



Hybrid assemblies by pyrrole polymerization on nano graphene oxide platelets



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ARTICLE INFO

Article history:

Received 18 March 2015

Received in revised form

15 May 2015

Accepted 20 May 2015

Available online 12 June 2015

Keywords:

Conducting polymer

Polypyrrole

NMR

Atomic force microscopy

Transmission electron microscopy

Polymerization kinetics

ABSTRACT

Oxidative polymerization of pyrrole on the surface of platelets of graphene oxide (GO) was demonstrated to generate polypyrrole/GO (PPy/GO) hybrid assemblies. The polymerization reactions were performed in GO acid dispersions using ammonium persulfate (APS) as an oxidant. Model kinetic reactions were carried out by ¹H NMR spectroscopy with APS at low temperatures. Evidence was found for an increase in the rate of polymerization of pyrrole in the presence of GO. IR and ESCA results indicate that the neutralization of the COOH groups on the GO may be due to interaction with the PPy. The morphology of PPy/GO assemblies analyzed by AFM revealed spherical particles of PPy agglomerated on the surface of GO platelets. Furthermore, TEM analysis indicated that polymerization of pyrrole occurred on both the surface of the GO and in between the GO layers.

This type of synthesis could offer an approach to the generation of new solid hybrids and allow systematic changes of their physical properties.

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1. Introduction

Polypyrrole (PPy) has remained an attractive target for the generation of nanostructured conductive materials with applications as antistatic coatings, chemical sensors, and molecular memory devices.

PPy is typically obtained by the polymerization of pyrrole initiated with strong chemical oxidants [1–11]. A variety of methods have been employed to synthesize nanostructures of PPy including the use of V₂O₅ nano-seeds, cationic surfactants or the application of hard templating techniques [12–15].

The direct formation of conductive polymer structures onto different surfaces has been limited to few investigations. For example, a solution-based method was used to grow transparent films of nanofibers of polyaniline, polythiophene and polythiophene derivatives on various substrates [16]. *In situ* polymerization of pyrrole onto printed circuit boards using a FeCl₃/5-sulfosalicylic acid oxidant complex was reported to produce uniform PPy films with good electrical conductivity [17].

Previously, we reported the electropolymerization of *N*-substituted PPy and its reactions with amino-substituted DNA

sequences [18], and the formation of PPy nanospheres by *in situ* polymerization of pyrrole in water soluble polymer templates [19]. We also investigated the chemical polymerization of pyrrole on polyimide (PI) films in the presence of FeCl₃ as oxidant and dopant resulting in conductive PPy nanospheres that increased the electrical conductivity of the surface of the PI film [20].

In recent years, graphene and its derivative GO have been the subject of several studies due to their electrical, mechanical strength and thermal attributes [21–27]. GO is obtained from stacked graphite oxide structures which are exfoliated into monolayers of few-layered stacks. According to the well-accepted Lerf–Klinowski model [28], GO platelets possess reactive carbonyl and carboxylic groups at their edges and epoxy and hydroxyl groups on the basal planes. A range of reactions involving the carboxylic groups have been carried out with small molecules including porphyrins and fullerenes [29]. The attachment of polymers to GO platelets by grafting onto or grafting-from approaches have been described also [30]. Several approaches have been reported for the preparation of PPy/graphene and PPy/GO composites for different applications with particular focus on electrochemical properties [31–33]. In an example, PPy/GO composites were prepared via *in situ* polymerization of pyrrole in GO dispersions with ferric chloride catalyst, followed by chemical reduction using hydrazine monohydrate [34]. In another study, graphene oxide/pyrrole-formaldehyde hydrogels were obtained by *in situ* non-

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catalyzed polymerization of pyrrole and formaldehyde in the presence of GO sheets [35]. Polypyrrole/GO nanoribbon composites with high electrochemical capacitance were synthesized by *in situ* chemical oxidation polymerization of pyrrole in the presence of GO nanoribbons (derived from multi-walled carbon nanotubes) and cetyltrimethylammonium bromide surfactant [36]. Graphene-supported PPy nanoparticles were obtained via *in situ* polymerization in the presence of sodium dodecyl sulfonate, which served as both surfactant and dopant [37]. Sodium dodecyl benzene sulfonate (SDBS) intercalated-reduced GO/PPy nanocomposites resulting from the polymerization of pyrrole on SDBS interposed graphene were reported to exhibit good capacitance and stability performance [38]. Covalently assembled graphene/PPy foams were obtained also via a multistep route and tested for oil sorption properties [39].

In the present study, the chemical polymerization of pyrrole on GO platelets was carried out in solution at low temperature using ammonium persulfate (APS) as an oxidant. Our objective was to determine whether PPy can be *in situ* generated on the two dimensional (2D) structure of the GO. The resulting system consisting of high surface area GO/PPy assemblies could be potentially useful to create ultrathin, uniform and mechanically and thermally resistant coatings with adjustable conductive properties. The electrical conductivity of such systems could be further modified by the reduction of the GO component, which is presumed to restore the graphitic network of sp^2 bonds [40].

