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Chemically grafted graphene-polyaniline composite for application in supercapacitor

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ABSTRACT

Chemically grafted p-aniline-functionalized graphene-polyaniline composite (a-G-PANI) is synthesized by covalent bonding and polymerization of aniline onto p-aniline functionalized graphene (a-G) substrate. To achieve this purpose, a-G substrate is initially synthesized *via* an easily-processible and powerful p-phenylenediamine diazotisation reaction, the modified p-aniline groups further serve as initiation sites for the chemical grafting and polymerization of aniline. The as-prepared a-G-PANI exhibits planar configuration with rich pores, which is formed by the conjugated bonding and coating of PANI nanofibers onto graphene sheet, endowing the composite with essential merits including high conductivity, efficient electrolyte diffusion channel and exposure of highly pseudocapacitive PANI to electrolyte, hence, a combined electric double-layer (EDL) capacitance and pseudocapacitance property is achieved. Supercapacitor based on a-G-PANI$_{200}$ composite with a-G to PANI ratio of 1:200 demonstrates high electrochemical capacitance ($422\,\mathrm{F\,g^{-1}}$) at discharge rate of $1\,\mathrm{A\,g^{-1}}$, which is dramatically higher than that based on sole a-G or PANI. The rate performance and cycling stability of a-G-PANI$_{200}$ based supercapacitor are also enhanced relative to sole PANI based counterpart, highlighting the structural advantage of chemically grafted a-G-PANI for capacitor applications.

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1. Introduction

With the rapid marketization of portable and smart electric products, as well as electric vehicles, reliable and sustainable energy storage and supply devices are increasingly demanded. Supercapacitors, also known as electrochemical capacitors, represent an attractive type of electrochemical energy storage devices with outstanding power density, charging-discharging rate, cycling stability and operational safety over other secondary batteries [1–3]. Therefore, supercapacitors are often directly utilized or coupled with other batteries for electrical energy storage and supply to certain electrical facilities.

In principle, supercapacitor can be basically classified into two types, the EDL capacitor and pseudocapacitor. The energy storage mechanism of EDL capacitor involves the rapid accumulation of ionic charges at electrode/electrolyte interface under external electric field, porous carbon materials with high surface area and conductivity are commonly employed as electrode materials in this type of supercapacitor, the specific capacitance is relatively low but stable. Whereas for pseudocapacitor, the charge storage mainly occurs through the redox or faradic transformation of capacitive materials such as metal oxides and conductive polymers, the specific capacitance is generally high but decays quickly due to the structural instability. Hence, the composites composing of conductive substrates and pseudocapacitive materials are highly desired to integrate the beneficial merits from EDL materials and pseudocapacitive materials, so as to enhance the overall capacitances, charging-discharging rate and cycling life [4,5].

Due to the ultrahigh surface area, excellent conductivity and flexible 2-dimensional single layer structure, graphene is widely accepted as ideal substrate for loading of capacitive materials in capacitors fabrication [6]. On the other hand, PANI is an attractive capacitive material owing to the excellent capacitance, easy synthesis, low cost and tunable morphology [7]. Hence, graphene-PANI composites were extensively investigated as efficient electrode materials of capacitors containing synergetic EDL capacitance and pseudocapacitance characteristics [8]. Various graphene-PANI composites with different morphological features were synthesized *via* in situ chemical or electrochemical deposition

techniques, and high capacitive performances were achieved [9–13]. Nevertheless, in these composites, the noncovalent inter-action between graphene substrate and PANI limits the charge transfer at graphene-PANI interface, and the weak interactions also incapable of enduring the volumetric changes during charging-discharging cycles, hence constrains the cycling stability. To overcome these problems, it is essential to design G-PANI compos-ites *via* covalent connection between graphene substrate and PANI. But as far as we know, only seldom reports involved the grafting of capacitive PANI to graphene *via* chemical interactions. Through chemical reaction of amino-protected 4-aminophenol with acy-lated GO and the following deprotection process, Baek et al. [14] grafted p-aniline to GO *via* ester linkage and further acted as initia-tor for the chemical grafting of PANI, the composite demonstrated a capacitance of 250 F g^{-1} and good cycling stability. Bhowmick et al. [15] employed toluene diisocyanate functionalized carbon nanofibers as substrate for chemically grafting of PANI, a capaci-tance of 557 F g^{-1} was achieved. In these chemically grafted com-posite, the linkage between PANI and graphene is not conjugated, limits the overall conductivity of the composite. If the connec-tion between PANI and graphene is through conjugated bond, the conductivity can be enhanced, so the capacitive performance of the corresponding device can also be improved. Diazotisation of arylamine is a powerful way to chemical immobilization of aro-matic rings on various surface including metal, polymer, graphite and even glass [16,17]. Conjugated connection of different motifs using p-phenylenediamine as bridging reagent by this means has proven to be able to improve the conductivity of the afforded composites [17,18]. Graphene-carbon nanotubes composite by the diazotisation attachment demonstrated superior conductivity, and the supercapacitor based on this composite offered a capacitance of 277 F g^{-1} at high current density and excellent cycling stability [18]. Through the controlled diazotisation of p-phenylenediamine, p-aniline could be tightly anchored to graphene, which facilitated the grafting and polymerization of aniline to afford conjugatedly grafted a-G-PANI composite, the donor-acceptor junction made a-G-PANI a promising material for photovoltaic device [19]. In view of the flexible skeleton of graphene with high conductivity and high specific surface area, the highly pseudocapactive PANI and the conjugated interaction between graphene and PANI, the capacitive performance of a-G-PANI is also expectable.

