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Fabrication of graphene foam supported carbon nanotube/polyaniline hybrids for high-performance supercapacitor applications

Abstract

A large-scale, high-powered energy storage system is crucial for addressing the energy problem. The development of high-performance materials is a key issue in realizing the grid-scale applications of energy-storage devices. In this work, we describe a simple and scalable method for fabricating hybrids (graphenepyrrole/ carbon nanotube-polyaniline (GPCP)) using graphene foam as the supporting template. Graphene-pyrrole (G-Py) aerogels are prepared via a green hydrothermal route from two-dimensional materials such as graphene sheets, while a carbon nanotube/polyaniline (CNT/PANI) composite dispersion is obtained via the *in situ* polymerization method. The functional nanohybrid materials of GPCP can be assembled by simply dipping the prepared G-py aerogels into the CNT/PANI dispersion. The morphology of the obtained GPCP is investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), which revealed that the CNT/PANI was uniformly deposited onto the surfaces of the graphene. The as-synthesized GPCP maintains its original three-dimensional hierarchical porous architecture, which favors the diffusion of the electrolyte ions into the inner region of the active materials. Such hybrid materials exhibit significant specific capacitance of up to 350 F g^{-1} , making them promising in large-scale energy-storage device applications.

Keywords

polyaniline, fabrication, hybrids, graphene, high, performance, supercapacitor, applications, foam, supported, carbon, nanotube

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Fabrication of Graphene Foam supported Carbon Nanotube/Polyaniline hybrids for High-Performance Supercapacitor Applications

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Abstract

Large scale energy storage system with high power is crucial for addressing the energy problem. The development of high-performance materials is a key issue in realizing grid-scale applications of energy storage devices. In this work, we describe a simple and scalable method to fabricate hybrids (graphene-pyrrole/carbon nanotube-polyaniline (GPCP) using graphene foam as the supporting template. Graphene-pyrrole (G-Py) aerogels are prepared by a green hydrothermal route from 2D materials – graphene sheets, while CNT/PANI composite dispersion is obtained via in-situ polymerization method. The functional nanohybrid materials of GPCP can

be assembled together by simply dipping the prepared G-py aerogels into the CNT/PANI dispersion. The morphology of the obtained GPCP are investigated by scanning electron microscopy (SEM) and transmission electron microscope (TEM), which revealed that CNT/PANI were uniformly deposited onto the surfaces of graphene. The as-synthesized GPCP maintains the original three-dimensional (3D) hierarchical porous architecture, which favor the diffusion of the electrolyte ions into the inner region of active materials. Such hybrid materials exhibit significant specific capacitance of up to 350 F g^{-1} , making them promising in large-scale energy storage device applications.

Keywords: Graphene; carbon nanotube; polyaniline; supercapacitor;

1. Introduction

Constructing three-dimensional (3D) graphene-based hybrid nanostructures with anticipated function has become one of the most active research fields in the past several years. The integration of individual 2D graphene sheets into a 3D macroscopic assembly and then into a functional system is an attractive strategy for realizing large scale applications. Lightweight graphene aerogel composed of interconnected 3D networks has attracted intensive attention because of their unique physical properties, such as low density, high electrical conductivity, rich porosity, and specific surface area [1,47-49]. These properties have caused rapid advance of various applications, extending from supercapacitors [2,3], stretchable electronics [4,5], catalysis [6,7], hydrogen storage [8], to environmental remediation [9]. Despite the aforementioned success, graphene in their pristine form are insufficient to satisfy diverse specific demands for practical applications, especially for large scale grid applications.

Carbon materials [10-13], transition metal oxides [14] and conducting polymers [15-18] are the three main types of greatly investigated electrode materials. Recently, polyaniline (PANI) has drawn much attention in electrochemical studies owing to its excellent properties such as low cost, ability to easily form various nanostructures, good biocompatibility and environmental stability [19,20]. However, PANI suffers from the mechanical degradation problem caused by swelling and shrinkage during the doping and dedoping process [21,22], leading to limited cycling life of PANI-based supercapacitors. In order to overcome these limitations, much effort has been devoted to preparing hybrid electrodes by combining PANI with other nanomaterials. To date, various attempts have been made to integrate PANI and carbon nanotubes [23-25,50] to obtain nanocomposites with excellent electrochemical properties and improved stability [26-28].

