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Full Length Article

Preparation of S/N co-doped graphene through a self-generated high gas pressure for high rate supercapacitor

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ABSTRACT

At present, the application of doped graphene have been widely studied in supercapacitor, but the preparation of co-doped graphene electrode materials for high rate performance supercapacitor is still a challenge. In this work, we reported an effective method to prepare S/N co-doped graphene (SNG-H) through a self-generated high gas pressure by heating graphene with $(NH_4)_2SO_4$ and melamine in a sealed vacuum copper tube under 600 °C. During heating treatment, the self-generated high gas pressure was formed by pyrolysis of the precursors in a sealed space. The X-ray photoelectron spectroscopy result showed that N and S atomic percentage of SNG-H were 6.22 at% and 2.82 at% which higher than that doped method using inert gas. This result indicated that the self-generated high gas pressure by pyrolysis of the precursors in a sealed space promoted the incorporation of heteroatoms into the lattice of graphene. Meanwhile, this method avoided the resources consumption of using inert gas (N_2 and Ar) and effectively reduced gas pollution emissions. As the supercapacitor electrode material, the specific capacitance of SNG-H electrode material reached 264.3 F g^{-1} at 0.5 A g^{-1} and showed excellent rate capability at 200 mV s^{-1} in a three-electrode system. SNG-H also exhibited high capacitance performance, excellent rate capability (82% capacitance retention from 1 to 20 A g^{-1}) and excellent cycling stability (95%) after 5000 cycles at 5 A g^{-1} in a symmetric two-electrode system. SNG-H was prepared through a self-generated high gas pressure in a sealed vacuum copper tube under 600 °C. This method improved the content of doped heteroatoms in SNG-H and enhanced the supercapacitor rate performance of SNG-H as an electrode material.

1. Introduction

Supercapacitors (SCs) with rapid charge and discharge rate, wide operating temperature range, long cycle life and high power density have become an important focus of energy storage device, and have been widely applied in various industries. Electric double-layer capacitors (EDLCs) and faraday pseudo-capacitors are two storage mechanisms for SCs [1,2]. To a large extent, the capacitance performance of SCs depends on electrode materials [3,4]. Graphene, 2D honeycomb lattice sheet of sp^2 hybridization carbon atoms, has high chemical and mechanical stability, high theoretical specific surface area, excellent electrical conductivity and environmentally friendliness [5–9]. Therefore, graphene has attracted attentions of researchers as electrode materials in SCs. However, poor ion permeability and surface wettability, few active edges and stack of graphene nanosheets make the practically achieved specific capacitance of graphene far below the theoretical value [10]. Doping of heteroatoms (N, S, P, B, etc.) is an effect method to change the electronic properties and modify the surface activity. Heteroatoms can increase the specific capacitance of graphene by introducing Faradaic pseudocapacitance [11,12]. Among the doped heteroatoms, nitrogen atom doping can effectively improve the capacitance of electrode material [13–16]. For example, Manikantan et al. synthesized nitrogen-doped three-dimensional graphene by annealing graphene oxide and melamine reaches 217 F g^{-1} at 5 mV s^{-1} with good rate capability (62%) [17]. The formation of pyrrole nitrogen and pyridine nitrogen in the graphene lattice can not only produce Faraday pseudocapacitance but also improve the hydrophilicity of electrode material [18,19]. In addition, sulfur atom doped has been also studied, because the formation of thiophene-S in carbon lattice can also improve charge-storage capability of electrode materials [20–24]. Recent studies have reported that S/N co-doping of heteroatoms has more excellent capacitance than single heteroatom doping due to the synergistic effect of doped atoms [25–31]. At present, numerous techniques have been used for preparing doped graphene such as chemical vapor deposition [32–35], plasma etching [36], ball milling [3], molecular layer deposition [37], hydrothermal [38] and pyrolysis of precursors in the

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atmosphere of rare gases [39]. Nevertheless, most of these methods are expensive, cumbersome, low doping content and air pollution. Therefore, it is necessary to seek a method which is a simple and effective preparation of doped graphene.

In this paper, an effective method of the self-generated high gas pressure was used to prepared sulfur (S) and nitrogen (N) co-doped graphene (SNG-H) by heating graphene with $(NH_4)_2SO_4$ and melamine in a sealed vacuum copper tube under 600 °C. A high gas pressure was formed by pyrolysis of the precursors in a sealed space, which promoted the incorporation of heteroatoms into the lattice of graphene. And this method avoided the resources consumption of using inert gas (N_2 and Ar) and effectively reduced gas pollution emissions. Meanwhile, as a supercapacitor electrode material, SNG-H exhibited excellent capacitance reached 264.3 F g^{-1} at 0.5 A g^{-1} and showed excellent rate capability.

2. Experimental section

2.1. Materials

Graphene (layers number: 4–8, and dimensional size: 0.5–5 μm) was purchased from Tangshan Jianhua Science and Technology Development Co., Ltd. The other analytical reagent grade chemicals reagents were purchased from Aladdin and used as received.

