In situ synthesis of interlinked three-dimensional graphene foam/polyaniline nanorod supercapacitor

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ABSTRACT

Three-dimensional (3-D) graphene foam/PANI nanorods were fabricated by hydrothermal treatment of graphene oxide (GO) solution and sequentially *in-situ* synthesis of PANI nanorods on the surface of graphene hydrogel. 3-D graphene foam was used as substrate for the growth of PANI nanorods and it increases the specific surface area as well as the double layer capacitance performance of the graphene foam/PANI nanorod composite. The length of the PANI nanorod is about 340 nm. PANI nanorods exhibited a short stick shape. These PANI nanorods agglomerate together and the growth orientation is anisotropic. The highest specific capacitance of 3-D graphene/PANI nanorod composite electrodes is 352 $F g^{-1}$ at the scan rate of 10 $mV s^{-1}$.

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1. Introduction

Emerging ecological concerns and the ever increasing energy demand of the modern society have become global problems being recognized as obstacles for the sustainable development of economy and society. Storage and efficient use of electrical energy is bound to depend on the development of power storage systems with high energy density and power density. Supercapacitor [1], also named electrochemical capacitor and ultracapacitor, is a new energy storage device between the traditional battery and capacitor. Supercapacitor is identified as a promising solution to solve the facing problems due to their higher rate capacity, long cycle life, high dynamic propagation, and low maintenance cost compared to the traditional batteries and capacitors [2].

According to the energy storage principle, the electrochemical supercapacitor can be divided into electric double layer capacitors and Faraday capacitance (pseudocapacitor). The major energy storage mechanism of double layer capacitors is the static accumulation of reversible ions on the surface of porous carbon, while as for the pseudocapacitor, the main energy storage mechanism is fast and reversible chemical reaction in the charging

and discharging process of the electrode materials [3,4]. Extensive explorations have shown that for achieving supercapacitor with high performance, the working electrode material is crucial. At present, it's a hot topic to produce composite electrode materials with synergistic effect.

Graphene, a crystalline allotrope of sp^2 bonded carbon with 2-D characteristics, has given rise to the new era of the nanocomposites [5,6]. As a result of its unique structural characteristics, graphene possesses a great majority of prominent intrinsic chemical and physical features, such as high electrical conductivity, large theoretical specific surface area (2675 $m^2 g^{-1}$), excellent in-plane thermal conductivity, and good chemical stability as well as extraordinarily high mechanical strength, etc [7]. Therefore, graphene based composite materials have been utilized in various practical applications, including energy storage and conversion, transparent conducting films, chemical sensors, and actuators, etc. Given the many extraordinary properties of graphene, such as the low mass density, good compatibility, highly conductive, large specific surface area and excellent flexibility, it is considered as one of the most suitable substrate materials for preparing super-capacitor electrodes. However, monolayer graphene tend to stack and self-aggregate due to the existence of strong π-π stacking interactions, van der Waals forces and high surface energy. Hence, the remarkable properties of graphene at the nanoscale can not be effectively translated to those at the macroscopic level. Recently,

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diverse 3-D graphene based on nanoporous scaffolds have been extensively reported [8–10]. According to these literatures, 3-D graphene nanocomposites with interconnected porous structures possess unsurpassed chemical and physical functionalities compared to 2-D monolayers. However, it was limited by the lithiation mechanisms of carbon material. 3-D graphene nanocomposites provided as an electrode material of supercapacitor is not very satisfactory because of its specific capacitance performance.

Polyaniline [9], a kind of semi-flexible linear polymer with many attractive processing properties, such as high electrical conductivity, mechanical flexibility, has three distinct oxidation states with different colors and acid/base doping response. These excellent properties make polyaniline promising for wide applications in the fields of actuators, supercapacitors and electrochromics and so on. Besides, the doped polyaniline not only have a relatively large surface area, but also the conductivity has been improved. Thus, it is a very attractive electrode material for supercapacitor. It is very important that the supercapacitor electrode with doped polyaniline film has a good performance whether in aqueous electrolytes or organic electrolytes.

The performance of supercapacitor is directly affected by the electrode materials. Graphene compounded with the conducting polymers [10–13] have high capacitance and good stability. The synthetic combination of the excellent conducting and mechanical properties of graphene and high pseudocapacitance of PANI lead to the high capacitance and improved cycle stability. Many researches have presented that the combination of 3-D graphene and PANI in a single system can take advantages of both the electrical double layer capacitance and pseudocapacitance. The conducting polymer is frequently used as supercapacitor materials for obtaining the efficient charge storage and delivery which strongly depends on the orientation of polymer chains into inorganic host. The polymer molecules are directed to grow along the large oriented tunnels of 3-D hosts or interlayer space of 2-D hosts where the structurally organized frameworks are provided by the inorganic host. But, the main problem is that nanoparticles tend to self-aggregate due to their high surface energy which effectively reduces the contact area among active materials, conductive materials and electrolyte. Thus, it is very much essential to preserve the maximum available surface area of the active nanomaterials for their full utilization. Recently, different types of hierarchical building blocks have been synthesized at the nanoscale as a new class of electrode materials, which enhance the features of both micromaterials and nanomaterials.

