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Synthesis of reduced graphene oxide nanoscrolls embedded in polypyrrole matrix for supercapacitor applications

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ABSTRACT

Reduced graphene oxide (rGO) nanoscrolls are synthesized in the presence of pyrrole (Py) by using oxidative polymerization method in the presence of sulphuric acid and ammonium persulfate. We report a simple method for the synthesis of rGO nanoscrolls in the presence of pyrrole, and this composite material is used for the supercapacitor applications. Supercapacitor electrodes show good cyclic stability by retaining 88% of the specific capacitance even after 200 cycles. Polypyrrole – reduced graphene oxide (PPy-rGO nanoscrolls) is characterized by Raman, TEM, FESEM, EDX, FTIR, TGA and UV–vis spectroscopy techniques.

1. Introduction

Carbon based materials have gained significant interest in the area of micro- and nano-device research due to their higher conductivity, electrochemical stability in ionic solutions, response to chemical treatments for surface property modifications, and biocompatibility [1]. Carbon materials are available in various allotropes such as diamond, graphite, carbon nanotubes (CNT) and glassy carbon. These materials have promising applications for electrodes in electrochemical sensors, energy storage/conversion devices and environmental applications [2,3]. Graphene is a 2D monolayer of sp^2-bonded carbon atoms packed into a regular hexagonal pattern; it is a promising material due to its high electrical conductivity and thermal conductivity, tunable specific surface area, strong mechanical strength and chemical stability [4]. These properties enables graphene based hybrid materials to find applications in the area of electronic, biosensing, energy generation and energy storage applications [4–6]. Zang et al. [7] have reviewed and discussed about the various synthesis techniques of graphene and carbon nanotube (CNT); and their applications in the area of MEMS (Micro-electro-mechanical Systems) and NEMS (Nano-electro-mechanical Systems) based sensors, actuators, and energy storage devices. Mecklenburg et al. [8] have reported about the synthesis of aerographite material which is having properties like lightweight, mechanically robust, electrically conductive, chemically resistant, better flexibility, compressibility, high temperature stability and superhydrophobicity; which are the important properties for materials to be used as an electrode material for batteries and supercapacitors.

Reduced graphene oxide (rGO) nanoscrolls are new class of graphene material different from that of multiwalled CNTs; it is a promising material for supercapacitor. It is formed by changing the topological structure of graphene by rolling, twisting, and by folding of the graphene sheets [9–11]. It consists of tubular graphene open ended sheet rolled from one side or from the corner to form spirally wrapped graphene sheets [10]; basically, it can be one-sided nanoscroll or two-sided nanoscroll and diagonal nanoscroll [11]. Nanoscrolls of rGO are reported to have varying interlayer distance due to its open-ended topology, which makes it different from CNTs. Scrolled graphene structure has different electronic and mechanical properties then that of multiwalled CNTs, they have very high current density $\geq 10^8$ A/cm^2 and reduced stiffness makes the scroll mechanically more flexible than a multiwalled tube structure [12,13].

Various techniques for the synthesis of graphene nanoscrolls have been reported by researchers, they are mainly by chemical route, Langmuir–Blodgett method, direct on SiO_2/Si substrate due to surface strain and well-controlled Lyophilization method [14–19]. Reduced graphene oxide nanoscrolls are used for hydrogen storage, supercapacitor, batteries, catalysts, sorbents and lightweight as-well-as high-strength materials [11,20–23].

Nanomaterials tends to agglomerate because of high surface energy which inhibits their cycle-life stability as an electrode material; to avoid this core-shell like structure or heterostructured

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nanocomposite materials are preferred [24]. Surface modification and addition of filler particles into polymer matrix helps in avoiding such agglomeration [25].

Graphene based nanocomposites materials with transition metal oxides, hydroxides and conducting polymers have been extensively investigated for supercapacitor applications, they shows superior electrochemical performance and are promising materials for achieving higher power density, good chemical stability and high energy density [4]. Primarily, supercapacitors can be divided into two classes' electric double layer capacitor (EDLC) and pseudocapacitor [4,26].

In this paper, we report an easy method for the synthesis of graphene nanoscrolls in presence of pyrrole, sulfuric acid and ammonium persulfate. The synthesized PPy-rGO nanoscroll composite is used for supercapacitor applications. Polymer-graphene composite is a hybrid capacitor possesses both Faradic and non-Faradic processes which help in achieving high energy and high power density greater than EDLC's. Several groups have reported about the synthesis PPy-rGO nanocomposite; however, they have not reported the formation of graphene nanoscrolls in the presence of pyrrole [26,27–31].

The objective of incorporation of graphene nanoscrolls into polypyrrole is to take advantage of higher surface area, open-ended topology and availability of higher accessible inter-wall area. Incorporation of graphene nanoscrolls makes the composite porous and forms an interconnected structure with polypyrrole. It also provides effective conductive path for the diffusion of ions into the material. Moreover, research work is going on in authors' laboratory to further incorporate these materials into high-aspect-ratio 3D structures to achieving better power and energy density.

