Graphene/polypyrrole nanofiber prepared by simple one step green method for electrochemical supercapacitors

Sima Pourbeyram⁎, Parinaz Kheyri
Department of Chemistry, Payame Noor University, PO Box 19395-3697 Tehran, Iran

ARTICLE INFO

Keywords:
Graphene
Polypyrrole
Nanofiber
Green method
Supercapacitors

ABSTRACT

In this work a simple green method has been developed to synthesize polypyrrole/graphene nanofiber (green-ppy/G) based on graphene oxide and pyrrole direct interaction without using reducing agent, oxidative agent, surfactant and organic solvent. The synthesis procedure was simple, inexpensive and eco-friendly. Morphology and structure of the synthesized nanocomposites was discussed by XRD, SEM, TEM and CV techniques. XRD pattern revealed that the resulting polypyrrole was not amorphous and the graphene oxide sheets improved the crystalline structure of the obtained polymer. SEM image looked like a very thin layer drawn over the underlay and implied that the ppy has been covered on the surface of graphene sheets. In the TEM image of the nanocomposite the nanofibers of ppy attached to the graphene layer were clearly seen. A maximum capacitance value of 480 F g⁻¹ was obtained by cyclic voltammetry at scan rate 5 mV s⁻¹ in 1 M NaCl solution. At the current density of 100 mA cm⁻² even after 1000 charge-discharge cycles on the green-ppy/G-PGE 94% of the initial capacitance remained. According to the noticeable electrochemical properties, the green-ppy/G-PGE has a very high potential for the design of supercapacitors.

1. Introduction

Supercapacitors possess much higher capacitances than those achievable with normal capacitors and can operate at substantially higher specific power than batteries [1]. In general, the supercapacitors can be classified into two categories: (i) Electrical double-layer capacitors; with electrodes made from carbonaceous materials. In this category, power density is generally high but the capacitance is poor. (ii) Pseudocapacitors; with electrodes made based on the transition metal oxides/hydroxides, or conductive polymers. In this category, capacitance is high but cycling stability is low because of low conductivity of the used materials [2]. In order to exploit the merits of both categories, the most effective outcome is expected from the incorporation of carbonaceous materials and metal oxides/hydroxides, or conductive polymers [3–5]. Supercapacitor electrodes and apparatuses that employ conducting polymers, are imagined to association the gap between existing carbon-based supercapacitors and batteries to form units of intermediate specific energy [6]. Graphene, monolayers of carbon atoms, has interesting properties such as big specific surface area (up to 2600 m² g⁻¹), extremely high electronic conductivity (7200 S m⁻¹), and superior mechanical strength (tensile modulus up to 35 GPa) has been extensively explored for nano-structure electrode materials in electrochemical supercapacitors [7]. It has been experimentally proved that, by importing graphene into a polymer matrix the electrical and mechanical properties of the neat polymer matrix could significantly improve [8]. Different specific morphologies of graphene/conductive polymer nanocomposites were prepared [9]. Polypyrrole (ppy) is one of the most popular conductive polymers that are extensively applied in energy storage devices due to its excellent energy storage ability, high conductivity, easy synthetic procedure, cost-effectiveness, and environmental stability [10,11]. In literature, G/ppy nanocomposite is mostly made by chemical polymerization of the pyrrole monomer using oxidants and surfactants in the presence of graphene, graphene oxide or functional graphene [8,9,11–14]. G/ppy was also synthesized by electro-polymerization of the pyrrole monomer on the electrode modified with graphene or graphene oxide [15] or electroreduction of graphene of the ppy/GO suspension [16].

In the present study, we reported a simple one step procedure for the construction of high-conductive ppy/G nanocomposite by in situ oxidative polymerization of pyrrole using graphene oxide both as an oxidant and as a dopant and as a support [17]. Mutually, with the obtained reduced graphene oxide the conductivity and dispersity of the prepared ppy/G nanocomposite was improved. Given that in this synthetic approach reducing agents such as sodium borohydride or hydrazine hydrate, oxidative agent such as ammonium peroxodisulfate, surfactants, as well as organic solvents were not used, it can be said that...
a green synthesis method has been developed. The morphology and structure of synthesized nanocomposites was discussed by SEM, TEM, XRD and CV techniques. Charge storage properties of the prepared nanocomposite were also described.

