

In situ one-pot preparation of reduced graphene oxide/polyaniline composite for high-performance electrochemical capacitors



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ABSTRACT

Reduced graphene oxide/polyaniline (rGO/PANI) composites are prepared through an effective in situ one-pot synthesis route that includes the reduction of graphene oxide (GO) by aniline under weak alkali condition via hydrothermal method and then followed by in situ polymerization of aniline. X-ray diffraction, Fourier transform infrared spectroscopy, Raman spectroscopy, ultraviolet-visible spectroscopy, X-ray photoelectron spectroscopy, scanning electron microscope and transmission electron microscope are employed to reveal that GO is successfully reduced by aniline under weak alkali condition and PANI can be deposited on the surfaces of reduced graphene oxide (rGO) sheets. The effect of rGO is optimized by tuning the mass ratios of aniline to GO to improve the electrochemical performance of rGO/PANI composites. The maximum specific capacitance of rGO/PANI composites achieves 524.4 F/g with a mass ratio of aniline to GO 10:1 at a current density of 0.5 A/g, in comparison to the specific capacitance of 397 F/g at the same current density of pure PANI. Particularly, the specific capacity retention rate is 81.1% after 2000 cycles at 100 mv/s scan rate, which is an improvement over that of pure PANI (55.5%).

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1. Introduction

Electrochemical capacitors (known as supercapacitors), a new type of energy storage devices, cause researchers' attention owing to their excellent electrochemical property [1]. Compared with conventional capacitor, supercapacitors possess obvious advantages, for example, higher energy density, longer cycle-life, wider application temperature range, maintenance-free, et al. [2,3]. As we all know, supercapacitors can be divided into two classes based upon charge-storage mechanism: (a) electrical double layer capacitors (EDLC), where in electrode/electrolyte system, direction arrangement of the electron or ion at the electrode/electrolyte interface forms electrical double layer [4]. (b) pseudocapacitors, where the pseudocapacitance arises from Faradic reactions taking place at the electrode/electrolyte interface [5]. Carbon materials (carbon nanotube, graphene, active carbon, et al.) are a typical electrode materials for the EDLC due to their high specific surface area and excellent conductivity [6], and the conductive polymer (polypyrrole, polyaniline, et al.) are often used for pseudocapacitors due to the high conductivity and large storage capacity [7]. Unfortunately, the specific capacitance of carbon materials is commonly

far less than that of conductive polymers and the storage capacity of conductive polymers gradually decrease with the increase of cycle number [8]. In order to alleviate the inherent drawback of single material, researchers have combined carbon materials and conductive polymers and obtained composite materials with both high specific capacitance and good cycle life.

Graphene is a kind of two-dimensional carbon-based material. It has achieved more and more attention due to its outstanding mechanical [9], optical and thermal properties [10]. The excellent characteristics of graphene have been applied to many electronic devices, such as nanoelectronics [11], solar cells [12], fuel cells [13], Li ion batteries [14], photocatalysis [15], and so on. Till now, graphene can be mainly obtained by using physical methods, for example, epitaxial growth via high temperature treatment of silicon carbide [16], chemical vapor deposition (CVD) [17], micromechanical exfoliation of graphite [18]. Chemical method is another important approach for preparation of graphene due to its low cost and easy to implement [19]. This method usually includes the liquid phase oxidation of graphite first and then reduction of graphene oxide (GO) [20]. In the current researches, many of chemical agents are used for reduction of GO, such as hydrazine and sodium borohydride. However, these chemical reducing agents are very hazardous and instable, thus bring many serious problems for safety and application [21]. Many researchers have reduced GO by some relative safe agents, such as aluminum powder and iron

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powder [22], but the as-prepared graphene is often prone to irreversible reunion. In addition, other reducing agents like amino acid [23,24], bovine serum albumin [25], dopamine [26], and so on are also studied for reduction of GO. However, these reduction processes needing a lot of time and energies and these costly reducing agents lead to the high cost of production. Particularly, the aggregation of graphene sheets is a main problem during the purification process.

