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Electrical and electrochemical properties of the expanded graphite filled polythiophene nanocomposites

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Charge capacity.

Abstract. In this study, graphite nanosheets were prepared by powdering expanded graphite with sonication in aqueous alcoholic solution. A facile process for the synthesis of expanded graphite filled polythiophene (PTh/EG) conducting composites was developed. The nanocomposites were fabricated via chemical polymerization of thiophene monomer in presence of expanded graphite nanosheets in various proportions. Nanocomposites were characterized by Fourier transform infrared spectroscopy (FT-IR), Scanning Electron Microscopy (SEM), Scanning Tunneling Microscopy (STM), X-Ray Diffraction (XRD), Cyclic Voltammetry (CV), and electrical conductivity measurements. SEM observations on cross-sections of EG were performed to understand the microstructure occurrence during interpenetration. Electrical conductivity of PTh/EG was notably enhanced by introduction of EG. The composite exhibited good electrical conductivity of 125 Scm^{-1} when the EG content was 0.5 wt %. CV is the most commonly used technique for evaluation of electrochemical properties of a film on the electrode surface. The composites also showed excellent electrochemical reversibility at the scan rate of 50 mVs^{-1} and maximum reversible electrochemical response was almost unchanged even up to 100 cycles. The stability of oxidation and reduction peaks of nanocomposites in cyclic voltammetry in up to 100 cycles shows that the obtained nanocomposites are very appropriate to be used in rechargeable batteries.

1. Introduction

Conducting composites have been extensively studied due to their diverse applications in electronics and antistatic devices, magnetic shielding [1], rechargeable batteries [2], thermistors [3], sensors [4], and supercapacitor [5].

Conjugated polymer semiconductors are highly desirable in electronic and optoelectronic fields for they provide easy treat, low cost, high light absorption, high electronic conductivity, and large area materials. Among them, polythiophene (PTh) [6-8] and polythiophene derivatives have drawn great attentions for large area applications, for instance in Polymer Solar Cells (PSCs) [9]. Moreover, the multifunctional property enhancements made possible with nanocomposites may create new applications of polymers [10].

Graphite nanosheets, obtained by delamination of expanded graphite, with excellent conductivity, have been successfully incorporated into polymer matrix via oxidative polymerization [11-13]. Functionalized Exfoliated graphite has a good bonding with polymers. Polymer can easily propagate along the surface of functionalized exfoliated graphite [14]. Therefore, expanded graphite or exfoliated graphite has been used for making conductive polymer composites. The nanosheets showed to be composed of thinner sheets and could be further intercalated by polymer

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molecules. The nanosheets are excellent conducting fillers for making conducting nanocomposites with polymer. It is observed that the electrical resistivity of exfoliated graphite filled polymers decreases with increasing exfoliated graphite concentration. Discovery of graphene with its combination of extraordinary physical properties and ability to be dispersed in various polymer matrices has created a new class of polymer nanocomposites [10]. Surface modification of graphene is an essential step for obtaining a molecular level dispersion of individual graphene in a polymer matrix.

More recently, fabrication of conducting polymer/graphite nanocomposites in presence of EG via an in-situ polymerization method has attracted great interest [15-18]. Owing to the high aspect ratio (width-to-thickness) of EG sheets, the resulting nanocomposites exhibited superior properties when compared with conventional unexpanded graphite-filled polymer composites. Because of its relatively low cost, high aspect ratio, and high anisotropy of physical properties in the plane and perpendicular to the planes, Expanded Graphite (EG) is regarded as a good filler material for preparation of conductive polymer composites. The promising mechanical, electrical, optical, thermal, and magnetic properties of graphene have led to creation of a new and exciting 'laboratory' for the study of fundamental sciences. A few studies have focused on nanocomposites based on EG and conducting polymers, for instance polyaniline and polypyrrole. However, to the best of our knowledge, the synthesis of Polythiophene/expanded graphite nanocomposites and study of their electrical and electrochemical behavior have not been reported so far. This study demonstrates preparation and characterization of the PTh/EG new nanocomposite. In addition, electrical and electrochemical properties of the nanocomposite have been investigated. Also, stability of oxidation and reduction peaks of nanocomposites by cyclic voltammetry has been studied.

