Synthetic Metals 243 (2018) 107–114

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet

Aniline oligomer-modified graphene for enhanced electrochemical performances

Sumin Wang, Lu Li, Qiguan Wang*, Yaru Fan, Jingwen Shen, Kai Zhang, Lei Yang, Wenzhi Zhang

Shaanxi Key Laboratory of Photoelectric Functional Materials and Devices, School of Materials and Chemical Engineering, Xi'an Technological University, Xi'an, 710021, People's Republic of China

ARTICLE INFO

Keywords:
Aniline oligomer
Graphene
Supercapacitance
Electrochemical sensing
Nifedipine

ABSTRACT

The surface of graphene (Gr) was covalently attached by an aniline oligomer, from the coupling of graphene oxide with aniline tetramer, followed by reduction process. After linked by tetramer aniline, the graphene materials showed remarkably enhanced electrochemical performances. The conductivity of the graphene was increased from 5.8 S cm^{-1} to 41.7 S cm^{-1}, under the strong doping effect between Gr and tetramer aniline by means of the π–π interactions, which was analyzed by FT–IR, UV–vis and XPS spectra. In addition, the aniline oligomer attached to reduced graphene oxide (AOAG) showed a remarkable energy-storage behavior due to the synergistic effect. The capacitance of AOAGs can be 370 F g^{-1}, while it is 114 F g^{-1} and 129 F g^{-1} for graphene oxide and tetramer aniline respectively. Because the covalent bonding between graphene and aniline oligomer can effectively combine the excellent mechanical strength of graphene and the large faradic pseudocapacitance of aniline oligomer, the AOAGs showed quite high charge-discharge cycle stability besides remarkable capacitance. In addition, the ease of electron motion mediated by the covalent bonding in AOAGs supports the sample significant electrochemical catalysis towards nifedipine. Compared with graphene and tetramer aniline, the oxidative current of nifedipine on AOAG showed five-fold increase.

1. Introduction

Graphene (Gr) has shown outstanding electronic, thermal and mechanical properties due to its characteristic structure [1,2]. So far different techniques have been employed for Gr synthesis, including the "Scotch tape"-based cleavage method [3], epitaxial growth [4,5], chemical vapor deposition [6], exfoliation of expanded graphite [7,8], and reduction of graphene oxide (GO) [9–11]. Among above techniques, the chemical reduction of graphene oxide needs no large complicated devices and shows low cost operation, which has been widely used [10]. However, in this process, the initial oxidation step ordinarily disrupts the sp^2 hybridized carbon, leading to bad thermal and electrical performance because of the formation of numerous oxidized carbon atoms. Although, by using thermal and/or chemical reduction, the sp^2 hybridized carbon structure can be restored. But the oxygen-containing groups may only be partially reduced due to significant influence of many structural defects, shown as crumpling, wrinkling and atomic vacancies in the sheets of reduced graphene oxide (rGO) [12], which has hindered realization of the promising macroscopic applications of Gr.

For the purpose of further enhancing its electrical and electrochemical performances of rGO suppressed by structural defects, combination of graphene with conjugative polymers, for instance, polyaniline (PANI) [13,14], polypyrrole (PPy) [15–17] and polythiophene (PTh) [18] has aroused rapidly growing research interest. By using in–situ polymerization method, Zhang et al. [19] prepared chemically modified Gr/PANI nanofiber composites. A high specific capacitance (SC) of 480 F g^{-1} measured at 0.1 A g^{-1} current density was achieved, and the electrical conductivity of composites is significantly increased to 2.3 S cm^{-1}. Nanofibered Gr/PANI composites stabilized by surfactant were prepared by Mao et al. [20], which showed SC value of 526 F g^{-1} measured at current density of 0.2 A g^{-1}. It was decreased to 321 F g^{-1} at higher current density of 1.0 A g^{-1}. The composite shows electrical conductivity of 0.61 S cm^{-1}. Basavaraja et al. [21] synthesized PPy/GO composites with conductivity values ranged from 0.0217 to 0.13 S cm^{-1}. By liquid – liquid interfacial polymerization, Bora et al. [22] developed a novel method to synthesize PPy/Gr composites with a noticeable conductivity of 8.45 S cm^{-1} and a high SC value of 260 F g^{-1} at 0.1 A g^{-1} current density. Similarly, from interfacial polymerization, PTh/GO nanocomposites can be synthesized [18]. The electrical conductivity could be 2.7×10^{-4} S cm^{-1} and the SC value was measured to be 99 F g^{-1}.

