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Strongly coupled polyaniline/graphene hybrids with much enhanced capacitance performance

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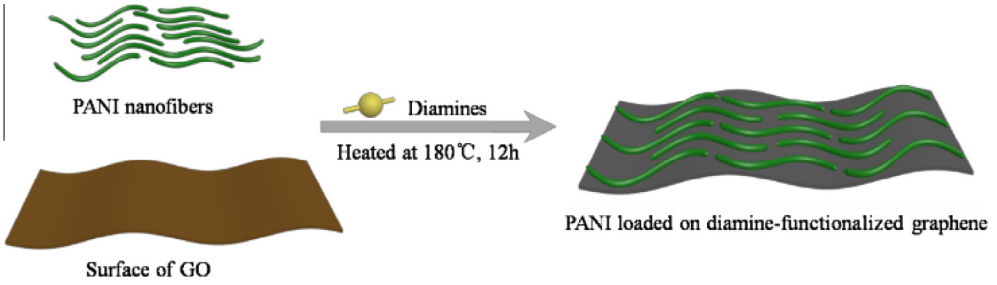
GRAPHICAL ABSTRACT

A facile strategy is developed in this work to fabricate the strongly coupled hybrids of polyaniline (PANI) and graphene (named as PAGs) by introducing different diamines to functionalize graphene oxide. As the electrode material in a two-electrode supercapacitor (SC), the ethylenediamine-functionalized hybrid (PAG-EDA) deliveries an excellent volumetric specific capacitance of 810 F cm^{-3} at 5 mV s^{-1}. The SC also manifests high cycling stability by maintaining 84.4% of the initial capacitance after 10,000 cycles. More importantly, PAG-EDA renders the SC to have both high energy density (92.15 W h kg^{-1}) and high power density (182.28 kW kg^{-1}), superior to most of the previously reported PANI based SC electrode materials.



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ABSTRACT

To enforce the interactions between polyaniline (PANI) and graphene, a facile strategy is developed in this work to fabricate the strongly coupled hybrids of PANI nanofibers and graphene (named as PAGs) by introducing different diamines to functionalize graphene oxide. As the electrode material in a two-electrode supercapacitor (SC), the ethylenediamine-functionalized hybrid (PAG-EDA) deliveries an excellent volumetric specific capacitance of 810 F cm^{-3} at 5 mV s^{-1}. The SC also manifests high cycling stability by maintaining 84.4% of the initial capacitance after 10,000 cycles. More importantly, PAG-EDA renders the SC to have both high energy density (92.15 W h kg^{-1}) and high power density (182.28 kW kg^{-1}), superior to most of the previously reported PANI based SC electrode materials.

1. Introduction

With high power density, fast charging rate as well as long cycling life, supercapacitors (SCs) have been regarded as one of the most promising energy devices for next generation electrical vehicles, portable electronics and grid energy storage [1–3]. Since the electrochemical behaviors of SCs is mainly determined by their electrodes, the development of unprecedented SC electrode materials thus holds the key for conquering the obstacles in the wide applications of SCs including low mass and volume energy densities. In this respect, polyaniline (PANI) has been intensively

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studied as SC electrode material owing to its large specific capacitance (>1000 F g^{-1}) with multiple redox states, relative low cost, good processability and high environmental stability [4–6]. The utilization of PANI alone in SCs is hardly applicable because of the relative low cycling stability of PANI and its poor conductivity in un-doped state [7–9]. Therefore, the loading of PANI on carbon nanomaterials (e.g., graphene, carbon nanofibers and carbon nanotubes) has become as an alternative solution since these carbon matrices can effectively enhance the stability of the PANI based SC electrodes [10,11]. However, PANI in these hybrids is usually physically absorbed on the carbon matrices [12–14]. Even for the hybrids obtained via the *in-situ* growth of PANI on the functionalized carbon nanomaterials, the coupling between PANI and carbon matrices is still weak [15–17]. As the results, the loose packing of PANI and the carbon matrices inevitably restricts the transportation of charge carriers within the electrode and reduces the electrochemical performances of the hybrids.

Very recently, a SC electrode material based on PANI and graphene composite monolith was reported by Yang's group, which exhibited a high volumetric capacitance over 800 F cm^{-3} [6]. Compared with previous work, the much improved performance of the hybrid was assigned to the π–π interactions between graphene sheets and PANI together with the physical confinement of PANI in the compact graphene framework [10]. Inspired by this work, it is envisioned that the enforcement of the coupling between PANI and the graphene matrices will improve the capacitive performance of the resulting hybrids, which is nevertheless still rare so far [15–17].

