Materials Chemistry and Physics 128 (2011) 283–290

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Preparation and optical/electrical/electrochemical properties of expanded graphite-filled polypyrrole nanocomposite

Surajit Konwer, Jatindranath Maiti, Swapan K. Dolui*

Department of Chemical Sciences, Tezpur University, Napaam, Tezpur, Assam 784028, India

ARTICLE INFO

Article history:
Received 9 November 2010
Received in revised form 3 March 2011
Accepted 7 March 2011

Keywords:
Semiconductors
Chemical techniques
Thermogravimetric analysis (TGA)
Electrical properties

ABSTRACT

Expanded graphite filled polypyrrole (PPy/EG) conducting composites were prepared by in situ polymerization of pyrrole by the addition of expanded graphite in various proportions (0.25%, 0.50% and 1.0%). The synthesized samples were characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), ultraviolet–visible absorption (UV–vis), X-ray diffraction (XRD) and electrical conductivity measurements. FTIR spectroscopy revealed the interaction between expanded graphite and polypyrrole (PPy). PPy/EG composites showed crystalline nature with rhombohedral structure. The band gaps of pure PPy and PPy/EG composites were determined by UV–vis absorption spectrophotometry and cyclic voltammetry. The electrical conductivities of the composites were enhanced dramatically to 110.04 $\mathrm{S\,cm^{-1}}$ compared to pure PPy. The composites also showed excellent electrochemical reversibility at the scan rate of 0.1 $\mathrm{V\,s^{-1}}$ and maximum reversible electrochemical response intaking charge capacity almost unchanged even up to 125th cycles.

1. Introduction

Conducting polymer composites with various conductive fillers have recently attracted much attention. They can exhibit significant levels of electrical conductivity suitable for use in electronic devices, rechargeable batteries, functional electrodes, electrochromic devices, sensors, conductive inks and so on [1–6]. Virgin conducting polymers like polyaniline, polypyrrole (PPy), polythiophene, etc. have poor processability and the lack of essential mechanical properties. To overcome these drawbacks, some fillers are incorporated into these polymer matrices to form composite materials [7–10].

PPy is one of the most studied conducting polymers because of its rather straightforward preparation methods. PPy materials are reasonably stable in air, and possess good electrochemical properties and thermal stability. PPy exhibits a wide range of volume conductivities ($10^{-3}\,\mathrm{S\,cm^{-1}} < \sigma < 100\,\mathrm{S\,cm^{-1}}$) depending on the functionality and substitution pattern of the monomer and the nature of the counter ion or dopant [11,12]. PPy shows its capability to store electrical charges. The stored electrical charges can be recovered upon demand, for that reason PPy can be considered as a good candidate of super-capacitors [13–15].

Graphite, which is naturally abundant and low cost, has widely been used as electronically conducting filler in preparing conducting polymer composites [16,17]. In most of the cases relatively large quantities of graphite are required to reach a critical percolation value. Large amount of graphite concentration is always leading to the poor mechanical property of the composite materials [18]. To overcome this problem the concept of expanded graphite (EG) has been extensively employed [19–25]. EG is produced from graphite flakes intercalated with concentrated H_2SO_4 followed by rapid thermal treatment which could lead expansion up to several hundred times of the original volume. This expansion splits up the graphite sheet into nanoplates with a very high aspect ratio [26]. The graphite intercalation compounds may provide a possible source for nanocomposite formation with polymers [27,28]. It is also well known that expanded graphite (EG) is much lighter, and has a higher specific surface area than carbon powder and carbon nanotubes [29].

In this paper, we have showed the effort of expanded graphite (EG) on the electrical and electrochemical behaviour of the polypyrrole/expanded graphite (PPy/EG) nanocomposite. The EG has been prepared by the standard method and this modified EG has been used for preparation of highly conducting PPy/EG nanocomposite. To the best of our knowledge, the synthesis of PPy/EG functional composites and study of their electrical and electrochemical behaviour have not been reported so far. The concept of optical and electrochemical band gap of the PPy/EG nanocomposite and comparison of both the techniques was studied thoroughly. Compared to the previous work of PPy/G composite [30], we have got the dramatic enhancement of the electrical conductivity, better electrochemical and optical behaviour of this modified nanocomposite.

