

Nitrogen-doped sandwich-like porous carbon nanosheets for high volumetric performance supercapacitors



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ABSTRACT

Nitrogen-doped sandwich-like porous carbon nanosheets (NPCG) have been prepared simply through carbonization of graphene/polyaniline hybrid materials. Due to its interconnected microporous structure, high nitrogen content (12.7 at.%), high surface area ($410.4 \text{ m}^2 \text{ g}^{-1}$) and high volumetric density (0.94 g cm^{-3}), the obtained sample prepared at 700°C (NPCG-700) shows both high gravimetric and volumetric capacitances of 305 F g^{-1} and 287 F cm^{-3} in 6 M KOH aqueous electrolyte, respectively. In addition, the assembled supercapacitor delivers a high energy density (16.3 Wh kg^{-1} and 15.3 Wh L^{-1}) in $1 \text{ M Na}_2\text{SO}_4$ aqueous electrolyte. Importantly, 97% of the initial capacitance is maintained after 5000 cycles, suggesting excellent cycling stability.

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1. Introduction

Supercapacitors have attracted intense research interest worldwide as ideal energy storage devices due to their unique advantages of high power density, long cycle life, superior reversibility and excellent rate capability [1,2]. Nowadays, a variety of porous carbon materials, such as activated carbon, mesoporous carbon, carbon nanotubes and graphene, are widely used as electrode materials for supercapacitors because of their high specific surface area (SSA), excellent physical/chemical stability, good electrical conductivity, relatively low cost and easily availability [3–7]. Due to the limited available SSA of porous carbon materials, their specific capacitance and energy density (less than 10 Wh kg^{-1}) are still unsatisfactory, and needed to be enhanced to meet the urgent requirement in further applications. Moreover, the electrical conductivity of porous carbon materials generally decreases with an increase of porosity due to the destruction of conductive pathways, which is detrimental to the power density and undesirable in practical application. Therefore, it is still an urgent challenge to develop advanced carbon materials with both large SSA and high energy density as well as excellent electrical conductivity without sacrificing the long cycle life.

In order to further enhance the specific capacitance of carbon materials, incorporating a pseudocapacitive component such as

metal oxides and conducting polymers on the surface or in bulk of carbon materials turns out to be a promising approach [8–13]. Alternatively, introducing heteroatoms such as N, B, P or S into carbon frameworks is a vital candidate to enhance the specific capacitance of carbon materials as these heteroatoms can give rise to pseudocapacitance and modify the electron donor-acceptor properties of carbon materials [14–19]. Among them, nitrogen-doping has been recommended as the most appealing and feasible way to enhance the specific capacitance of carbon materials in recent years while keeping remarkable cycling stability [16,20–22]. Nevertheless, the greatly developed electrode materials still can not be widely used where space is limited due to the low density of traditional carbon materials (typically less than 0.5 g cm^{-3}) [23]. In other words, the volumetric performance of the current carbon materials is less competitive although they exhibit outstanding gravimetric performance. In order to design and fabricate the compact and portable energy storage devices, it is urgently required to synthesize carbon-based material with high volumetric density [24,25].

In this paper, we elaborately synthesized the nitrogen-doped sandwich-like porous carbon nanosheets (NPCG) through one-step carbonization of graphene/polyaniline (PANI) hybrid materials. Due to its high SSA, enriched nitrogen and high volumetric density, the as-prepared NPCG sample possesses superior gravimetric and volumetric capacitances of 305 F g^{-1} and 287 F cm^{-3} in 6 M KOH aqueous electrolyte, respectively. Additionally, the assembled symmetric supercapacitor achieves a high volumetric energy density of 15.3 Wh L^{-1} in $1 \text{ M Na}_2\text{SO}_4$ aqueous electrolyte.

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2. Experimental

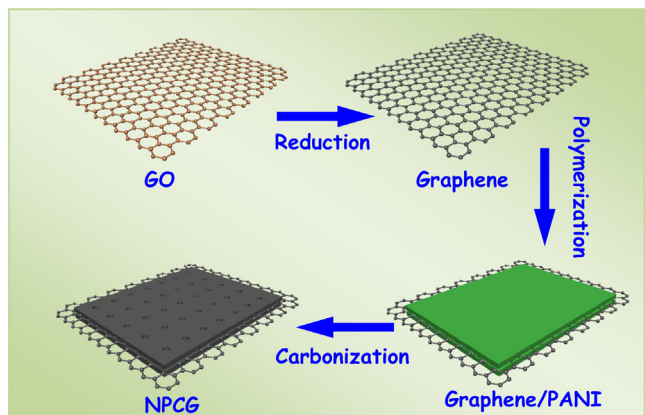
2.1. Synthesis of NPCG composite

NPCG composite was synthesized as follows (Scheme 1): Firstly, the graphene/PANI precursor was prepared through in-situ polymerization according to the previously reported procedure [26]. Briefly, graphene (0.13 g) prepared by hydrazine hydrate reduction was ultrasonically dispersed in 40 mL of distilled water at room temperature for 30 min and cooled to 2 °C in an ice-water bath. Then 40 mL of 0.25 M aniline monomer (solvent: 1 M HCl) was added into the above suspension and stirred for 10 min. Subsequently, 40 mL of 0.25 M ammonium persulfate solution was added dropwise into the mixed suspension and further stirred at 0–4 °C for 4 h. Finally, the black-green precipitation was filtered, washed repeatedly with distilled water until the filtrate was neutral and dried in a vacuum oven at 80 °C for 12 h to obtain graphene/PANI precursor.

