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Porous graphene-polyaniline nanoarrays composite with enhanced interface bonding and electrochemical performance

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ABSTRACT

There are ever increasing interests in three dimensional (3D) graphene for the construction of wearable electrics and flexible energy storage devices. Herein, we report a 3D porous graphene supported polyaniline (PANI) nanoarrays composite with enhanced interface bonding and high load fraction of PANI for supercapacitor application. We demonstrate that by utilizing benzenesulfonic acid functionalization followed by a pre-immersion treatment, surface chemistry and permeability of the porous graphene can be improved significantly, which favors the controllable growth of high-quality PANI nanoarrays. The resulting composite used as a freestanding electrode exhibits excellent electrochemical performance, hence a maximum specific capacitance of 752 F/g with retention of 90.8% over 10000 cycles was achieved.

1. Introduction

Energy conversion/storage is emerging as one key technology in 21st century due to widespread concern on energy supplies and environmental issues. Supercapacitor is one type of known energy storage devices for high power density, durable cycle life, and high efficiency etc. [1,2]. The research about supercapacitors mainly focuses on electrode materials, for which two categories of materials electric double-layer capacitance (EDLC) material and pseudocapacitance material have been developed [3–5]. As EDLC material, 3D graphene [4] has attracted increasing attention for its good electrical conductivity, fast conductive path for electrons, large specific surface area, as well as strength and flexibility. Nevertheless, the essentially low capacitance limits its practical applications. As pseudocapacitance material, PANI has advantages like high capacitance, ease of synthesis and low cost, but suffers from low conductivity and stability [5,6]. The hybrid of 3D graphene and PANI combines the advantages of the two components, and has established a valid strategy to afford high-performance flexible energy storage devices [7,8].

So far, three kinds of 3D graphene have been developed to prepare 3D graphene/PANI composites for supercapacitor electrodes: porous graphene foam (GF) [9,10], porous graphene aerogel (GA) [8,11,12] and graphene paper (GP) [13–15]. For example, Kulkarni et al. [9] reported PANI nanofibers grown on GF as an electrode material with enhanced electrochemical performance. Zhao et al. [11] prepared a GA/PANI composite via in-situ polymerization, and obtained the specific capacitance of 322.8 F/g (1 A/g) for GA/10 wt% PANI. Yang and coworkers [15] designed a smart routine to obtain GP/PANI nanotube papers, where MnO_2 nanotubes were used as both the template and oxidant. The composite paper exhibits high specific capacitance and excellent rate capability. In these works, the used GF that was usually fabricated by CVD technique on nickel foam as the sacrificial template is costly, and its large dimension macropores would produce non-uniform structure of the composite. On the other hand, though GA and GP can be economically obtained from graphene oxide (GO), their compact structure limits the load of pseudocapacitive PANI, hence reduces electrochemical performance of the 3D graphene/PANI composites. Furthermore, the lack of interface design and control hampers the improvement in composite structure and properties.

In present work, we report a porous GA/PANI composite with enhanced interface bonding and high load of PANI and its well-

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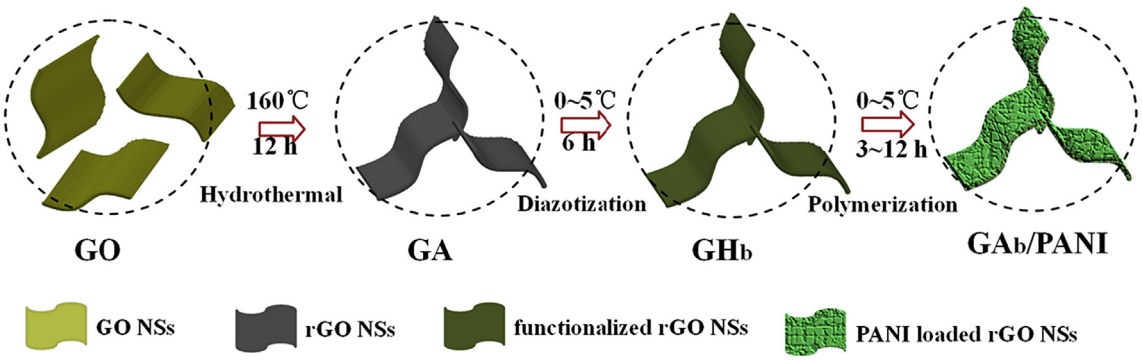

Fig. 1. Illustration for preparation processes of GA_b/PANI composite.

defined preparation routine for high-performance supercapacitor application. The products were characterized by various instrumental techniques, the obtained composites as freestanding electrodes and assembled supercapacitor were evaluated, and the effects of composite composition and interface bonding on electrochemical properties were discussed.