---

* Corresponding author. Fax: +91 03712 267006; mobile: +91 9957198489.
E-mail address: dolui@tezu.ernet.in (S.K. Dolui).

0254-0584/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.matchemphys.2011.03.013

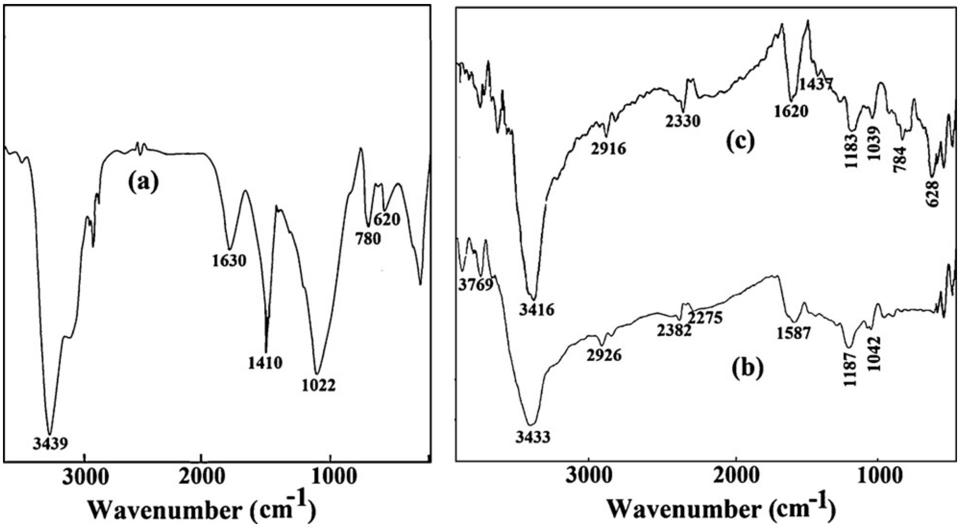

Fig. 1. FTIR spectra of (a) expanded graphite, (b) polypyrrole and (c) PPy/EG (1%) composite.

2. Experimental

2.1. Materials

Pyrrole was obtained from Aldrich Co. and used without further purification. The natural graphite flake of size −50 +100 BS mesh, hydrochloric acid (HCl), sulphuric acid (H_2SO_4), nitric acid (HNO_3) and anhydrous ferric chloride ($FeCl_3$) were obtained from Merck and used as received. The solvent methanol (CH_3OH) was distilled before used. Acetonitrile (CH_3CN) was obtained from Merck and purified by standard methods. Lithium perchlorate ($LiClO_4$) was obtained from Fluka and used as received. For all purposes double distilled water was used.

2.2. Preparation of expanded graphite

EG was prepared by following the chemical oxidation method described elsewhere [31]. The natural graphite flake was dried at 348 K in vacuum oven for 10 h to remove the moisture. It was then mixed with concentrated H_2SO_4 and HNO_3 in a volume ratio 3:1 for 10–15 h to form graphite intercalated compound (GIC) where HNO_3 served as an oxidizer and H_2SO_4 as an intercalant. The mixture was stirred to get the uniform intercalation of each flake. After filtration the flakes were washed with distilled water until the pH level of the solution reached up to 7 (neutral). After washing, the flakes were dried at temperature 333 K in a vacuum oven for 5 h to remove the solvents and water molecule. GIC was rapidly expanded in between temperature 1073 and 1173 K within 10–20 s in muffle furnace to form EG.

