Fabrication of highly ordered polyaniline nanocone on pristine graphene for high-performance supercapacitor electrodes

Ningning Song, Wucong Wang, Yue Wu, Ding Xiao, Yaping Zhao [*]

School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, 800 Dong Chuan Road, Shanghai 200240, PR China

ABSTRACT

The hybrids of pristine graphene with polyaniline were synthesized by in situ polymerizations for making a high-performance supercapacitor. The formed high-ordered PANI nanocones were vertically aligned on the graphene sheets. The length of the PANI nanocones increased with the concentration of aniline monomer. The specific capacitance of the hybrids electrode in the three-electrode system was measured as high as 481 F/g at a current density of 0.1 A/g, and its stability remained 87% after constant charge-discharge 10000 cycles at a current density of 1 A/g. This outstanding performance is attributed to the coupling effects of the pristine graphene and the hierarchical structure of the PANI possessing high specific surface area. The unique structure of the PANI provided more charge transmission pathways and fast charge-transfer speed of electrons to the pristine graphene because of its large specific area exposed to the electrolyte. The hybrid is expected to have potential applications in supercapacitor electrodes.

1. Introduction

A supercapacitor is a promising energy device for electrical vehicles, mobile electronic devices, and grid energy storage due to its high power density, long cycle life and fast charging rate [1,2]. Carbon-based materials, transition metal oxides and conducting polymers are commonly used as electrode materials in supercapacitor [3]. Graphene has attracted increasing attention for making the supercapacitors with fast charge-discharge rate and excellent cycle stability because of its superior electrical conductivity, high specific surface area, and outstanding mechanical performance [4,5]. The composite of graphene with a conductive polymer or a transition metal oxide was preferred [6–8].

Polyaniline (PANI), a conductive polymer, has been widely studied as a supercapacitor electrode because it has high capacitive characteristics and low cost [9]. The PANI can form a π-π conjugated structure with graphene via their rich π-electrons. Thus, the graphene/polyaniline (G/PANI) hybrid is regarded as a promising candidate material for a supercapacitor electrode [10–12]. Recently, various methods have been proposed to fabricate the G/PANI hybrid [13–17] using graphene oxide (GO) or chemically reduced GO (RGO). However, the performance of the supercapacitor electrode [18] made from GO or RGO was inadequate because the GO contains oxygen-containing groups and the RGO could not recover to its original graphene structure. Cao et al. [19]

synthesized a microsphere composite of the graphene/PANI to improve the supercapacitor performance by adopting pristine graphene. But the improved performance was not too much because the graphene used was restacked and the loading amount of the PANI on the graphene was small also. To solve this issue, Cao et al. [20] prepared a graphene nanomesh by a chemical vapor deposition method (CVD), and then let an aniline monomer polymerized on the resulted graphene via chemical oxidative polymerization. In this way, the PANI nanorod arrays were formed on the graphene, and the performance of the supercapacitor electrode made accordingly was improved considerably. Unlike the PANI nanorod, Yu et al. [21] synthesized a polyaniline nanocone array on the three-dimensional (3D) graphene network in which the PANI nanocone arrays offered a large area exposing to the electrolyte, and the space between the nanocones provided a free-diffusion path for electrolyte ions. This structure of the nanocone array and the 3D graphene facilitated the charge transfer between the electrode and the electrolyte resulting in enhanced performance. However, the synthesis method was complicated and expensive. To our best knowledge, there are few published papers on the PANI nanocone. Moreover, reports on fabricating the hybrid of the nanocone PANI with the pristine graphene are much less. Therefore, it is worth to explore the fabrication of the PANI nanocones with the pristine graphene for boosting the performance of supercapacitor electrodes.

---

* Corresponding author.
  E-mail address: ypzhao@sjtu.edu.cn (Y. Zhao).

The purpose of this research is to prepare a hybrid of the nanocone polyaniline with the pristine graphene to enhance the performance of the supercapacitor electrode using a novel and facile approach. The strategy is to make aniline monomer in situ polymerized on the fresh exfoliated pristine graphene sheets. The aniline monomer absorbed onto the surface of the pristine graphene via π-π interaction not only provided active nucleation sites for the PANI nanocones but also avoided the aggregation of the graphene sheets. The length of the PANI nanocones could be controlled via the amount of the aniline monomer initially used. The morphology and structure of the as-resulted G/PANI composites were characterized by scanning electron microscope (SEM), transmission electron microscope (TEM), Fourier transform infrared spectroscopy (FTIR), and Raman spectroscopy. The specific capacitance and the cycle stability of the hybrid were investigated by cyclic voltammetry, galvanostatic charge-discharge, and electrochemical impedance spectroscopy.

2. Experimental

2.1. Materials

Graphite powder (99.85%, CP), aniline (AR), ammonium persulfate (AR) and sulfuric acid (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd.. Carbon dioxide (99.90%) was obtained from Shanghai Chemical Co., Ltd. Absolute ethanol was purchased from Changshu Yangyuan Chemical Co., Ltd. Deionized water was used in all experiments.

2.2. Preparation of pristine graphene and G/PANI composites

The pristine graphene was prepared by exfoliating graphite using a fluid dynamic force in supercritical CO_2 as reported in a previously published paper [22]. At first, an amount of graphite was put into the reactor made from stainless steel 304, and then carbon dioxide was pumped into the reactor by a manual pump. When the pressure and the temperature reached to 15 MPa and 45 °C, the shear mixer started to run at the desired speed of 3000 rpm for 3 h. The as-exfoliated graphene was collected in a 200 mL beaker filled with a certain amount of ethanol to obtain the ethanol dispersion of the graphene.

