Teller (BET) surface area was measured with a Quantachrome NOVA4200e surface area detecting instrument by N₂ adsorption at 77.3 K. X-ray diffraction (XRD) curves were observed on a Ultima III X-ray diffractometer using Cu K α radiation at $\lambda = 0.15406$ nm. Micro-Raman spectra for the structure modifications were obtained on a LabRAM Aramis Raman system with a 532 nm laser as an excitation source. X-ray photoelectron spectroscopy (XPS) analysis was operated on thermo ESCALAB 250XI with an excitation source of Al K α radiation ($\lambda = 1486.6$ eV).

2.4. Electrochemical measurements

Electrochemical measurements were carried out on a CHI660E electrochemical analyzer (Chenhua, Shanghai, China) with a conventional three electrode system in a 6 M KOH aqueous electrolyte at room



Scheme 1. Schematic representation of preparation procedure of PNGC.

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