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Effect of graphene oxide on the structural and electrochemical behavior of polypyrrole deposited on cotton fabric

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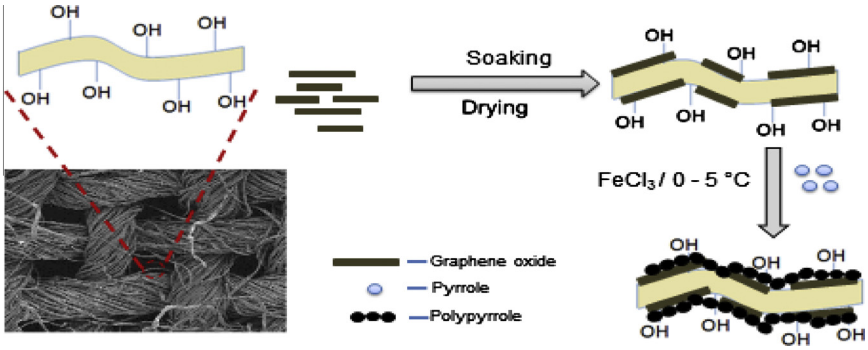
HIGHLIGHTS

- Polypyrrole/graphene oxide/cotton are prepared by chemical polymerization process.
- The physical and electrochemical properties of polypyrrole/graphene oxide/cotton.
- Conductivity-physical properties relationship of polypyrrole/graphene oxide/cotton.

GRAPHICAL ABSTRACT



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ABSTRACT

Improving the electrical response of polypyrrole–cotton composite is the key issue in making flexible electrode with favorable mechanical strength and large capacitance. Flexible graphene oxide/cotton (GO/Cotton) composite has been prepared by dipping pristine cotton in GO ink. The composite‘s surface was further modified with polypyrrole (Ppy) via chemical polymerization to obtain Ppy/GO/Cotton composite. The composite was characterized using SEM, FTIR and XRD measurements, while the influence of GO in modifying the physicochemical properties of the composite was also examined using TG and cyclic voltammetry. The achieved mean particle size for Ppy/Cotton, Ppy/GO/Cotton and GO estimated using Scherrer formula are 58, 67 and 554 nm, respectively. FTIR spectra revealed prominent fundamental absorption bands in the range of 1400–1800 cm^{-1}. The increased electrical conductivity as much as 2.2×10^{-1} S cm^{-1} for Ppy/GO/Cotton composite measured by complex impedance, is attributed to the formation of continuous conducting network. The partial reduction of GO on the surface of cotton (GO/Cotton) during chemical polymerization can also affect the conductivity. This simple, economic and environmental-friendly preparation method may contribute towards the controlled growth of quality and stable Ppy/GO/Cotton composites for potential applications in microwave attenuation, energy storage system, static electric charge dissipation and electrotherapy.

Introduction

Modification of the electrical properties of cotton fibers and fabrics by incorporating conducting polymers in order to achieve exotic functional properties has been an active research domain.

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Generally, conductive polypyrrole (Ppy) is chemically coated on cotton fabrics using ferric chloride as the oxidizing agent. Ppy-coated cotton fabrics are topically attractive due to their widespread applications in chemical and biological sensors [1], rechargeable batteries [2], actuators [3], light-emitting diodes [4], memory devices [5], photo-voltaic [6], corrosion resistance [7], and many more. Ppy is well known for its high electrical conductivity [8], facile preparation [9], biocompatibility and appreciable thermal stability [10]. This new generation of conductive polymers-coated fabrics is promising due to their electrical heating behavior, nonlinear optical properties, superior mechanical properties and processing advantages [11,12]. Intrinsic conducting polymers that mimic metallic conductivity, which can be achieved by the well-known approach of inserting conductive fillers into an inherently insulating resin or coating a plastic substrate with a conductive metal solution, are found to be promising [13].

Conductive fabrics can be prepared from fibers or fabrics that can be metalized with a conductive layer. The preparation methods for Ppy include chemical [12], vapor phase [14], electrochemical [15] and plasma enhanced chemical polymerization methods [16]. Chemical method offers several advantages over the other methods, such as free from contamination, simplicity, lower cost, more homogenous mixing of the components and better control over the particle size of Ppy [17,18]. The *in situ* chemical polymerization that renders relatively high conductivity is the most suitable method for dielectric coating. Methods for improving the electrical properties of such conducting polymer-coated fabrics have also been developed [19]. Additional functionality of conducting polymer-coated fabrics using triethoxysilane has also been demonstrated [20]. However, the insoluble and infusible nature of synthetic conductive Ppy restricts their processing and applications in other fields. Lately, the problem has been extensively addressed to explore applications in emerging areas.