In this work, 3-D graphene/PANI nanorods were fabricated by hydrothermal treatments using graphene oxide (GO) solution and then in-situ synthesis of PANI nanorods on the surface of graphene hydrogel. The detailed synthesis procedure as well as the morphology and structure of the as-obtained composite were presented. The electrochemical capacitive properties of the composite were measured for the special 3-D structure and the corresponding mechanism was analyzed.

2. Experimental

2.1. Synthesis of three-dimensional graphene hydrogel

The schematic diagram and the samples of 3-D graphene/PANI nanorods are presented in Fig. 1. GO was obtained by modified Hummers methods. Briefly, first, the low temperature ($0\,^{\circ}$C) reaction, 1 g flake graphite and Na_2SO_3 mixed with 50 mL concentrated sulphuric acid were stirred by magnetic stirring apparatus in ice water bath. Then 6 g $KMnO_4$ was put into the solution slowly in order to reduce the heat caused by the redox reaction. The reaction was maintained at this temperature for 1 hour and the color of the solution was dark green in this step. And
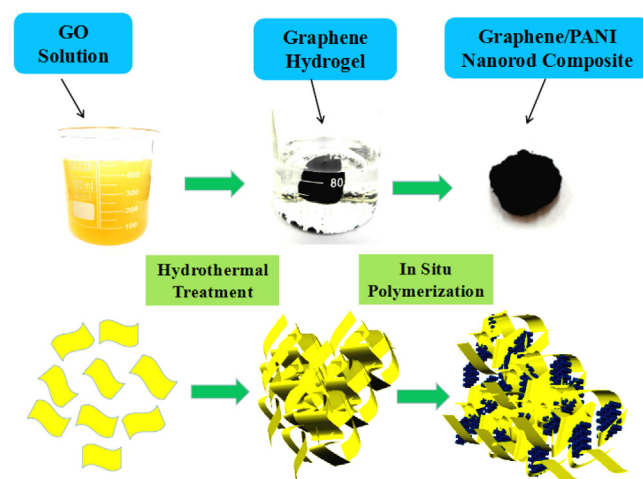

Fig. 1. Schematic diagram (down) and pictures (up) of 3-D graphene/PANI nanorods.

then followed by the middle reaction, the beaker with the reactant was transferred to $35\,^{\circ}$C in water bath, stirring for 1 hour. Finally, the high temperature reaction, the temperature of the water bath increased to $95\,^{\circ}$C and meanwhile 80 ml distilled water was added to the solution slowly. The reaction time was 30 minutes in this step. After the reaction, 200 mL distilled water was poured into the solution and added 6 mL H_2O_2 though drop by drop. Some bubbles appeared in the solution and the color changed into luminous yellow. The obtained sample was washed until neutral by centrifugal machine and then dried at $40\,^{\circ}$C for latter application. To synthesize the graphene hydrogel, 0.09 g GO was dispersed into 40 mL deionized water. Then the solution was treated with magnetic stirring and ultrasonic dispersion for 30 minutes. The solution became homogeneous and the color changed into yellow. The homogeneous solution was transferred to Teflon autoclave and treated at $140\,^{\circ}$C for 12 hours. After the reaction, the 3-D graphene hydrogel was obtained. Using for reference [8], the hydrothermal treatment produces a reduction of GO to graphene through recovery of π-conjugated system from GO sheets.

2.2. Synthesis of PANI nanorods on the surface of 3-D graphene

After the synthesis of graphene hydrogel, polyaniline was in situ formed inside in the hydrogel on the surface of graphene. During the reaction, aniline monomers were slowly added into 1.5 mol L^{-1} hydrochloric acid solution and mixed homogeneously with magnetic stirrers. Then as-prepared hydrogel was put into the solution. $(NH_4)_2S_2O_8$ was dissolved in the hydrochloric acid solution. The mol ratio of $(NH_4)_2S_2O_8$ versus aniline monomers was 1:1. The $(NH_4)_2S_2O_8$ hydrochloric acid solution was dropwisely added into the aniline monomers hydrochloric acid solution. The chemical oxidation polymerization method is usually in acid medium, triggered by using water-soluble initiator to polymerize the monomer. The $(NH_4)_2S_2O_8$ was used as initiator. The velocity of polymerization is controlled by the dropwise speed of $(NH_4)_2S_2O_8$. The solution color was gradually changed into dark green. The reaction temperature was set as $0\sim5\,^{\circ}$C using refrigerator. The total reaction time was 6 hours.

2.3. Characterization

Transmission electron microscope (TEM, JEOL JEM-3100), field emission scanning electron microscope (SEM, JSM-6700F), X-ray diffraction patterns (XRD, X'Pert PRO) and the Raman scattering spectrum (LabRAM HR800, HORIBA) are used for qualitative