2. Experimental details

2.1. Materials

Thiophene was obtained from Aldrich Co. and purified by a standard method (thiophene washed successively with 7M HCl, 4M NaOH, and distillated water, dried with $CaCl_2$ and fractionally distillated) [19]. Natural graphite flake with 10 μm of size, 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 (from Merck) was distilled before use. Acetonitrile (from Merck) was distilled over P_2O_5 (from Merck) and used as a solvent directly. Lithium perchlorate ($LiClO_4$) was obtained from Fluka and used as received. For all purposes, double distilled water was used.

2.2. Instruments

Infrared spectra were recorded on a Shimadzu FTIR-8400S, Japan. X-Ray Diffraction (XRD) experiments were performed using a Rigaku X-Ray Diffractometer, Japan. SEM images and EDAX spectra were obtained by a Field Emission Scanning Electron Microscope (FE-SEM) (Hitachi Model S-4700, operating voltage; 15 kV, Japan). Morphology of the films was investigated using a Scanning Tunneling Microscopy (STM) Nano system Pars (SS-1), Iran. STM images were obtained in a constant current mode using Pt/Ir tips, previously tested on an HOPG (highly ordered pyrolytic graphite) standard sample in order to verify their suitability for topographic performances. The STM measurements were performed at a tunneling current of 0.1 nA and at bias of +0.1 V relative to the tip, and characterization was performed in air and at room temperature. Cyclic voltammetry Model (PARSTAT2273 potentiostat-galvanostat (Princeton Applied Research, USA)) and four-point probe instrument (Jandel Engineering, model CMT-SR1060N, Japan) were used for electrochemical methods and conductivity measurements, respectively.

2.3. Preparation of expanded graphite

Expanded Graphite was prepared by following the chemical oxidation method described elsewhere [18]. Natural flake graphite was first dried in a vacuum oven for 24 h at 120°C. Then, a mixture of concentrated sulfuric and nitric acids (ratio 3:1, v/v) was slowly added to a glass flask containing graphite flakes with vigorous stirring. After 36 h of reaction, the acid-treated graphite flake was filtered and washed with deionized water until pH level of the solution reached 6.6. After being dried at 100°C for 72 h, the resulting graphite intercalation compound was subjected to a thermal shock at 1050°C for 30 seconds in a muffle furnace to form exfoliated (expanded) graphite.

2.4. Preparation of graphite nanosheets

Expanded graphite (1 g) was placed in a mixed solution (400 mL) of alcohol and distilled water with 68:32 v/v ratio for 24 h. The mixture was then subjected to ultrasonic irradiation with a power of 400 watt for 24 h. After 24 h of sonication, exfoliated graphite particles were effectively fragmented into foliated (nanosheets) graphite. The foliated graphite dispersion was then filtered and dried at 100°C to remove residual solvents. The as-prepared foliated graphite powder will be called graphite nanosheets (G) throughout the paper.

2.5. Preparation of polythiophene

The polymer has been prepared using a standard procedure described elsewhere [17]. $FeCl_3$ (2.5 M) in methanol (20 ml) was placed inside a three-neck round-bottom flask (250 ml) equipped with thermometer, nitrogen inlet, and dropping funnel. The solution was cooled to 273-278 K by salt/ice mixture and then thiophene (thiophene/$FeCl_3$=1:2.33 molar ratio) was added dropwise with stirring for 6 h. The polymer so obtained was filtered, washed with distilled water followed by methanol until the solution became colorless and dried in vacuum.

2.6. Preparation of polythiophene/expanded graphite nanocomposites

Expanded graphite powders were washed with a 2 M NaOH solution at 313 K for 2 h to improve their surface conformation. In a three-neck round-bottom flask (250 ml), 2.5 M $FeCl_3$ was taken in 20 ml methanol and 0.25% or 0.50% EG particles (w/v (g/ml)) were also dispersed in methanol. The mixture was cooled (273-278 K) in a salt/ice mixture and sonicated for 1 h. Thiophene (molar ratio to $FeCl_3$: 1:2.33) was added slowly in the temperature range close to 273-278 K under vigorous stirring for 6 h. The polymers (PTh/EG 0.25% and PTh/EG 0.5%) so obtained were filtered, washed with water and methanol until the solution became colorless and dried in vacuum.