2. Experimental

2.1. Reagents

Graphite powder, hydrogen peroxide, pyrrole, cetyltrimethylammonium bromide (CTAB), potassium permanganate, phosphoric acid, sulfuric acid, ammonium persulfate (APS), hydrazine hydrate and other materials used were all analytical grade obtained from Sigma-Aldrich (Chemical Co., St. Louis, US). The used solutions were prepared with double distilled water.

2.2. Synthesis of nanocomposites

2.2.1. Synthesis of green-ppy/G

GO was synthesized by the improved Hummer method [18]. GO dispersion (1 mg mL\(^{-1}\)) was prepared by adding 100 mg of GO into 100.0 mL of the distilled water and then ultrasonication for 30 min. the \( \text{pH} \) was adjusted to 1.0 by addition of concentrated HCl under ultrasonication. Then 0.5 mL pyrrole was added into the reaction system under ultrasonication for 30 min, and then the reaction system was kept at 4 \(^\circ\)C for 24 h. Essentially, the in-situ polymerization of pyrrole into polypyrrole and the reduction of GO to G occur promptly at the same time after the adding the pyrrole monomers, as the color of the solution was changed from creamy to clear black. According to the ratio between pyrrole and GO, green-ppy/G(1) and green-ppy/G(2) were obtained in which 0.5 or 1 mL pyrrole was added into 100 mL of 1 mg mL\(^{-1}\) GO dispersion, respectively.

2.2.2. Synthesis of chem-ppy/G

Reduced graphene oxide (G) was prepared according to the literature [19]. 100 mg of G and 2 g CTAB were dispersed in 100 mL of 0.1 M HCl aqueous solution under ultrasonication for 30 min. Then 0.5 mL pyrrole and 0.1 g APS were added into the reaction system under ultrasonication. After 30 min ultrasonication the reaction system was kept at 4 \(^\circ\)C for 24 h. The black product was washed two times with ethanol and three times with water, and dried in a vacuum oven at 60 \(^\circ\)C over night.

2.3. Instrumentation

Electrochemical studies were done on Potentiostat/Galvanostat Autolab30 in a conventional three-electrode glass cell, comprising pencil graphite electrode (PGE), Pt rod and Ag/AgCl (3 M KCl) as working, auxiliary and reference electrodes, respectively. PGE was the commercial pencil lead (Tombow Co., Ltd. Japan) with a diameter of 0.5 mm that was implanted into a teflon tube revealing 0.5 cm of its tip (\( A = 0.15 \text{ cm}^2 \)). Electrical contact was done through joining a metallic wire to the unprotected reverse side of the PGE. The structure of the nanocomposites was examined by scanning electron microscope (SEM, HITACHI 54160) and TEM (JEOL, Tokyo, Japan). Powder X-ray diffraction (XRD) data were gained with a D8-ADVANCE diffractometer (Bruker AXS, Germany) using CuKa radiation with a secondary graphite monochromator.

3. Results and discussion

3.1. X-ray powder diffraction (XRD)

The crystalline nature of the prepared materials was studied by the XRD as shown in Fig. 1. The diffration pattern of GO at 2\( \theta \) = 10.1\(^\circ\) indicating a large distance between the sheets of GO because of the existing of oxygen containing functional groups on the surface and in the edges of GO. In the XRD pattern of G the characteristic peak at 10.1\(^\circ\) had a shift to around 25\(^\circ\) indicating the hexagonal structure of graphene, confirming the conversion of GO to G [20]. In the case of green-ppy/G(1), in comparison with the GO, the height of peak at around 10.1\(^\circ\) was decreased and shifted to 8.7\(^\circ\) and the new broad peak around 25\(^\circ\) was appeared. Decreasing the height of the peak at around 10\(^\circ\) can be due to partial reduction of GO to G and shifting the peak can be due to the increasing intersheet because of intercalation of polymer between adjacent graphene oxide layers in the nanocomposites [21,22]. Indeed, the negative charge functional groups of GO, acting as anchor...