



Graphene oxide-polythiophene derivative hybrid nanosheet for enhancing performance of supercapacitor



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HIGHLIGHTS

- S-doped graphene oxide hybrid nanosheets were prepared by a facile method.
- Hybrid nanosheets exhibits good capacitive performance.
- Large energy density of the GO-TB-based three-electrode device was obtained.

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ABSTRACT

S-doped graphene oxide hybrid nanosheets are prepared by a facile in situ-polymerization method. The electrochemical performance is evaluated using cyclic voltammetry, galvanostatic charge/discharge techniques and impedance spectroscopy in 2 M KOH. As an electroactive material, it exhibits good capacitive performance in alkali aqueous electrolyte, high specific capacitance (up to 296 F g⁻¹) at a current density of 0.3 A g⁻¹, which is calculated via charge/discharge curve in three electrode systems. The electrical conductivity is also measured. More importantly, over 91.86% of the long-term stability is retained after repeating the galvanostatic charge/discharge over 4000 cycles. Furthermore, larger energy density (up to 148 W h kg⁻¹ at a power density of 41.6 W kg⁻¹) of the GO-TB-based three-electrode device is obtained with alkali aqueous electrolytes.

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1. Introduction

At present, great efforts have been dedicated to the development of new microstructure materials with novel physiochemical properties utilized as supercapacitors (SCs) [1]. The electrochemical energy storage devices have received increasing attention because of their adorable properties, such as high power [2–4]. SCs are the furthest candidate for energy storage device of this century, which has the ability to protect the environment from pollution as well as to satisfy the robust demand of energy presently. It can be divided based on the energy storage mechanisms into electrical double layer capacitor (EDLC) and pseudo-capacitor (PC) [5]. EDLC can

store energy via reversible ions absorption at the electrode/electrolyte interface. However, its energy density and specific capacitance are analogous to a conventional capacitor due to the nature of electrode materials and the limited surface area [6]. On the contrary, PCs possess a higher energy density and a fast loss of power density and life cycle. Currently, the real challenge in the development of supercapacitors is to promote their energy density and preserve their high power capability and long cycle life [7,8].

To achieve this goal, numerous multifunctional materials have been prepared. Among them, heteroatom (e.g. B, N, S and Si)-doped porous carbon materials and heteroatom with graphene, has attracted great attention and been proved to be a boosting candidate for electrode materials because of their unique physical properties [9,10]. Graphene is a two-dimensional sp² hybridized carbon sheet with high electrical conductivity, thermal stability and mechanical properties [11,12]. The most important is the graphene

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oxide (GO) derived from graphite, composed of both conjugated sp^2 systems and electronically isolated oxygen functional groups that possesses the unique characteristics such as easy synthetic functionalization, a high aqueous dispersibility and biocompatibility [13]. GO usually results from the chemical exfoliation of graphite [14]. Chemical method adopted based on Hummers oxidation route, that have been used to produce a large number of functional groups within the graphene oxide composite, such as hydroxyl ($-OH$), aldehyde ($-CHO$), carboxyl ($-COOH$) and epoxy groups, thus reducing the interior forces and enhancing the hydrophilic characteristic [15]. Moreover, numerous functional moieties as well as polymer chains have been linked onto the graphene oxide sheet by various chemical approaches. Thus, the presences of oxygenic functional groups on the surface, like carboxyl and hydroxyl groups are supportive for the growth of other layers within inorganic materials. Therefore, GO is more appealing for its ability to display a multiple range of energy and charge exchange interactions with polymers and organic molecules, which contribute to GO ability to allow both ionic and nonionic bonding with a variety of molecules [16]. For instance, Polythiophenes (PTs) and their derivatives considered to be one of the most conductive polymers, have the ability to conduct electricity and possess high charge mobility [17]. Therefore, PT derivatives as supercapacitor candidates, are capable of forming composites with GO. Although S-doped graphene oxide (SGO) had been prepared, but the atomic configurations of the S dopants within the graphene oxide lattices, the nature of the dopants and the doping concentration has not been studied yet. Shuai et al. synthesized GO–P3HT and r-GO–P3HT hybrids via the noncovalent binding of P3HT molecular films on GO and r-GO sheets, which showed that synergistic interactions in this molecular layer-on-GO assembly enhances optical absorption, charge transfer, and photocatalytic properties [18]. Zhao et al. successfully prepared the GN/PT composites at different mass ratios of GN to Th by in situ polymerization [19] and Takahashi et al. succeeded in synthesizing P3HT-b-GPT for organic solar cells application [20].