2.7. Electrochemical method and conductivity measurements

The electrochemical method was carried out using a digital potentiostat/galvanostat. This technique is composed of a graphite electrode disk (4 mm φ diameter) covered with polythiophene and nanocomposites as the working electrode in cyclic voltammetry experiments. In each case, a platinum wire was used as the counter electrode and a glass Ag/AgCl (Azar Electrode Company, Iran) was employed as the reference electrode (Figure 1). Prior to CV experiments, the purge removes oxygen by purging argon gas through the solution. The blanketing function is to maintain an inert atmosphere above the sample to keep oxygen from re-entering the sample solution.

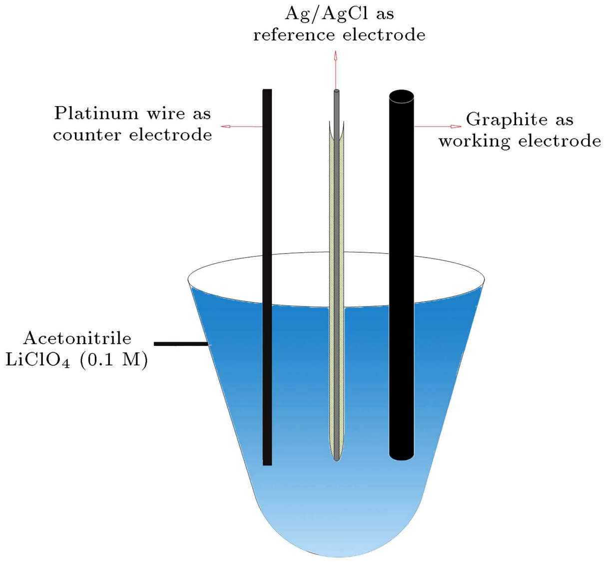


Figure 1. Schematics of the electrochemical cell.

The material was suspended using an Ultrasound bath. The suspension was slowly poured on a vertically placed electrode, with its surface horizontally positioned, and the *N*-methyl pyrrolidone solvent was allowed to evaporate naturally. After two days and complete vaporization of the solvent, the nanocomposite was casted on the electrode surface. Finally electrodes were washed with acetonitrile and placed in electrolyte solution. All cyclic voltammetry studies were performed in a conventional three-electrode cell with working electrode coated with polythiophene or composite film. The electrolyte solution was 0.1 M $LiClO_4$ in acetonitrile.

Conductivity measurement results were obtained by four-probe instrument. The electrical conductivities of PTh and their composites were measured using four-probe instrument at ambient temperature employing the method on a pressed pellet. The pellets were obtained by subjecting the powder sample to a pressure of 30 MPa. By measuring the resistance three times for each pellet, reproducibility of the result was checked.

3. Results and discussion

3.1. Characterization of PTh/EG nanocomposites

The PTh/EG nanocomposites are synthesized via oxidative polymerization. Figure 2 represents a scheme of the synthesis of expanded graphite and PTh/EG nanocomposite. Solute thiophene may has been adsorbed on the surface of dispersed EG particles. This adsorbed thiophene on the EG and the remaining free thiophene got polymerized in the presence of oxidizing agent to yield the PTh/EG nanocomposite.

The surface morphology of expanded graphite, composites, and polythiophene was examined by scanning electron microscopy. SEM observations from cross-sections of expanded graphite were performed to understand the microstructure occurrence during interpenetration. Figure 3(a) and (b) show the SEM images of graphite before and after expanded graphite nanosheets, respectively. By imposing thermal shock, graphite sheets expanded and so graphite nanosheets were produced. It is clearly apparent that the expanded graphite worms have been completely torn into foliated, named graphite nanosheets.

Figure 3(c) and (d) present SEM images of nanocomposites. Treatment of EG with NaOH created negatively charged functional groups (such as carboxylic and hydroxyl) on its surface. On the other hand, via polymerization of thiophene in the presence of EG, firstly cations radicals of thiophene monomers

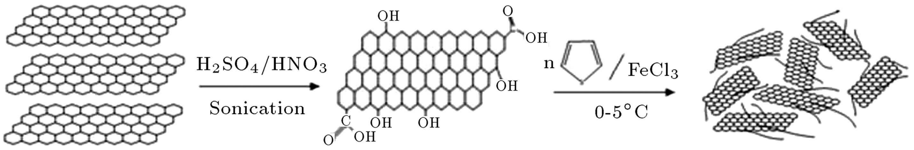


Figure 2. Schematic representation of the synthesis of PTh (oxidative polymerization process of thiophene by $FeCl_3$) on a graphite nanosheets surface.