Chemical coating of Ppy on isolated substrate has recently been developed due to their superior physical, optical and electrical properties [21]. The solution-based coating and printing techniques are intensively exploited to synthesize conductive carbon nanotubes (CNTs)-based papers and textiles for electrodes and/or current collectors in batteries and super-capacitors [22]. However, the low specific capacitance resulted from the energy storage mechanism of carbonaceous nanomaterials, limits their usage as efficient electrodes. Despite unusual and interesting properties exhibited by these CNTs-incorporated papers and textiles, the significant cost reduction for large-scale energy storage applications remains a challenge. Graphene materials, being an emerging unique class of carbon based nanoscale building blocks, possess substantial potential towards energy conversion and storage devices. Their exceptional characteristics, such as superior electronic and mechanical properties, good electrochemical stability and large specific surface area, make them viable for a variety of energy applications such as photovoltaic, batteries and super-capacitors [23]. It is commonly known that graphene acquires unique electronic band structure in the presence of Dirac point which facilitates both electron and hole to transport. This distinct band structure allows them to fabricate field-effect transistor (FET) devices with ambipolar properties [24]. Tuning of their electronic properties for electronic devices and related applications has been recently explored by different kinds of doping and also by preparing graphene nanoribbon, nanomesh and bi-layer structures [24]. Through these methods, doping of graphene is the most feasible way to control its electrical property [24]. Substitutional doping is the functionalization of graphene by covalent bonding that introduces defects into the graphene's structure. In other kinds of doping, which is basically the functionalization of graphene by non-covalent bonding, no defects are generated. Nevertheless, functionalization of graphene by covalent bonding possesses similar drawbacks to the common doping technique because defects generation decreases mobility and the on/off ratio in a graphene field-effect transistor [25]. Conversely, the non-covalent physisorption inherently driven by favorable molecular self-assembly involves dispersive interactions. This process does not remarkably modify the band structure properties, leaving the exceptional electronic structure of the graphene derivatives [25]. This strategy is predicted to be one of the keys to solve the drawbacks of common doping processes [24,25]. To date, much work has been carried out to develop GO-based nanomaterials in order to study their applications in biosensors, electronics and optoelectronics [23,26]. Based on the unique properties of GO and its derivatives, extensive efforts are dedicated to integrate GO or its derivatives into Ppy-based composite materials. In a recent study, relatively large anionic GO functions as a weak electrolyte and is captured in the Ppy composites through the electropolymerization of pyrrole, performing as an active charge-balancing dopant within the Ppy film [26]. It is proposed that the π–π interactions and hydrogen bonding between the GO layers, aromatic polypyrrole rings and the carboxyl groups of GO are efficient dopants in the polymerization. It is acknowledged that GO/Ppy composites are potential candidates for energy storage [26] and sensing application [27]. GO produced by modified Hummer's method displayed higher capacitance (as much as 189 F g^{-1}) than graphene, due to an additional pseudo-capacitance effect originated from the attached oxygen-containing functional groups on its basal planes. GO may be considered as a better electrode material than graphene in account of higher capacitance, lower cost and shorter processing time [28]. Controlled syntheses and careful characterizations of high quality stable Ppy/GO/Cotton composite with tunable structural and conducting properties have ever-growing interests in energy storage system and electronic application.

Herein, we report the preparation of high quality Ppy/GO/Cotton composite using chemical method and subsequent characterizations to examine their electroactive and conductive nature. The physicochemical and mechanical properties of these conducting fabrics are determined and compared with Ppy/Cotton composite. The mechanisms responsible for considerable improvement in conductivity and structural properties of these composites were also analyzed. The successful attachment of the solution-exfoliated GO sheets on three-dimensional, porous textiles support structures for controlled loading of active electrode materials is demonstrated. The controlled deposition of electroactive Ppy and graphene oxide nanomaterials facilitated the access of electrolytes onto the composite's structures.

Experimental

Raw materials of analytical grade such as graphite (HmbG), sulfuric acid (H_2SO_4, 97%, Grade AR, QREC), hydrochloric acid (HCl, 37%, Grade AR, QREC), ethanol (96%, Grade AR, QREC), potassium permanganate ($KMnO_4$, 99%, Sigma–Aldrich), sodium nitrate ($NaNO_3$, 99.99% Sigma–Aldrich), anhydrous sodium carbonate (Na_2CO_3, 99.9% Sigma Aldrich, USA), pyrrole (C_4H_4NH, 99.99%, Sigma–Aldrich) and iron(III) chloride ($FeCl_3$, Sigma–Aldrich) were used. GO was synthesized by modified Hummer's method [29] via chemical oxidation without further purification. The solution of GO (5 mg ml^{-1}) and deionized water was sonicated for 1 h at 100 W to form a stable dispersion. In the scouring treatment, the cotton textile was boiled for 5 min at 100 °C in deionized water. Following Nilghaz et al. [30], the first treatment was performed using 10 mg ml^{-1} anhydrous sodium carbonate. After the treatment, the samples were washed with water until the pH was reverted to the neutral range (pH = 7).