In order to obtain NPCG composite, the graphene/PANI precursor was carbonized according to the following procedure: The sample was firstly stabilized in a horizontal tubular furnace at 280 °C in air for 1 h with a heating rate of 8 °C min⁻¹ and then carbonized under N₂ atmosphere with a heating rate of 5 °C min⁻¹ to the target temperature for 2 h. The resulting carbon materials prepared at 600, 700 and 900 °C were denoted as NPCG-600, NPCG-700 and NPCG-900, respectively. The contents of graphene in NPCG-600, NPCG-700 and NPCG-900 are 25.3 wt.%, 28.1 wt.% and 31.2 wt.%.

2.2. Characterization methods

The crystallographic structures of the materials were determined by a powder X-ray diffraction system (XRD, TTR-III) equipped with Cu K α radiation ($\lambda = 0.15406$ nm). The morphology of the samples was investigated using a scanning electron microscope (SEM, Hitachi SU70) and a transition electron microscope (TEM, JEOL JEM2010). Raman spectra were recorded with a Jobin-Yvon HR800 Raman spectrometer with 457.9 nm wavelength incident laser light. X-ray photoelectron spectroscopy (XPS) analysis was carried out on a PHI 5700 ESCA spectrometer with a monochromatized Al K α X-ray source (1486.6 eV). N₂ adsorption and desorption isotherms of the samples were performed at 77 K using an automated gas sorption analyzer (Autosorb iQ2, Quantachrome). The SSA of samples was determined according to the Brunauer-Emmett-Teller (BET) method. The pore size distribution was calculated from the adsorption branch of the isotherm based on the Density Functional Theory (DFT) model.



Scheme 1. Schematic illustration of the preparation of NPCG composite.

2.3. Preparation of electrodes and electrochemical measurement

To prepare the working electrode, the as-prepared NPCG materials, carbon black and poly(tetrafluoroethylene) were mixed in ethanol (75:20:5, w/w) and coated onto nickel foam with area of 1 cm², followed by dried at 100 °C overnight. All the electrochemical performances of the NPCG were firstly tested in a standard three-electrode system on a CHI 660C electrochemical workstation, in which a Pt foil (1.5 cm × 1.5 cm) and a Hg/HgO electrode were used as the counter and reference electrodes, respectively. The electrolyte was 6 M KOH aqueous electrolyte. A symmetric two-electrode system composed of two identical electrodes was also used to characterize the capacitive and energy-storage properties of NPCG-700 using 1 M Na₂SO₄ aqueous solution as electrolyte.

3. Results and discussion

3.1. Microstructure characterizations

Fig. 1 shows the SEM and TEM images of pristine graphene and the graphene/PANI composite. Graphene nanosheets exhibit two-dimensional (2D) structure with a relatively flat surface, thin layer (~2 nm) and few corrugations (Fig. 1a). After *in situ* polymerization, thin PANI films uniformly coat on both surfaces of graphene nanosheets to form a sandwich structure, maintaining the 2D morphology of graphene sheets (Fig. 1b). The PANI film consists of numerous nanoparticles with sizes of 2–4 nm (Fig. 1c and d). After carbonization at high temperatures, the obtained NPCG samples still inherit the 2D sheet-like structure of graphene/PANI composite as shown in the SEM image (Fig. 2a). Due to volume shrinkage and the release of non-carbon elements during the carbonization process, the surface of carbon film derived from PANI becomes rougher and rougher with an increase in temperature from 600 to 900 °C (Fig. 2b–d), resulting in the formation of porous carbon film as energy storage units loosely anchored on the graphene sheets. Considerable pores with diameters of ~2 nm could be clearly observed from the TEM images, which are created by the release of non-carbon elements during carbonization process. Additionally, the carbonization temperature has a great influence on the graphitization degree of samples. In the case of NPCG-900, the graphite lattice fringes with an interlayer spacing of 0.35 nm are obviously observed in Fig. 2d, suggesting the formation of highly conductive carbon networks that are favorable for electron transfer during rapid charge/discharge process.

XRD was performed to characterize the resulting samples as shown in Fig. 3a. For graphene/PANI composite, the crystalline peaks appear at $2\theta = 15.3^\circ$, 20.7° and 25.2° , corresponding to (011), (020) and (200) crystal planes of PANI in its emeraldine salt form, respectively [26]. XRD pattern of NPCG-600 exhibits two weak and broad diffraction peaks at around $2\theta = 24.8^\circ$ and 42.8° assigned to the (002) diffraction of the graphitic layer-by-layer structure and the (100) diffraction of graphite, respectively, indicating the amorphous nature of carbon, which is in good agreement with previous reports [27–29]. The intensity of these two peaks gradually increases and the peak position shifts a little to higher angle while the full-width at half-maximum decreases with increasing carbonization temperature, revealing the increased graphite crystallite size and decreased interspacing of graphene layer. In other words, the graphitization degree of the NPCG samples is improved with the increase of carbonization temperature, which is in good agreement with TEM observations (Fig. 2b–d). Fig. 3b displays the Raman spectra of the NPCG samples prepared at different carbonization temperatures. Two obvious peaks centered at ~1360 and 1573 cm⁻¹ can be observed for all the samples. The former corresponding to the D band is caused by structure defects and

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