Conducting polymers have been widely studied in the electronic field because of their easy synthesis, excellent chemical and thermal stability [5]. Yahiaoui and his coworkers synthesized conjugated co-polymers (PTB) [17]. Yokozawa et al., have separately developed Grignard metathesis (GRIM) polymerization, a promising synthetic method for conjugated block copolymers containing PT segments and regular PTs [21]. Later, Ueda group have succeeded in synthesizing a polythiophene bearing phenyl group (P3PhT), which demonstrates an intramolecular oxidative coupling of P3PhT to generate novel polythiophenes with graphene-like structures (GPTs) [20]. Farah Alvi et al. prepared G-PEDOT and G-PTh nanocomposites with maximum capacitance of 374 F g^{-1} and the long term stability about 88% in 2 M HCl after 100 cycles [22]. In perspective of obtaining conducting polymers with long time stability during charging/discharging, higher reversibility and high ohmic resistance are great challenges to obtain a high power supercapacitor [23]. Currently conducting polymers combining with graphite or graphene composite were synthesized to resolve these issues [11,24]. However, till present there is no report available that shows the behavior of graphene oxide–polythiophene for electrochemical properties such as a capacitance or conductivity.

Generally, sulfur (S) doping on graphene oxide surface can modulate the electron structure of GO. Because the S atoms integrated into graphene, requires a large formation energy than N atom [25], so the synthesis of S-doped GO is very difficult. Nevertheless, the thermal annealing reduction has been reported for synthesis of S-doped GO. The electrical properties of S-doped GO remain entirely undiscovered. Besides, two types of S bonding configurations (thiophene-S and oxidized-S) have been mentioned for S-doped GO samples [26,27]. This hinders a conclusive study of

the doping effect of S on the GO properties, because various types of S-bonding configurations lead to different properties.

Herein, a facile route to synthesize graphite- (Thiophene-2,5-diyl)-co-(benzylidene) (G-TB) and graphene oxide- (Thiophene-2,5-diyl)-co-(benzylidene) based on the in-situ polymerization of conjugated polymer poly [(thiophene-2,5-diyl)-co-(benzylidene)] (PTCB) via the non-covalent binding of PTCB film on G and GO sheets has been explored, which demonstrates the synergistic effect of structure and doping in the graphene by designing and fabricating G-TB and GO-TB. The electrochemical characteristics of the as-synthesized G-TB and GO-TB in alkaline media have been investigated. GO-TB exhibits more superior electrochemical performance in the aspect of less internal resistance, excellent capacitance, and high cycle stability. These exceptional properties are attributed to the high ionic conductivity, excellent compatibility with electrode material, and long-term stability of S-doped on GO surface.

2. Experimental

2.1. Materials

Graphene was obtained from Sinocarbon Materials Technology Co. Ltd., China. Thiophene and raw-Magnite were supplied by Aladdin Industrial Corporation Shanghai, China. Benzaldehyde, potassium permanganate, hydrogen peroxide and sodium nitrate were purchased from Sinopharm Chemical Reagent Co., Ltd. Potassium Chloride was purchased from Sinopharm Chemical Reagent Co., Ltd. (SCRC), which was used as electrolyte solution for the electrochemical characterizations. All chemicals were used directly without any further purification.

2.2. Synthesis

2.2.1. Preparation of GO

Graphene oxide was synthesized using a modified Hummers method. Graphite powder (1 g) was first added to concentrated sulfuric acid (98%, 30 ml). Then, sodium nitrate 0.5 g was added. The mixture was cooled to 0°C . Potassium permanganate (3.5 g), an oxidizing agent, was gradually added to the graphite solution with vigorous stirring for 10 min. After allowing the reaction to proceed at 35°C for 2 h, the solution was cooled in an ice bath and diluted with deionized water (200 ml). Following 1 h of stirring, hydrogen peroxide (100 ml) was added to the reaction solution. The color turned from brown to yellow. The mixture was then filtered and washed several times with hydrochloric acid (10%). The remaining solvent was evaporated under vacuum at room temperature for 12 h.

2.2.2. Preparation of GO-TB composites

Poly [(Thiophene-2,5-diyl)-co-(benzylidene)] was synthesized by the condensation of thiophene and benzaldehyde as monomers in the presence of Mag-H^+ as a catalyst. In a 50 ml round flask, graphene oxide (GO) (0.5 g), thiophene (8 mmol) benzaldehyde (8 mmol) and 1 g of Mag-H^+ were dissolved in 10 ml of 1,2-dichloroethane. The mixture was heated at 80°C for 1 h. At the end of the reaction, the resulting mixture was filtered and washed with methanol and the polymer was dried under vacuum at room temperature for 24 h. The product sample labeled GO-TB, The same procedure was used to prepare G-TB from graphite.

2.3. Characterization methods

Scanning Electron Microscopy (SEM, SIRION 200) operated at 5 kV and High resolution Transmission Electron Microscopy (HR-

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