---

* Corresponding author.
E-mail address: qiguanwang@163.com (Q. Wang).

https://doi.org/10.1016/j.synthmet.2018.06.011
Received 22 February 2018; Received in revised form 3 June 2018; Accepted 19 June 2018
0379-6779/ © 2018 Elsevier B.V. All rights reserved.

Composited with those conductive polymers (CPs) having large pseudo-capacitance, the electrochemical capacitance of the graphene based electronic double layer capacitor was greatly enhanced. In addition, the disrupted sp^2 hybridized carbons and the defected structures in rGO formed during graphite exfoliation were partly repaired by the π–conjugative faces of conductive polymers under the π–π interactions, which facilitate the electron motion in the Gr-based composites and enhances their electrical conductivity. However, because of the weak interactions between Gr and CP, the cycling stability of aforementioned composites cannot yet meet the practical requirement. To increase the interactions among the components, many studies have been performed on the ionic and/or covalent linked Gr/CP materials. Liu et al. [23] synthesized the hierarchical polypyrrole/sulfonated reduced graphene oxide (SrGO) nanocomposites via liquid interfacial fabrication. A high specific capacity of 265.6 F g^{-1} measured at 1.0 A g^{-1} current density was obtained, and around 90% of the initial capacity was retained after 1000 cycles. Because of the ionic interaction and the doping effect between PPy and SrGO, the composites showed the conductivity as high as 5.45 S cm^{-1}. Moghadam et al. [24] synthesized a highly crystalline and conductive composite fabricated from GO and PANI by using in–situ polymerization method. Electrical conductivity of the doped GO/PANI composite is 5.8 S cm^{-1}. They attributed the high conductivity to the creation of common conjugated pathways between PANI and GO, based on the higher crystallinity and/or chemical grafting of PANI to GO. In our group [25], a facile strategy was developed to synthesize GO/PANI nanotube composites by using an in–situ alkaline polymerization method. The obtained GO/PANI nanotubes showed electrical conductivity of around 1.4 S cm^{-1}, with the maximum SC value of 277 F g^{-1} at a current density of 1.0 A g^{-1}. The ionic interaction between PANI and GO makes the nanotubed GO/PANI hybrids show high stable charge-discharge cycles. The SC value just decreased less than 6% upon 1000 charge-discharge cycles at 1.0 A g^{-1} current density.

As far as the preparative methods of Gr/CP composites concerned, the interfacial polymerization and in–situ polymerization are usually used. During these processes, the deposition of CP towards Gr surfaces happens after the polymerization process of conjugative monomer. That is, the CP chains have already been hardened and aggregated to be granules when attached to GO surface from the liquid phase. Therefore, the interface contact between Gr and CP components is bad in those Gr/CP composites, which strongly limits the electron motion and the further enhancement of electrochemical performances.

In order to modify the contact state between Gr and CP, introduction of stronger interactions such as covalent bonding is undoubtedly an effective approach. Meanwhile, to suppress aggregation of CP, maintainess of CP in the monodispersed state during being attached to the surface of GO is needed. However, this is difficult to take place in the in–situ polymerization case. For the purpose of keeping CP in a monodispersed state during attachment to GO, making CP dissolved in liquid phase is the feasible approach. However, the bad solubility of CP limits the utility of this method. Considering the similar electrochemical and spectroscopic properties as polyconjugated conducting polymers [26], the well-defined CP oligomers possessing good solubility in organic solvents are appropriate candidates as model compounds in the synthesis of covalently linked Gr/CP materials. In this case, the polymerization process of monomer is avoided, which can effectively suppress the significant aggregation of CP particles. Here we report a Gr-based material, in which the Gr surface was covalently attached by tetramer aniline (Fig. 1). Because the interfacial contact was enhanced and the aggregation of CP was effectively suppressed, the aniline oligomer attached reduced graphene (AOAG) showed fast charge transfer and enhanced electronic communication, leading to large specific capacitance, excellent cycling stability, high electrical conductivity and better electrocatalytic behavior.