In this work, highly porous graphene scaffolds containing pyrrole (Py) with 3D intercrossed structures were synthesized via a green hydrothermal route (the resulting material is referred to as G-Py aerogel). CNT/PANI composite solution was prepared using a simple in-situ polymerization method. The GPCP hybrid materials are then obtained via dipping the G-Py foam into the CNT/PANI dispersion. The incorporation of CNT/PANI into the porous structures of graphene-based foam could prevent aggregation/restacking of graphene sheets to maintain the foam architectures during the following treatment and testing processes. Also, the well deposition of PANI nanorods on CNT effectively increases the electrochemical utilization of PANI, and reduces the ion diffusion path during charge–discharge process. Moreover, CNTs serve as conducting wires to provide electronic transport paths for the conductive networks inside the bulk electrode matrix and improve the stability of GPCP hybrid materials upon electrochemical cycling. The as-prepared GPCP hybrid porous electrodes have the significant potential to be used as promising 3D electrode materials for lightweight and flexible energy storage devices with stable high performance.

2. Experimental

2.1 Chemicals. All analytical grade reagents were used without further purification. Aniline (ANI, Tianjin Damao Chemical Reagent Factory), Pyrrole (Py, Aladdin), ammonium persulfate (APS, Sigma Aldrich) and carbon nanotubes (CNT, Beijingdekedaojing Co., Ltd, China).

2.2 Preparation of Graphene-Py aerogel. GO was prepared by oxidation of natural graphite powder according to the modified Hummers' method [29,30]. We first prepared 3D graphene by hydrothermal treatment of 6 ml 2 mg mL⁻¹ homogeneous graphene oxide (GO) aqueous dispersion with 5 vol% pyrrole (Py) in a Teflon-lined autoclave at 180 °C for 12 h. Then the

autoclave was naturally cooled to room temperature and the product was freeze-dried for 12 h to obtain the G-Py aerogel [31].

2.3 Preparation of CNT/PANI solution. The CNT/PANI solution was synthesized by chemical oxidative polymerization in an ice-water bath. In-situ chemical polymerization was conducted according to the following procedure. MWNT (6 mg) were dispersed in 15 ml 1M HClO₄ for 2 h under sonication. Then, different amounts of ANI (from 20 to 50 mM) were dispersed into the mixture under the protection of N₂. Ethanol (500 μ L) was added into the mixture to prevent the mixture from freezing. 5 ml of 1M HClO₄ solution containing APS (the molar ratio of ANI to APS was 3 : 1) was added dropwise into the reaction mixture and mixed for 7 h. The dark green product was collected by centrifugation and washed with large amount of water/ethanol solution (1:1 volume ratio). The products were dried in vacuum for 12 h.

2.4 Preparation of Graphene-Py/CNT/PANI hybrid. The as-prepared Graphene-Py aerogel (20 mg) was dipped into as-prepared CNT/PANI ethanol solution (5 ml) with various PANI concentration for 2 h and dried in vacuum for 12 h. The final Graphene-Py/CNT/PANI samples were referred to as GPCP-X where X=20, 30, 40, 50 representing the aniline monomer concentration during the preparation of CNT/PANI composites.

2.5 Characterization. The morphologies of the obtained structures were characterized by field-emission scanning electron microscope (FE-SEM, JSM 7500F) and transmission electron microscopy (TEM) (JEM-2100). X-ray diffraction (XRD) patterns of samples were measured on a Y-2000 X-ray Diffractometer with copper K α radiation ($\lambda=1.5406$ Å) operating at 40 kV and 40 mA. The Raman measurements were carried out on a Renishaw Microscope System RM2000 with a 50 mW Ar⁺ laser at 514.5 nm. Fourier transform infrared spectra (FTIR) were recorded on a TENSOR 27 FTIR spectrometer (Bruker) in the absorption mode with resolution of 2 cm⁻¹. X-

ray photoelectron spectroscopy (XPS) measurements were made on a ESCALABMK spectrometer using electrostatic lens mode with a pass energy of 100 eV.

2.6 Preparation of working electrode and electrochemical measurements. The working electrodes for supercapacitors were prepared by thoroughly mixing the electroactive nanocomposites, carbon black and poly(tetrafluoroethylene) in a mass ratio of 80:10:10, respectively. The obtained slurry was coated and pressed onto a foam nickel to prepare a working electrode, and then dried at 80 °C for 24 h in a vacuum oven. The electrochemical performance of the as-prepared hybrid composites as working electrodes was carried out on a CHI660D electrochemical station in a three-electrode configuration with platinum foil and Ag/AgCl as counter and reference electrode, respectively. The cyclic voltammetry and galvanostatic charging/discharging techniques were employed to investigate the electrochemical performance of the composites. The applied potential window ranged from -1 V to 0 V in 1 M KOH electrolyte.