The G/PANI composites were synthesized by a modified method [23]. Typically, a certain amount of aniline monomer and 9.8 g H_2SO_4 were slowly poured into 100 mL graphene dispersion (1 mg/mL) in aqueous ethanol solution (20 wt %) and stirred for 1 h. Then, another 100 mL ethanol aqueous solution (20 wt %) containing ammonium persulfate was added to the above mixture solution under stirring at 0 °C. The reaction lasted for 6 h. The blackish-green G/PANI formed was filtered and repeatedly washed with deionized water and absolute ethanol for several times, and finally was dried under vacuum at 60 °C for 24 h. A series of the G/PANI composites were prepared corresponding to the concentration (C_{AN}) of the aniline monomer 0.01, 0.02, 0.03, 0.04 and 0.05 M, respectively (named as G/PANI1, G/PANI2, G/PANI3, G/PANI4 and G/PANI5, respectively). The mass ratio of the graphene to the PANI in the composites was determined via their mass change after high-temperature calcination (Fig. S1). They were 1:0.24, 1:0.49, 1:0.73, 1: 0.98 and 1: 1.22, respectively. The PANI without graphene was prepared at C_{AN} = 0.05 M using the same process to the method above, which was as a contrast sample.

2.3. Characterization

The graphene concentration (C: mg/mL) was analyzed using a UV–vis spectrophotometer at a 660 nm wavelength. It was calculated from the formula A/l = αC based on the Lambert-Beer law. Herein, A/l (m^{-1}) is the absorbance per cell length, and α is the absorption coefficient, which is 528 mL mg^{-1} m^{-1} (Fig. S2). The as-prepared samples were characterized by a field-emission scanning electron microscope (FE-SEM, Nova Nano-SEM 450, FEI Company, USA), Transmission Electron Microscope (TEM, JEM-2100 JEOL Ltd., Japan), Atomic Force Microscopy (AFM, Bruker

ICON), Raman spectroscopy (DXR), Fourier Transform Infrared Spectroscopy (FTIR, Spectrum 100, Perkin Elmer, Inc., USA) and Thermogravimetric Analyzer (TGA7, Perkin Elmer, Inc., USA), respectively.

2.4. Electrochemical measurements

A three-electrode system was carried out to evaluate the electrochemical performance of the samples. The preparation procedure of constructing the three-electrode was as follows: 85 wt% G/PANI composite, 10 wt% acetylene black and 5 wt% polytetrafluoroethylene (PTFE) were mixed for 2 h. Then the mixture was pressed onto a stainless-steel grid served as a current collector (5 cm × 1 cm) at 2 MPa and dried at 60 °C for 12 h. The electrochemical measurement was carried out on a CHI 660E electrochemical workstation (Shanghai Chenhua Instrument Company, China) using a three-electrode cell, in which the platinum and Ag/AgCl electrode were used as a counter electrode and a reference electrode, respectively. An aqueous solution of 1 M H_2SO_4 was used as the electrolyte. Electrochemical characterization of the prepared materials was performed as follow: cyclic voltammetry (CV) curves were carried out from −0.2–0.8 V at the scanning rates of 10, 20 and 50 mV/s, respectively; galvanostatic charge/discharge (GCD) tests were measured at the current densities of 0.1, 0.5, 1, 2 and 5 A/g with a scanning range of −0.2–0.7 V, respectively; electrochemical impedance spectra (EIS) was recorded at the open circuit voltage amplitude of 5 mV at a frequency ranging from 0.01 Hz to 100 kHz.

3. Results and discussion

3.1. Morphology and structure

The characterization of the pristine graphene sheets is shown in Fig. 1. We can see from Fig. 1a–b that the graphene sheets are irregular ultrathin and semitransparent, and the lateral size is about 4 μm. The sharp shape and position (2683 cm^{-1}) of the 2D peak shown in Fig. 1c indicates that the layer number of the graphene is few [24]. Fig. 1d suggests that a typical graphene flake is 3 layers according to its thickness of about 1.5 nm. We measured over 100 sheets of the graphene, and the mean thickness is approximately 1.5 nm. It indicates that the average layer number of the graphene is around three.

The G/PANI hybrids with different weight ratios of the PANI to the G were prepared by changing the C_{AN} while fixing the amount of the graphene sheets as 100 mg. SEM images in Fig. 2a–e displays that the surface of the graphene sheets was entirely covered with the PANI made at all conditions. The highly-ordered PANI array was formed on both sides of the graphene sheets. It can be ascribed to the π-π interaction between the PANI and the graphene. The PANI was guided by□π-conjugated graphene to grow on the graphene sheets. The length of the PANI increased from 70 nm to 440 nm with increasing from 0.01 M to 0.05 M. However, the disorder PANI nanowires were formed when the C_{AN} was 0.05 M as shown in Fig. 2e. The excessive aniline monomer might produce these isolated PANI nanowire clusters which were formed via self-nucleation and polymerization [25] in the ethanol solution rather than on the graphene sheets. The aligned PANI on the graphene sheets was created at the optimum concentration of 0.04 M as shown in Fig. 2a–e, and its length is about 400 nm (Fig. 2c).

Fig. 3a–b indicates that the pure PANI consisted of randomly stacked nanowires which are different with that in the hybrids. The SEM image of the G/PANI4 shown in Fig. 3c suggests that all of the PANI are vertically arranged on both sides of the graphene sheets, and the PANI has a nanocone structure as shown in Fig. 3d. It might be attributed to the interactions of the graphene and the PANI.

FTIR analysis can illustrate the combination of the PANI and the pristine graphene sheets in the hybrids. The characteristic peaks of the PANI at 1570, 1486, 1296, 1108 and 801 cm^{-1} suggest the presence of the C═C stretching vibration of a quinoid structure, and a benzene ring, stretching vibration of C—N, C═N, and C—H, respectively [26,27], as