2. Experimental

2.1. Materials

Graphite powder, N-phenyl-1,4-phenylenediamine, nifedipine and $SOCl_2$ were received from Aladdin Chemical Co. in China. Ferric chloride hexahydrate, potassium permanganate ($KMnO_4$, 99.9%), phosphoric acid (H_3PO_4, 85%), hydrogen peroxide (H_2O_2, 30%), hydrogen chloride (HCl, 37%), hydrazine hydrate, ammonium persulfate (APS), ethanol and acetone were obtained from Shanghai Chemical Co., Ltd., and were used without any purification. N,*N*-dimethyl formamide (DMF) was distilled under vacuum prior to use.

2.2. Synthesis of GO

GO was prepared by a modified approach based on the reported method [27]. By addition of 3 g of graphite powders in 400 ml of H_2SO_4/H_3PO_4 (9/1, v/v) mixture, followed by further adding 18 g of $KMnO_4$, graphite oxide was obtained. The mixture was stirred for 72 h. Then, adding 3 ml of H_2O_2 solution, an acidic mixture showing bright yellow color was gained. The obtained graphite oxide was washed by using hydrogen chloride solution (1.0 M) and then high-purity water until the pH value was 4–5. After decanting the supernatant, concentrated GO solution was resulted to form GO gel. The GO powder was collected after filtered and dried at 65 °C in a vacuum oven.

2.3. Synthesis of tetramer aniline

Tetramer aniline was synthesized from the N-phenyl-1,4-phenylenediamine which was suspended in 1.0 M HCl aqueous solution, oxidized by ferric chloride hexahydrate according to the reported method [28]. After recrystallized from ethanol, the tetramer aniline was obtained.

2.4. Covalently attaching tetramer aniline to GO

For the sake of covalent attachment of tetramer aniline to GO, 20 mg of GOs was firstly chlorinated by refluxing in 30 ml of $SOCl_2$ at 70 °C for 10 h. After evaporating the unreacted $SOCl_2$ from the flask, aniline oligomer attached GOs were then obtained by reaction with 80 mg of tetramer aniline in 40 ml dry N,*N*-dimethyl formamide at 80 °C for 48 h. The obtained powders were filtered, and repeatedly washed by N,*N*-dimethyl formamide and acetone, and collected after vacuum drying at 50 °C for 48 h. The obtained black powders were loosely packed with high uniformity, and the synthesis yield was 96.3%.

2.5. Reduction of GO in AOAG

In order to decrease the content of unreacted oxygen-containing groups, chemical reduction of GO was done by dispersing 50 mg of as-prepared AOAG in 60 ml of hydrazine monohydrate, which was agitated at 80 °C for 6 h. Then the product was collected by filtering, thoroughly washed by water and dried in a vacuum oven at 60 °C. The resultant product was suspended in 50 mL 1 M hydrogen chloride solution containing 0.5 g APS. After agitation for 24 h at 25 °C, the mixture was filtered and thoroughly washed by high-purity water and ethanol. The resultant materials were desiccated at 60 °C under vacuum condition for 1 d. In contrast, the rGO was also synthesized by reduction of GO according to the same procedure.

2.6. Characterization

The morphologies of the prepared nanocomposites were detected by using a scanning electron microscopy (SEM, Hitachi S–4800, Japan) and a transmission electron microscopy (TEM, JEOL JEM–2010, Japan). A Fourier transform infrared (FTIR) spectrometer (Nicolet 750,

Download English Version:

https://daneshyari.com/en/article/7873427

Download Persian Version:

https://daneshyari.com/article/7873427

Daneshyari.com