2.3. Preparation of polypyrrole

The polymer has been prepared using a standard procedure described elsewhere [32]. In a three-necked round-bottomed flask (250 ml) equipped with a thermometer, a nitrogen inlet, and a dropping funnel, 2.5 M $FeCl_3$, was taken in 20 ml methanol and pyrrole (pyrrole/$FeCl_3$ = 2.33:1 molar ratio) is then added drop wise with stirring for 6 h. The solution was cooled to 273–278 K by salt/ice mixture. The polymer so obtained is filtered, washed with distilled water followed by methanol until the solution became colourless and dried in vacuum.

2.4. Preparation of polypyrrole/expanded graphite composites

EG powders were washed with a solution of NaOH (2 mol L^{-1}) at 313 K for 2 h to improve its surface conformation. In a three-necked round-bottomed flask (250 ml) 2.5 M $FeCl_3$ was taken in 20 ml methanol and 0.25%, 0.50% and 1.0% EG particles (w/v) were also dispersed in methanol. The mixture was cooled (273–278 K) in a salt–ice mixture and sonicated for 1 h. Pyrrole 2.33:1 molar ratio (with 2.5 M $FeCl_3$) was then added slowly at the temperature range close to 273–278 K under vigorous stirring for 6 h. The polymer so obtained is filtered, washed with water and methanol until the solution became colourless and dried in vacuum.

3. Characterization

Fourier transform infrared spectroscopy (FTIR) was used to record FTIR spectra by Impact 410, Nicolet, USA, using KBr pellets. The ultraviolet–visible (UV–vis) absorption spectroscopy of the samples in 1-methyl-2-pyrrolidon solvent was recorded using Shimadzu UV-2550 UV–vis spectrophotometer in the range of 300–800 nm. The surface morphology of the composites was observed by scanning electron microscope (SEM) of model JSM-6390LV, JEOL, Japan. The surface of the sample was coated with platinum before SEM analysis. Transmission electron microscope (TEM) measurements were conducted on a PHILIPS CM 200 microscope at 200 kV. The TEM sample was prepared by dispensing a small amount of dry powder in ethanol. Then, one drop of the suspension was dropped on 300 mesh copper TEM grids covered with thin amorphous carbon films. To study the thermal degradation of the samples, thermogravimetric analysis (TGA) was performed using TG 50, Simadzu thermogravimetric analyser, Japan from temperature range 298 to 973 K with a heating rate of 283 K min^{-1} under the nitrogen flow rate of 30 ml min^{-1}. The X-ray diffraction (XRD) study was carried out at room temperature (ca. 298 K) on Rigaku X-ray diffractometer with Cu $K\alpha$ radiation (λ = 0.15418 nm) at 30 kV and 15 mA using a scanning rate of 0.050° s^{-1} in the range of $2\theta = (10–70)^{\circ}$. Using a compression-moulding machine, pellets of composite samples were made. High pressure was applied (1.5–2 tonnes) to the sample to get hard round shaped pellet (1.5 cm diameter, 2 mm thickness), which was used to measure the electrical conductivity. The DC electrical conductivity of PPy and PPy/EG composites was measured using four probe technique in the temperature range of $300\,K \le T \le 413\,K$. The electrical conductivity of the composite was calculated by using the following equation [33]

$$\rho = \frac{V}{I} 2\pi S, \tag{1}$$

where ρ is the resistivity of the sample, V is the applied voltage, I is the measured current through the sample and S is the distance between probes. Current–voltage (I–V) characteristics of prepared samples were recorded by Keithley 2400 source meter at the room temperature in the frequency range 102–106 Hz and at the scan rate 0.1 V s^{-1}. The electrochemical behaviour of the prepared samples was studied using Sycopel AEW2-10 cyclic voltammeter.

4. Results and discussion

The EG filled PPy composites were prepared by in situ oxidative polymerization technique. The monomer pyrrole may get adsorbed on the surface of the dispersed expanded graphite sheets. This adsorbed pyrrole on expanded graphite as well as remaining free pyrrole gets polymerized in the presence of oxidizing agent $FeCl_3$ to yield PPy/EG composites.