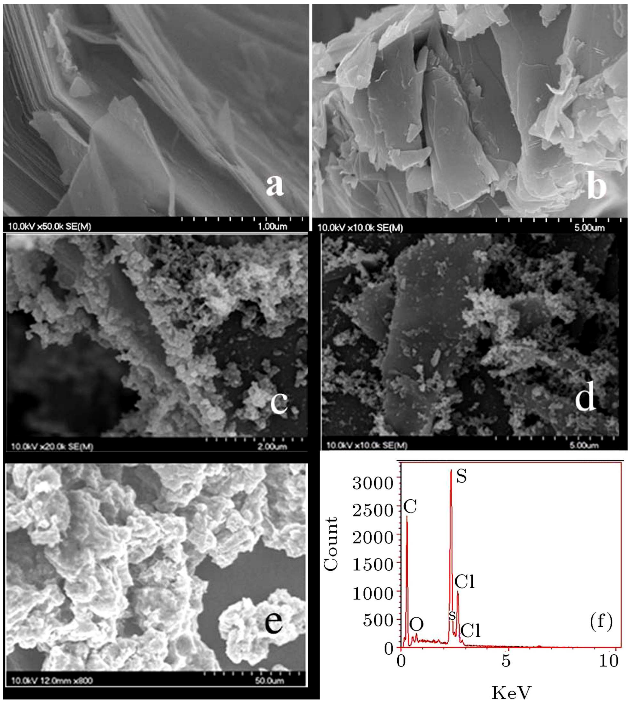
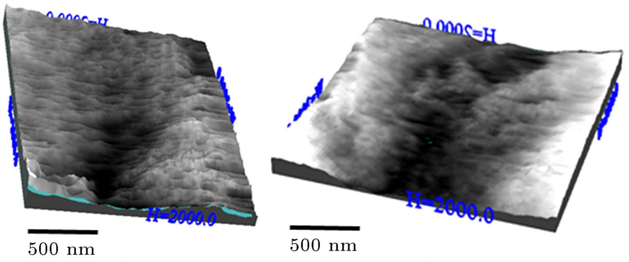


Figure 3. SEM images of a) graphite before expanded, b) expanded graphite, c) PTh/ EG 0.25% nanocomposite, d) PTh/ EG 0.5% nanocomposite, e) pure PTh, and f) analysis of the nanocomposite elements with EDAX.

are produced and the negative sites on the surface of EG act as anchor and adsorb positive charges of cations radicals and finally polymerization of polythiophene continues to process. The polymers are absorbed on the surface of EG, which gives the nanocomposites without distinguishing the individual phase, i.e. EG and polythiophene. There is no accumulation of polythiophene separated from nanosheets which is a good proof that functional groups on the surface of expanded graphite are the proper ambient for polymerization of polythiophene. This fact is very critical in polymerization of monomers. Also Figure 3(e) shows SEM image of pure polythiophene with amorphous structure.

Nanocomposites possess a significant electrical conductivity. So, typical morphology of nanosheets is shown in the STM images (Figure 4). As can be seen from Figure 4(a), expanded graphite layers are observable. Also Figure 4(b) shows the structure of nanocomposite (PTh/ EG 0.25%) where no separate growth of polythiophene is visible in this image.



(a) (b)

Figure 4. STM images of a) graphite nanosheets and b) PTh/EG 0.25% nanocomposite.

There is good correlation between SEM and STM images.

The EG sample exhibits broad peaks at $2\theta = 24$, 26.7°, 34, and 54.5 (Figure 5(a)). Figure 5(b) shows the XRD pattern of PTh/EG, a nanocomposite that is similar to X-ray pattern of EG. The image demonstrates that EG crystal structure stayed firm during the composite deposition. Also the characteristic peaks of PT ($2\theta = 26.73°$) can hardly be observed. Figure 4(c) shows the region of 2θ=23-28° in detail. As it is shown, this may be due to the adsorption and growth of polymer on the surface of EG sheets.