3. Results and Discussion

A schematic illustration of the fabrication process for the nanocomposites is depicted in Figure 1. The GPCP-X nanohybrids were prepared by simply dipping the G-Py aerogel (prepared via a one-step hydrothermal method) into the CNT/PANI nanocomposites solution (prepared via in-situ polymerization).

3.1 Morphology and structure characterization of GPCP-X.

Small graphene sheets are usually constructed or assembled into macroscopic materials for practical applications. The critical issue typically encountered in this process is the irreversible aggregation or restacking of graphitic structures. In this work, pyrrole was introduced to prevent aggregation of the graphene sheets. Shown in Figure 2a are the G-Py hydrogel and aerogel. The

density of the G-Py aerogel is 12 mg cm^{-3} . The corresponding SEM investigation revealed that G-Py possesses 3D interconnected framework with randomly opened macropores. Considering the conjugated structure of pyrrole with its electron-rich N atom, it can attach to the surfaces and galleries of GO sheets through hydrogen-bonding and/or π - π interactions. During the hydrothermal process, pyrrole works as a swelling agent to effectively prevent GO from self-stacking, thereby obtaining a graphene aerogel with larger volume than pure graphene hydrogel. Figures S1b and c illustrates that G-Py had a loose structure with much thinner connection walls compared to pure graphene hydrogel [31]. The pore sizes of the G-Py network range from submicrometer to several micrometers [32]. The interconnected macropores within the GO framework are favorable for the transfer of buffering ions for they minimize the diffusion distance from the external electrolyte to the interior surfaces [33]. The morphology of the as-prepared materials was further observed by TEM. The curled and wrinkled morphology of graphene sheets indicate the porous structure of the obtained G-Py [34], which is in agreement with SEM images. The FTIR spectra of the G-Py aerogel, pyrrole, and polypyrrole shown in Figure 2d show the appearance of representative bands at 617, 685, 1407, 1485 and 1517 cm^{-1} , which indicate the presence of Py.

The SEM images of CNT/PANI nanocomposites with different concentration of ANI (30, 40 and 50 mM) are shown in Figure 3 and Figure S2a, c. It can be observed that CNT/PANI nanocomposites with uniform morphology have been successfully prepared. The magnified SEM image clearly shows that the PANI nanorods align vertically on the surface of the CNT, which is due to the π - π stacking interaction between the graphitic structures of CNT and the aromatic rings of PANI [35]. As seen in the Figure 3b, c and d, the average diameter of the CNT/PANI composites increases with increasing ANI concentration. It is apparent that the length of the

vertical PANI nanorods grown on CNT can be controlled by changing the initial concentration of ANI, which will allow the controllable electrochemical performance of the supercapacitor [36].

The typical SEM and TEM images of the obtained GPCP nanohybrids are shown in Figure 4 and Figure S2b, d. As shown in the Figure 4b, c and d, it can be clearly observed that CNT/PANI was uniformly grown on the surfaces of graphene. They act as bridges between different graphene sheets to form a conductive network [37], as well as preventing the stacking of graphene sheets. In addition, the multi-composition can have synergistic effects to take advantage of both Faradaic and non-Faradaic processes for capacity-charge storage with excellent electrochemical properties [38].

Figure 5a shows the X-ray diffraction spectra of GPCP-50 nanohybrids. The X-ray data of the GPCP-50 nanohybrids show weaker crystalline peaks to that of neat PANI that has a semi-crystalline structure. The main peaks in the XRD pattern of pure PANI are located at 9.0° , 21.5° and 25.3° , which are the characteristic peaks of PANI [39]. Compared with PANI, the XRD pattern of the GPCP-50 nanohybrids exhibits one peak (21.5°) similar to that of PANI, indicating that in the hybrids the PANI exhibits poor crystallinity because of the existence of G-Py aerogel [40].