In this work, we for the first time developed a facile strategy to fabricate the strongly coupled hybrids of PANI nanofibers and graphene (named as PAGs) by introducing diamines including hydrazine (HA), ethylenediamine (EDA), hexanediamine (HDA) and *p*-phenylenediamine (PDA) to functionalize graphene oxide (GO). The subsequent characterization indicates these hybrids have different structural features, which are believed to lead to the varied coupling effects between PANI and the diamine-functionalized graphene. Among the obtained samples, the hybrid using EDA (PAG-EDA) exhibits the most improved electrochemical behavior in SCs. As the electrode material in a two-electrode capacitor, PAG-EDA deliveries a very high volumetric specific capacitance of 810 F cm^{-3} at the scan rate of 5 mV s^{-1}. The capacitor also manifests high cycling stability by maintaining 84.4% of the initial capacitance after 10,000 cycles. More importantly, the excellent electrochemical performance of PAG-EDA renders the capacitor to have both excellent energy density (92.15 W h kg^{-1}) and high power density (182.28 kW kg^{-1}), which are superior to most of the previously reported PANI based SC electrode materials (Table S1).

2. Experimental section

2.1. Chemicals

Aniline (99.5%), sodium dodecyl sulfate (SDS), ammonium peroxydisulfate (APS), hydrazine (85%), ethylenediamine, hexanediamine and *p*-phenylenediamine were purchased from Sinopharm Chemical Reagent Co., Ltd. All the reagents were of analytical grade and used as received. Ultra-pure water was used throughout the experiment.

2.2. Materials synthesis

2.2.1. Synthesis of graphene oxide (GO)

GO was prepared from natural graphite powder according to a modified Hummers method [18].

2.2.2. Synthesis of PANI nanofibers

PANI was synthesized by a dilute polymerization process. Typically, aniline (228 μL) was first added to the aqueous solution of $HClO_4$ (1 M, 50 mL). SDS (7.6 mg) was then added to the mixture to improve the dispersion of aniline. Before polymerization, the mixture was sonicated for 30 min and cooled in an ice bath (ca. 0–5 °C) for another 30 min. Then, APS (380.3 mg) dissolved in the aqueous solution of $HClO_4$ (1 M, 5 mL) was added slowly into the above solution. The resulting mixture was stood in the dark and maintained 0–5 °C for 24 h. Consequently, the dark green colloidal solution was centrifuged at 5000 rpm for 6 min and $HClO_4$ doped PANI nanofibers can be obtained after washing with water for several times.

2.2.3. Synthesis of PAGs

The obtained PANI nanofibers (180 mg) were first dispersed in water (25 mL) by sonicating for 30 min. Then, the dispersion of PANI was added into the aqueous suspension of GO (2 mg mL^{-1}, 25 mL) under stirring. After half an hour, the diamine was added (0.225 mmol) to the above mixed solution and the mixture was stirred for another half an hour. The mixture was then transferred into a Teflon lined stainless steel autoclave (100 mL) and hydrothermally treated at 180 °C for 12 h. Subsequently, the resulting samples were immersed in $HClO_4$ (0.01 M) overnight to re-dope PANI. Finally, diamine functionalized PAGs were obtained after the residue solvent was removed by freeze-drying. According to the diamine used during the fabrication process, the products are named as PAG-HA (hydrazine), PAG-EDA (ethylenediamine), PAG-HDA (hexanediamine) and PAG-PDA (*p*-phenylenediamine), respectively.

In controlled experiment, the mixture of PANI nanofibers (180 mg, 25 mL) and the aqueous suspension of GO (2 mg mL^{-1}, 25 mL) was transferred into a Teflon lined stainless steel autoclave (100 mL) without the addition of any diamine and hydrothermally treated at 180 °C for 12 h. Subsequently, the resulting sample was immersed in $HClO_4$ (0.01 M) overnight to re-dope PANI. After removing the residue solvent by freeze-drying, the final sample was obtained and denoted as PAG.

3. Results and discussion

The fabrication process of PAGs is illustrated in Fig. 1. Typically, PANI nanofibers derived from a dilute polymerization procedure [19] are first mixed with GO and diamines in aqueous solution. Subsequently, the mixture is hydrothermally treated at 180 °C for 12 h. During this step, the reactions between the amine groups of the diamine and GO sheets can create pyrrolic structures and imine bonds to link them, which will not only reduce the amount of oxygen atoms in the hybrids but also enhance the coupling between PANI and graphene [15,20]. According to the different diamines used in this work, the obtained PAGs are named as PAG-HA (hydrazine), PAG-EDA (ethylenediamine), PAG-HDA (hexanediamine) and PAG-PDA (*p*-phenylenediamine), respectively. In controlled experiments, PAG without the addition of diamines were also prepared (see Section 2).

As indicated by their scanning electron microscopy (SEM) images (Figs. 2 and S1), the addition of diamines indeed has obvious impact on the morphology of the resulting hybrids. In the SEM images of PAG, the aggregated PANI fibers with the diameters ranging from ~30–80 nm can be easily observed between the reduced GO sheets (Fig. 2a and b). In PAG-HA, the phase separation of PANI and graphene can still be found (Fig. S1a and b), suggesting the insufficient effect of HA on the dispersion of PANI. By contrast, PANI nanofibers are discretely loaded on the surface of graphene in PAG-EDA (Fig. 2c and d), which implies that EDA is efficient in