In FTIR spectrum of EG (Figure 6(a)), the peak at 1458 cm^{-1} is of the C-C-C symmetric stretching vibration. The peak at 1643 cm^{-1} is of the C=O stretching of ketone group. The broad absorption band at 3425 cm^{-1} indicates the O-H stretching vibration of phenolic or alcoholic functional groups present on the EG surface, whereas the band at 2924 cm^{-1} is due to the stretching of the C-H bonds [19]. However, some peaks are observed within a lower wave number range in between 400 and 800 cm^{-1}. In the course of treatment of natural graphite by strong acids, some of the carbon double bonds are oxidized, which leads to the formation of oxygen-containing functional (carboxylic and hydroxyl) groups on exfoliated graphite surface, that can facilitate the physical and chemical interactions with the functional groups of polymeric matrix [17].

The infrared absorption spectra of PTh/EG nanocomposite and pure polythiophene are shown in Figure 6(b) and (c). In PTh/EG nanocomposites, the absorption peaks were relatively similar to those of thiophene, except that the absorption bands assigned to C=C ring stretching of thiophene at 1590 cm^{-1} were shifted to 1625 cm^{-1} for the composites, which might

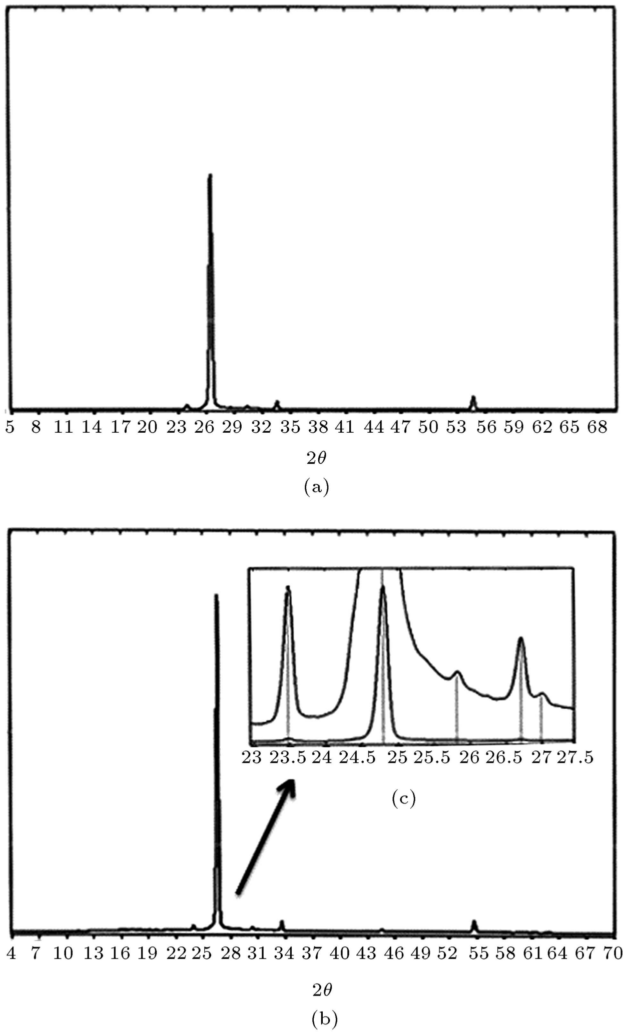


Figure 5. Presentation of the X-ray diffraction pattern of a) EG, b) PTh/EG 0.25% composites, and c) region 23-28 2θ in detail.