Herein, a-G-PANI with chemically bonding and coating of PANI nanofibers onto graphene substrate was synthesized by controlled diazotisation modification and bridging. Mainly due to the suffi-cient coating of PANI on graphene substrate and the conjugated network, the specific capacitance of device based on a-G-PANI was dramatically improved relative to that based on sole a-G or PANI. The rate performance and cycling stability were also enhanced in comparsion with sole PANI based capacitor.

2. Experimental

2.1. Synthesis of a-G-PANI$_{200}$

Graphite oxide (GO) was initially prepared by a modified Hummers method [20,21]. To synthesize graphene, 1.6 g NaBH$_4$ dissolved in 40 mL water was rapidly added to 200 mL GO suspen-sion (1 mg mL^{-1}) and then heated at 80 °C for 1 h until the color of suspension turned to black. The suspension was centrifuged and washed repeatedly to afford graphene. To synthesis the a-G, 200 mg graphene was re-dispersed in 200 mL water to form an aqueous sus-pension, 3 mL 12 M HCl was added to form an acidic medium, then added were 0.1226 g p-phenylenediamine and 0.0266 g NaNO$_2$ for diazotization modification under continuous stirring in ice-bath for 2 h. After being washed thoroughly with deionized water, the

afforded a-G was vacuum dried for 2 days for chemical modification of PANI.

To synthesis a-G-PANI$_{200}$, 1 mL of a-G suspension (1 mg mL^{-1}) was diluted with 100 mL 1 M HCl, 0.2 mL of aniline monomer was then added into the suspension under ice-bath and vigorous stir-ring. Subsequently, 0.12 g ammonium peroxydisulfate dissolved in 100 mL 1 M HCl was added to the above mixture to initiate the chemical grafting of aniline to p-aniline groups on a-G and the fol-lowing polymerization to form a dark green floccule, the afforded product was denoted as a-G-PANI$_{200}$. Other a-G-PANI composites with mass ratios of a-G to aniline monomer as 1:400, 1:20 and 1:4 were also synthesized for comparsion, which were denoted as a-G-PANI$_{400}$, a-G-PANI$_{20}$ and a-G-PANI$_4$, accordingly. Sole a-G or PANI was also synthesized likewise in the absence of PANI or a-G.

2.2. Characterizations

The morphologies and structures of the products were char-acterized by scanning electron microscopy (SEM, JEOL JSM-6390), high resolution transmission electronic microscopy (HRTEM, JEOL JEM-2100), X-ray powder diffraction (XRD, Bruker D diffractome-ter with Cu Ka radiation), Fourier Transform Infrared Spectroscopy (FTIR, Bio-Rad FTS-40) and X-ray photoelectron spectroscopy (XPS, ThermalFisher ESCALab 250 X-ray photoelectron spectrometer with Al Ka radiation). The Brunauer-Emmett-Teller (BET) specific surface area and Barrett-Joyner-Halenda (BJH) pore size distribu-tion of the products were measured on a Micromeritics Gemini 2380 surface area analyzer at 77 K with N$_2$ gas as adsorbate.

2.3. Electrochemical measurements

Cycling voltammetry (CV) and electrochemical impedance spec-troscopy (EIS) were performed on a CHI 660D electrochemical workstation. The conventional three-electrode test system for CV measurement includes an active material coated glass carbon elec-trode (GCE) as working electrode, a Ag/AgCl reference electrode and a platinum wire auxiliary electrode immersed in 1 M H$_2$SO$_4$ over the potential range of 0-0.8 V at scan rates of 10-200 mV s^{-1}. In EIS measurement, the active materials were individually coated onto stainless steel net (500 mesh) serving as working electrode, other conditions were the same as CV measurement. Impedance was recorded in the frequency range of $10^5 \sim 0.01$ Hz at open circuit potential with an ac perturbation of 5 mV. Galvanostatic charge-discharge curves of the symmetrical capacitors in double-electrode mode were measured on a Land CT2001A cell test system (Wuhan, China) in a voltage range of -1~1 V. The slurry consisting of 85 mw% active material, 10 mw% acetylene black and 5 mw% polytetraflu-oroethylene aqueous dispersion was coated onto stainless steel net and served as working electrode, the weight of active materials were accurately measured for mass capacitance calculation.

3. Results and discussion

3.1. Morphological and structural characterizations

The protocol for the synthesis of a-G-PANI composite was illustrated in Scheme 1. Firstly, the reduction of GO by NaBH$_4$ mainly removes most of the carbonyl, hydroxyl, epoxy and car-boxyl groups [22,23]. The addition of equal stoichiometric ratio of p-phenylenediamine and NaNO$_2$ in acid media causes the conver-sion of one amino group in p-phenylenediamine to aryldiazonium salt, the readily decomposition of aryldiazonium salt *via* releas-ing of N$_2$ results in reactive aryl cations that can rapidly bond to skeletal carbon atoms of graphene to afford a-G [16,17]. Due to the large steric hindrance, the covalently bonded p-aniline groups act as spacer inhibiting the restack of graphene sheets, facilitating