2. Experimental

2.1. Synthesis of rGO

Graphene oxide (GO) was synthesized from graphite (GRP) powder (purity > = 99.99% Sigma-Aldrich) by using Hummers Method and further reduced by hydrazine hydrate to form reduced graphene oxide (rGO) [32]. The procedure adopted for the synthesis of rGO was as per our previous report [33]. All the chemicals and reagents used in the experiments were of analytical grade. Synthesized rGO was filtered by using deionized (DI) water and methanol, and dried under vacuum. The TEM, Raman and TGA techniques were used to characterize rGO.

2.2. Synthesis of PPy-rGO nanocomposite

For the synthesis of PPy-rGO (sample-1) see Fig. 1, at the beginning freshly vacuum distilled 0.5 M pyrrole (Aldrich make) monomer solution was prepared in deionized (DI) water in which 2 ml of H_2SO_4 was added, and later the mixture was sonicated for 10 min. In another beaker the solution of 2.5 g of rGO and 1 ml of ethanol was prepared in DI water, and sonicated for 90 min. After these steps, glass substrate cleaned with nitric acid, acetone, and DI water, dried, and, fitted in jigs mounted vertically into the beaker containing pyrrole solution. Now the prepared rGO solution was added gradually to it under continuous stirring. Thereafter, ammonium persulfate (APS) solution which was separately prepared in 30 ml of DI water was added slowly into it. After 6 h of chemical reaction the glass slides were taken out from the beaker and cleaned thoroughly by DI water to wash away unreacted monomers and adsorbed particles, and then dried under vacuum. The prepared PPy-rGO (sample-1) thin film shows the synthesis of rGO nanoscrolls embedded into polypyrrole matrix. FESEM, TEM, Raman and UV–vis spectroscopy were used to confirm the formation of rGO nanoscrolls.

Further, to analyze the formation of rGO nanoscrolls sample-2 was also prepared (see Fig. 1). Sample-2 was synthesized in a similar manner to that of sample-1 without adding H_2SO_4. No scrolling was observed in sample-2. All the experiments were performed at room temperature, i.e., 25 °C.

Synthesis of Sample-3 shows the formation of rGO nanoscrolls in presence of pyrrole and sulfuric acid. Nanoscrolls of rGO were synthesized under solution phase.

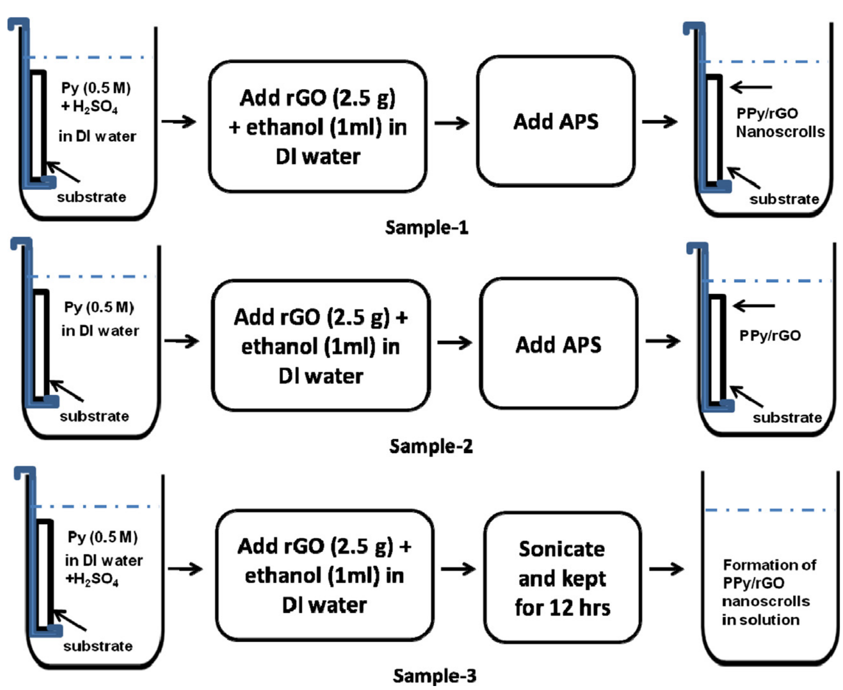

Fig. 1. Schematic representation of sample preparation of PPy-rGO; in case of sample-1 the H_2SO_4 is added at the beginning stage followed by addition of APS leads to the formation of rGO nanoscrolls embedded into PPy; sample-2 is polymerized without adding H_2SO_4 it does not show rGO nanoscrolls formation; sample-3 shows the synthesis of rGO nanoscrolls in solution phase.