2.2. Preparation of SNG-H

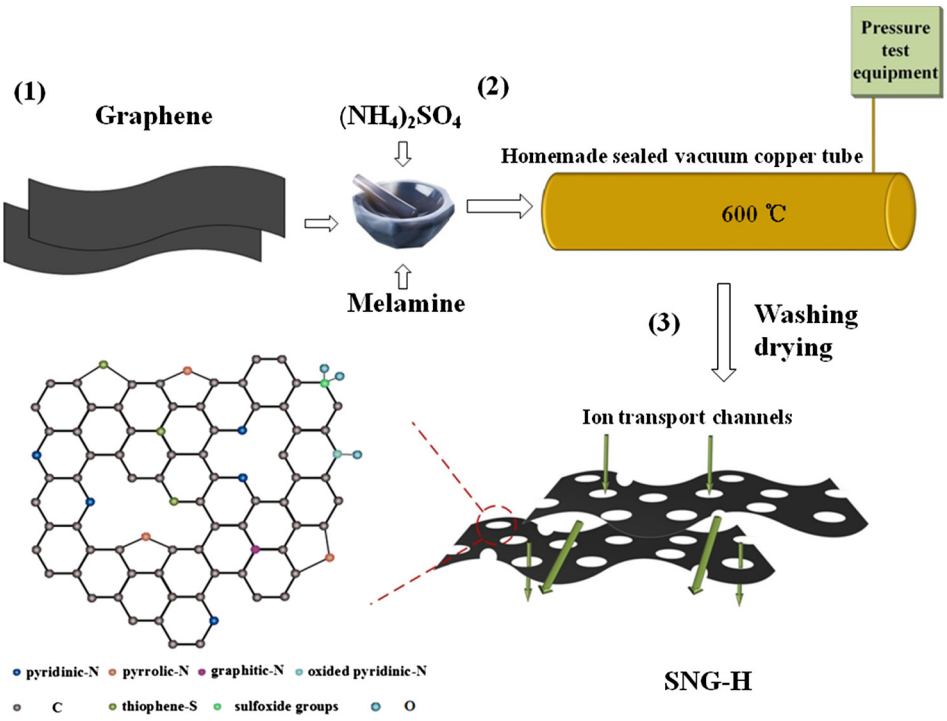
The SNG-H was synthesized in a sealed vacuum copper tube under a self-generated gas pressure as illustrated in Scheme 1. The specific experimental process was as follows: firstly, 30 mg of graphene, 900 mg $(NH_4)_2SO_4$ and 120 mg melamine were placed in the agate mortar to mechanical mixing uniformly. Secondly, the uniform mixture was loaded into a copper tube with one of the ends sealed by mechanical folding extrusion, and then the other end was sealed by mechanical folding extrusion after vacuum degree of the copper tube inside up to 3×10^{-2} Pa tested by the gas pressure test equipment (vacuum thermocouple, ZD0-2). The homemade sealed vacuum copper tube size was 9.52 mm in outer diameter and 0.70 mm in wall thickness and approximately 100 mm in length and connected with pressure gauge (YN60). Thirdly, the sealed vacuum copper tube was put into a 600 °C muffle furnace maintained for 3 h. After 3 h, the copper tube was removed from the muffle furnace and cooled rapidly in the air. This method can effectively shorten the experimental period. During the heating treatment, the gas produced by the pyrolysis of the precursor formed a high gas pressure in the sealed copper tube which was as high as 25 MPa. Finally, the obtained sample was washed with 1 M hydrochloric acid and deionized water until pH = 7 and dried at 80 °C for 12 h and then it was marked as SNG-H. For comparison, the same components sample was heat-treated at 600 °C for 3 h in a tubular furnace under a nitrogen atmosphere, which was denoted as SNG.

2.3. Characterization

Transmission electron microscopy (TEM) JEM-2010EX with an image filter (Gatan GIF) at 200 kV was used to survey the microscopic morphology of samples. The active material was dispersed in ethanol and then dropped on a 200 mesh copper mesh micro-gate for TEM testing. The elemental composition, content and different doped configurations were measured though X-ray photoelectron spectroscopy (XPS) (PHI Quantera IIXPS) with a monochromatic Al KX-ray source. The structural characterization was analyzed by The structural characterization was analyzed by Micro-Raman Spectroscopy System of Renishaw (inVia, the laser wavelength at 532 nm).

2.4. Electrochemical measurement

All SCs performance was measured by using a Germany Zennium electrochemical workstation in 6 M KOH electrolyte (30 mL). An Hg/HgO (1 M KOH) was served as the reference electrode and a platinum foil (1 cm^2) was served as counter electrode throughout all experiments test in a three electrode system. Galvanostatic charge/discharge (GCD) and cyclic voltammetry (CV) were tested on the voltage range of −0.8–0 V. The amplitude of electrochemical impedance spectroscopy (EIS) measurements was fixed on 5 mV with the frequency from



Scheme 1. Preparation process of the SNG-H.