The kinetic of the polymerization in the presence of GO platelets was followed by ^1H NMR spectroscopy. This study provides preliminary evidence for an increase in the pyrrole reaction rate when the polymerization was performed in GO dispersions. The external structure of PPy/GO assemblies was examined by AFM and identified to exhibit a PPy cluster-type morphology in which the spherical particles agglomerated to form a “cauliflower-like” microstructure on the surface of GO platelets. This structure was distinctly present on the platelets and TEM revealed that the polymerization of pyrrole occurred not only on the surface of GO but also between the GO layers. This suggests the participation of the carboxylic acid groups in the polymerization reaction, since no additional dopant was used.

2. Experimental

2.1. Materials

All reagents were obtained from Sigma–Aldrich Chemical Co. and used as received unless otherwise indicated. Pyrrole was distilled under vacuum immediately prior to use. Ammonium persulfate $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$ was used as received. Solutions of GO in different concentrations were obtained from Angstrom Materials Inc., 1240 McCook Avenue, Dayton, OH 45342, described as Nano Graphene Oxide Platelets/Water Suspensions with characteristics shown in Table 1.

2.2. Methods

2.2.1. Polymerization of pyrrole in aqueous dispersions of GO

The polymerization of pyrrole was performed in the presence of the GO platelets and APS without an additional acid dopant. Typical

polymerization reactions were carried out as follows. APS (0.45 g, 0.001982 mol) was dissolved in the minimum amount (0.56–0.6 mL) of deionized water and cooled in ice for 3 h before use. An amount of 20 mL of the dispersion (0.5%) of GO in water was weighed out into a 50 mL three-necked flask. To this, 0.3 g (0.004472 mol) of pyrrole monomer was added with constant magnetic stirring. The contents of the flask were cooled to 0 °C in an ice bath and a thermocouple was used to measure any fluctuations in temperature. The apparatus was flushed with nitrogen throughout the experiment as a safety precaution. The flask was also connected to a condenser with a constant flow of recirculated water and ethylene glycol. The cold APS solution was added dropwise over a period of 3 min. The reaction mixture turned darker and became more viscous immediately. In some cases, there was a small temperature increase, but usually, the reaction set-up allowed for the temperature to remain close to the desired 0 °C. The reaction mixture was left stirring magnetically for 3 h before adding deionized water to a total volume of 100 mL. This gave a uniform aqueous dispersion of PPy/GO.

Attempts were made to increase the percentage solids of these dispersions. In these cases, solutions with higher GO solids were used for the reaction. However, the resulting products were not as easily dispersed due to the degree to which agglomeration of the particles occurred. The lower oxygen content of these samples also needs to be considered, since it is thought to be due to the carboxylic groups on the GO interacting with the N–H groups on the PPy that these reactions were successful. As an example, 100 g of N002-PDR was weighed out into a 200 mL three-necked flask and 1.5 g (0.02236 mol) of pyrrole was added whilst stirring and cooling. At the same time, a solution of 2.25 g (0.00986 mol) of APS in the minimum amount (2.82–2.9 mL) of deionized water was made up and cooled to 0 °C for about 3 h before use. This was added dropwise to the flask with constant stirring at a temperature of 0 °C. As the reaction proceeded, a very small change in temperature was observed, from 0 °C to 1.2 °C. The viscous black mixture was left stirring for 3 h to ensure the completion of the reaction.

Using the N008-P-(40) solution with higher solids, the same procedure was followed. In this case the temperature increase after the addition of the APS initiator was 1.6 °C. The experiment was repeated using a larger amount of monomer and initiator (in order to match the optimum molar ratio that had been determined in previous similar experiments). The GO solution (100 g) was weighed out into a 200 mL three-necked flask and 15 g (0.2236 mol) of pyrrole was added whilst stirring and cooling. At the same time, a solution of 22.5 g (0.0986 mol) of APS in the minimum amount (28.2–29 mL) of water was made and cooled to 0 °C for about 3 h before use. This was added drop wise to the flask with constant stirring at 0 °C.

GO (N008-N) (25 g) was weighed out into two three-necked flasks and the same general method was followed again; this time using 0.375 g (0.00559 mol) of pyrrole and 0.5625 g (0.00246 mol) of APS and 7.5 g (0.1118 mol) of pyrrole and 11.25 g (0.0493 mol) of APS.

The product from the polymerizations using the GO (N002-PS) sample was diluted using different amounts of deionized water in order to obtain the best dispersion and conductivity. The resulting reaction mixture was blended with 0, 8, 16, 24, 32, 40, 48, 56, 64,

Table 1
Characteristics of water suspensions of GO platelets.

Sample	GO (%)	Mean x–y dimensions (μm)	Avg. thickness (μm)	Oxygen (%)	Surface area (m ² /gm)
N002-PS	0.5	<1	1.0–1.2	≤46	NA
N002-PDR	0.5	≤10	<1	≤2.1	400–800
N008-P-(40)	5	≤44	50–100	≤1.4	≤110
N008-N	10	≤5	50–100	≤0.80	≤13

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