Polyaniline (PANI), as a kind of significant conductive polymer, has been used as the electrode material for supercapacitors due to its highly π -conjugated polymeric chains, good conductivity and uncommon conducting/insulating fast transition by doping/dedoping process [27]. The combination of graphene/reduced graphene oxide (rGO) with PANI can obtain electrode materials with improved electrochemical properties. The rGO/PANI composites are generally prepared by the following methods: (a) physical mixing, (b) electropolymerization of aniline (An) on the rGO sheets, (c) chemical bond connects rGO and PANI, (d) in situ polymerization of An in presence of GO/rGO. The last method is commonly used to prepare rGO/PANI composites due to facile synthesis and suitable for large-scale production. To improve the disperse extent of rGO and the properties of rGO/PANI composites prepared by in situ polymerization of An, the researchers have developed many methods. A graphene/polyaniline nanofiber composite [28] was prepared by in situ polymerization of An in the presence of GO and followed by a reduction (using hydrazine), reoxidation and reprotonation process. However, the specific capacitance of this composite was only 480 F/g at a current density of 0.1 A/g. Hasan et al. [29] reported the synthesis of camphor sulfonic acid doped polyaniline/graphene composite by the in situ chemical oxidative polymerization of An in the graphene dispersion containing cationic surfactant cetyltrimethylammonium bromide (CTAB). Jin et al. [30] synthesized graphene/polyaniline composites through a one-pot method that includes the reduction of GO by aniline and then followed by in situ polymerization. The as-synthesized composites exhibited a good electrochemical performance. They proposed that An can release electrons during reduction process and the released electrons are used to convert GO to graphene. It took 24 h at 95 °C to reduce GO with An as a reducing agent. As everyone knows, $-\text{NH}_2$ group of An has different forms in different pH solutions. At high pH, the basic $-\text{NH}_2$ group involve in the reduction process, whereas at low pH the $-\text{NH}_2$ group will be largely protonated. The increased nucleophilicity of $-\text{NH}_2$ group of

An at high pH can increase the efficiency of reduction. To the best of our knowledge, there is no report on preparing rGO/PANI composite through reduction of GO by An under weak alkali condition via hydrothermal method and then followed by in situ polymerization.

In this work, rGO/PANI composites are prepared by an effective in situ one-pot synthesis route. We first reduce GO by An under weak alkali condition via hydrothermal method and then obtain the rGO/PANI composites by in situ chemical oxidative polymerization of An. It takes 10 h to reduce GO with An as a reducing agent under weak alkali condition. The effect of rGO is optimized by changing the mass ratios of aniline to GO to improve the electrochemical performance of rGO/PANI composites. The electrochemical tests show that the composite with the optimal ratio not only exhibits a high specific capacitance, but also possesses an excellent rate capability and a good cycling stability.

2. Experimental

2.1. Preparation of GO

Graphene oxide was prepared from purified natural graphite by the modified Hummer's method [31]. Briefly, concentrated H_2SO_4 (50 mL), natural graphite (1.0 g) and NaNO_3 (1.0 g) were added into a 250 mL flask placed in an ice bath. Solid KMnO_4 (6.0 g) was slowly added into the solution with stirring and cooling the temperature of the mixture remained below 5 °C for 2 h with the aid of an ice bath. And then, the mixture was stirred for another 30 min at 35 °C. After that, excess DI water was added into the above mixture, the temperature was allowed to rise to 90 °C and stirred for 30 min. Finally, 30% H_2O_2 aqueous solution was added to the deep brown mixture until the color of the mixture changed to brilliant yellow. The resulting suspension was filtered while it was still hot and then washed in succession with HCl (5%) and DI water. The solid GO was obtained after filtering and drying in air.

2.2. Preparation of rGO/PANI composites

Composites of rGO/PANI with different mass ratios were synthesized by a new in situ one-pot synthesis route. The mass ratio of An to GO is varied as 10:1, 30:1, 50:1, and the product signed as rGO/PANI-n, such as rGO/PANI-10 composite, indicating the mass ratio of An to GO is 10:1. The synthesis route is illustrated in Fig. 1. For example, the type preparation process of rGO/PANI-

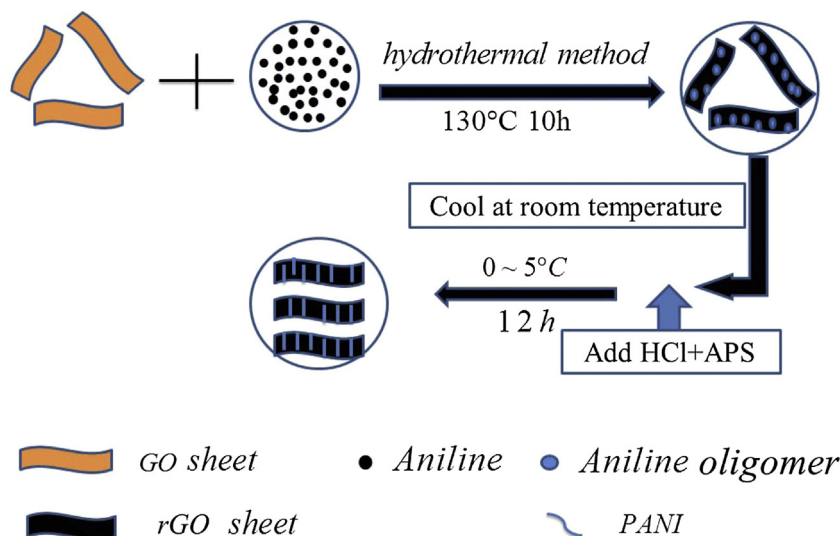


Fig. 1. Illustrations of the preparation process of rGO/PANI composites.

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