To further study the interaction between these carbon materials and PANI, Raman spectroscopy analysis is employed. The Raman spectra of the pristine CNT, GO, G-Py, neat PANI and GPCP-X hybrids are presented in Figure 5b. The obvious peaks at about 1350 and 1600 cm^{-1} can be attributed to the disordered structure (D band, sp^3 carbon atoms of defects and disorders) and graphitic structure (G band, sp^2 carbon atoms in graphitic sheets) of GO, respectively [41]. For the Raman spectrum of GPCP-50 sample, the band at about 419 cm^{-1} is ascribed to out-of-plane amine ring deformations and the band at 574 cm^{-1} is a confirmation of

the existence of ring deformation and phenazine- or phenoxazine-like segments. The bands around 779 and 818 cm^{-1} is in agreement with amine and imine deformation (C-N-C bending) [42]. However, the GPCP-50 nanohybrids show sharp peaks at about 1180 cm^{-1} representing the C-H bending in the benzene- or quinine-type rings. The peak at 1350 cm^{-1} is a clear symbol of C-N⁺ stretching, and the peak at 1485 cm^{-1} stands for the C=N stretching vibration in the emeraldine base of imines due to the n-doping effect of PANI. The Raman results further confirm that the GPCP-50 nanohybrids with strong π - π interactions was successfully synthesized [43,44].

A surface elements analysis was carried out on the GO film and G-Py aerogel using X-ray photoelectron spectroscopy (XPS). The obtained XPS full spectrum (Figure 5c) shows signals from C, N and O elements, indicating the presence of Py on the G-Py aerogel. The peaks with lower binding energy located at 397.8 and 399.9 eV correspond to pyridine-like and pyrrole-like nitrogen, respectively [45], as illustrated in Figure 5d. During the hydrothermal reaction, the loss of oxygen-containing groups is confirmed by XPS spectrum. As shown in Table S1, after hydrothermal reaction, the ratio of C/O decreases significantly, which is similar to the literature reported by Shi et al [32].

3.2 Electrochemical performance of GPCP-X.

To demonstrate the potential of GPCP-X electrodes for supercapacitor applications, we further evaluated their electrochemical performance in a three-electrode system using 1 M KOH as electrolyte. The experimental results are shown in Figure 6. The average specific capacitance was calculated from the CVs according to equation (1);

$$C = \frac{1}{mv\Delta V} \int i(V)dv \quad (1)$$

where C is the specific capacitance, m is the mass of active materials, v is the potential scan rate, ΔV is the potential window in the CV, $\int i(V)dv$ is the integrated area of the whole CV loop.

It can be seen in Figure 6a that the area of the CV curve of the GPCP-50 hybrids is larger than those of the CNT/PANI and G-Py at the same scan rate, indicating a higher specific capacitance of the nanohybrids. The exceptionally high specific capacitance and superior rate capability of the multiphase composite over those binary composites imply that the CNT/PANI hybrids combined with the G-Py aerogel has a strong synergistic effect between the components. It can be suggested that the introduction of CNT/PANI into the G-Py structure provides synergistic effects on both the microscale and nanoscale level, i.e., it facilitates efficient electron transport from CNT/PANI to the G-Py. The interwoven porous structure ensures effective access of the electrolyte ions to such an ultralight active material, substantially reducing the dead volume. The GPCP nanocomposite has the longest discharge time, meaning the highest specific capacitance. Figure 6c show the comparison of specific capacitance of the various components of GPCP-X. The specific capacitance of the GPCP-50 electrodes (350 F g^{-1}) is 5 times that of G-Py aerogel electrode (69.8 F g^{-1}) and 2.2 times that of CNT/PANI electrodes (162 F g^{-1}), which clearly demonstrate superior performance. Figure 6d and e show the cyclic voltammetry (CV) and galvanostatic charge/discharge of GPCP-X nanohybrids. It can be observed that the area of the CV becomes larger and the discharge time becomes longer with increasing ANI concentration, which signifies higher specific capacitance. From Figure 6f, it can be seen that the shape of CV curves was maintained at high scan rates (up to 100 mv s^{-1}), which implies efficient charge transfer and electrolyte diffusion within the 3D GPCP-50 nanohybrids. To further understand the superior performance of the GPCP-50, electrochemical impedance spectroscopy (EIS) analysis was performed. As shown in Figure 6g, the Nyquist plots show a small arc in the

high frequency region and a straight line in the low frequency region for all samples. It can also be observed that the GPCP-50 electrode displays the smallest semicircle at high frequencies suggesting it has that lowest charge transfer resistance, and a transition to linearity at low frequency that exhibits an ideal capacitive behavior. From these, it can be inferred that the assembly of CNT/PANI on G-Py consisting of GPCP nanohybrids can increase the accessible surface area of electrode as well as reduce the ion diffusion length during the charge-discharge process. From Figure 6h, it indicates that GPCP-50 results in an improved capacitance compared to other GPCP-X samples with lower PANI content. Moreover, the specific capacitance GPCP-50 displayed a high specific capacitance of 406 F g^{-1} at 1 mV s^{-1} .