2. Experimental

2.1. Materials

P-aminobenzene sulfonic acid (*p*-ABSA), ascorbate acid, sodium nitrite ($NaNO_2$), hydrochloric acid (HCl), aniline (An) and ammonium sulfate (APS) were purchased from Aladdin Industrial Corporation. All chemicals were of analytical grade. GO was prepared from natural flake graphite (300 meshes, Qingdao Meilikun) by an improved Hummers method [16].

2.2. Characterization

The morphology and phase structure of samples were characterized by field-emission scanning electron microscopy (FESEM; JEOL, JSM-6701F), transmission electron microscope (TEM; JEOL, JEM-2000FX) and X-ray powder diffractometer (XRD; Bruker, D8 ADVANCE, Cu-K_a radiation). Chemical components were analyzed using Fourier transformation infrared spectroscopy (FTIR; Bruker, IFS660V) and X-ray photoelectron spectroscopy (XPS; Kratos, Axis Supra). For XPS, all C1s line was corrected at 284.6 eV. The weight loss of the samples was obtained by thermal gravimetric analyzer (TGA; TA, SDT Q600) at a heating rate of 10 °C/min under an Ar air flow of 30 mL/min.

2.3. Electrochemical tests

Electrochemical properties were evaluated according to cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS) based on the three-electrode system for electrode materials and two-electrode system for symmetric supercapacitor device. Herein, CV and EIS tests are conducted on an electrochemical workstation (CHI660E, Chenhua), GCD data was taken by a Battery Test System (Land2001, Kingnuo).

To construct the three-electrode system, a GA_b/PANI (GA or GA/PANI) slice services as the free-standing working electrode, a Pt plate as counter electrode and a SCE as reference electrode, with 1 M H_2SO_4 solution as electrolyte. The supercapacitor is assembled in the ambient condition using two PANI/GA_b (GA or PANI/GA) slices as positive and negative electrodes, 25 μm-thickness film (Celgard 3501) as the separator and H_2SO_4 + PVA as gel electrolyte [14].

The specific capacitance of working electrodes can be calculated according to CV and GCD curves, and respectively expressed as C_1 and C_2 (F/g) as follows:

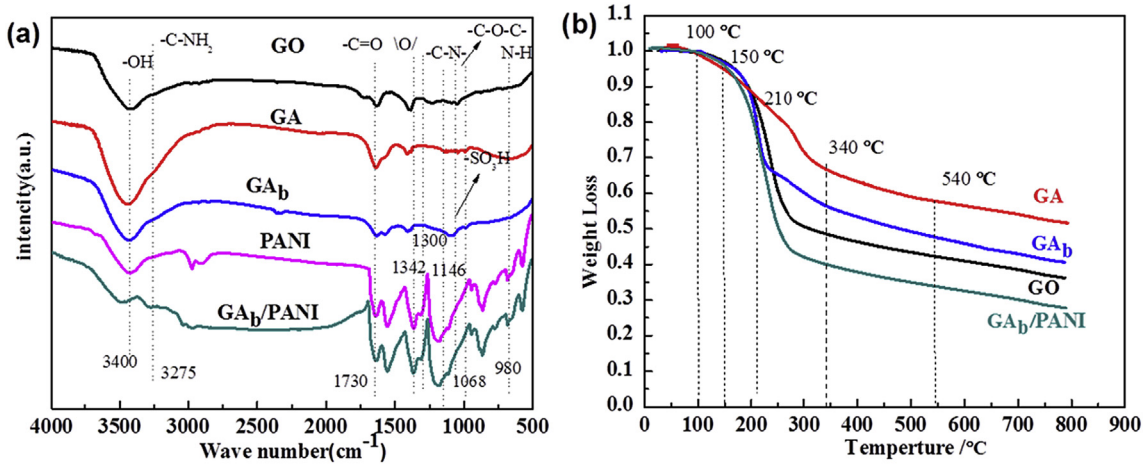

Fig. 2. (a) FTIR spectra of GO, GA, GA_b, PANI and GA_b/PANI, and (b) TGA of GO, GA, GA_b and GA_b/PANI.