The long-term cycle stability is a crucial parameter for supercapacitor electrode materials. The cycle stability of GPCP-50 nanohybrids was measured by long-term charge/discharge cycling at a current density of 2 A g^{-1} , as shown in Figure S3. 84% of specific capacitance can be retained even after 2,000 cycles. Usually, the degradation in capacitance is ascribed to swelling and shrinkage, which induced gradually deterioration of the conductivity and volumetric changes [46]. As a result, the good stability of GPCP comes from the synergistic effect between aligned PANI nanorods on CNT and G-Py aerogel. To sum up, the outstanding performance of GPCP can be attributed to two key reasons. First, the 1D conductive CNT/PANI not only prevent the aggregation and restacking of graphene sheets in some extent but also locally improve the conductivity of the aerogels by providing conductive pathways through defects of graphene and bridging the neighboring graphene sheets. Second, the incorporation of conductive polymers into the G-Py aerogel can effectively improve their energy density due to the pseudocapacitance originating from conducting polymers. As shown in Figure 3, the morphology of PANI exhibits an interesting change related to the increase of the concentration of ANI. Apparently, the

acanthine structure of PANI protrudes more with the increase of aniline concentration. So the high capacitance of GPCP is mainly due to the high content of CNT/PANI, which can provide more pseudocapacitance contribution.

4. Conclusions

In summary, we have demonstrated that the architectures of 3D graphene-pyrrole/carbon nanotube/polyaniline (GPCP) nanohybrids can be successfully prepared via a simple method. When the G-Py aerogel was dipped into the CNT/PANI solution, the CNT/PANI were sandwiched between layers of G-Py and served as spacers to create gaps between neighboring graphene sheets, which can effectively reduce the layer-to-layer stacking of G-Py sheets. The calculated specific capacitances in supercapacitors using the 3D GPCP-50 electrodes are 5 times that of G-Py aerogel and 2.2 times that of CNT/PANI – its two main components. The experimental results presented here are a proof of concept that the ideal electrode templates for supporting high-performance active materials are necessary to achieve excellent electrochemical properties. The methods described demonstrates a simple way to design new functional materials that can be used as electrode materials for lightweight and flexible energy storage devices.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version.

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Figure captions:

Figure 1. Schematic illustration of the fabrication process: the assembly of 3D graphene-pyrrole/carbon nanotube/polyaniline architectures.

Figure 2. Morphological characterizations and FTIR spectra of the nanocomposites. (a) Photographs of G-Py hydrogel (left) prepared with a 2 mg mL^{-1} homogeneous aqueous dispersion via hydrothermal reduction at 180°C for 12 h and G-Py aerogel obtained by freeze-drying (right); (b) The SEM image and (c) TEM image of G-Py aerogel; (d) FTIR spectra of the Py, PPy and G-Py aerogel.

Figure 3. SEM images of CNT/PANI nanocomposites with different ANI concentration (a, d) 50mM; (b) 30mM; (c) 40mM.

Figure 4. SEM and TEM images of GPCP nanohybrids. The nanohybrids achieved with different concentration of ANI: (a, d) 50mM; (b) 30mM; (c) 40mM.

Figure 5. X-ray diffraction spectra, Raman spectra and XPS of the nanohybrids. (a) XRD patterns of the CNT, G-Py, GO, neat PANI and GPCP-50 hybrid samples; (b) Raman spectra of pristine CNT, Graphene, G-Py, neat PANI, and GPCP-50 hybrids; XPS survey scan (c) and High-resolution N1s peaks (d) of the G-Py aerogel.

Figure 6. Electrochemical performance of GPCP nanohybrids. (a) Cyclic voltammetry at 5 mV s^{-1} and (b) Galvanostatic charge/discharge curves of the G-Py, CNT/PANI and GPCP-50, at a current density of 1 A g^{-1} ; (c) Relational graph of specific capacitance to different nanomaterials, and the schematics representation of the microstructures of different nanomaterials; (d) Cyclic voltammetry at 5 mV s^{-1} and (e) Galvanostatic charge/discharge curves of the GPCP-X, at a current density of 1 A g^{-1} ; (f) Cyclic voltammetry curves of the GPCP-50; (g) Nyquist impedance plots of GPCP-30, 40, 50. (h) The variation of specific capacitances with different scan rates for GPCP-X.

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Graphical abstract

3D GPCP architectures for High-Performance Supercapacitor Applications