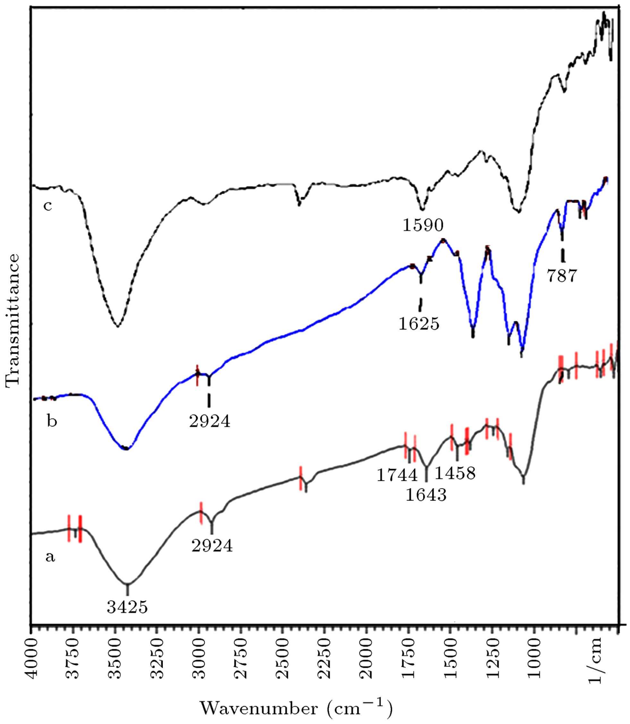


Figure 6. FT-IR spectra of a) EG, b) PTh/EG 0.25% nanocomposite, and c) pure polythiophene.

be ascribed to the conjugate effect between C=C of thiophene and surface of the EG layers [17]. The peak at 1136 cm^{-1} is due to C-C stretching [19].

3.2. DC electrical conductivity

One of the most important parameters of conducting polymers and of nanocomposites is their electrical conductivity. The conductivity of conductive polymers depends on the concentration and mobility of carriers. Mobile charge carriers in conducting polymers are called polarons and bipolarons. Density of these species is the function of oxidation (doping) level. As a conclusion, any enhancement in the order of molecules depending on the procedure of synthesis of conducting polymers will contribute to increase in mobility and electrical conductivity of carriers. We believe that this development in mobility and electrical conductivity leads to a more efficient function of electronic devices.

In order to investigate the electrical conductivity of obtained nanocomposites and compare their conductivity with polythiophene, we have used four-probe device. The results show that the conductivity of polythiophene is low without the graphite nanosheets. According to the X-ray study, the polymer structure is amorphous, without a regular order. It explains a low value of conductivity. The specific electrical conductivity for polythiophene film is 3.5×10^{-2} Scm^{-1}. Moreover, we have measured the electrical conductivity of nanocomposites pills by a four-point device. This measurement is performed to evaluate the presence of various amounts of nanosheets in the structure of nanocomposites. The results corroborate that as the amount of graphite nanosheets increases, the value of electrical conductivity increases too. The obtained electrical conductivity values for 0.25 and 0.5 percent of nanosheets are 45 Scm^{-1} and 125 Scm^{-1}, respectively.

In order to determine the elemental composition of prepared polythiophene and its corresponding nanocomposites with EG, EDAX analysis was performed and the resulting data is reported in Table 1. As can be seen in Table 1, nanocomposites at 0.25% and 0.5% of EG show rather higher carbon values because of the addition of EG as a carbon source in the source polythiophene. The results indicate that by increase in the amount of carbon as graphite, electrical conductivity also increases. Therefore, the higher carbon content in PTh/EG 0.5% compared to PTh/EG 0.25% can be regarded as the main reason behind the increased electrical conductivity. Also presence of oxygen, iron, and chlorine elements in polythiophene

Table 1. Elements analysis of polythiophene and its composites with EDAX.

Sample/ element	**PTh**	**PTh/EG (0.25%)**	**PTh/EG (0.5%)**
C	64.39	64.89	66.66
O	-	2.12	2.52
S	24.20	21.91	22.23
Cl	8.56	9.07	6.47
Fe	2.85	2.01	2.12

and its composites has its roots in the oxidized state of functionalized EG and counter ion of $FeCl^{4-}$ as dopant, respectively.

Therefore, increase in the fraction of nanosheets inside the composite results in a greater electrical conductivity since the specific conductivity of nanosheets is much higher than that of the polymer. Each of the calculated electrical conductivities is the average of five measurements for each pellet.

3.3. Evaluation of electrochemical behavior of polythiophene and its nanocomposites by cyclic voltammetry

Cyclic voltammetry is the most commonly used technique for evaluation of electrochemical properties of a film on the electrode surface. Due to the change of potential in the course of cyclic voltammetry, components of the film may be subjected to oxidation or reduction.

Figure 7(a) shows the cyclic voltammetry of polythiophene without graphite nanosheets. The shape of the measured CV curve for the pure PTh film was compared with those in literature [8,20]. As it is clear, showing an agreement with reported behavior, the oxidation and reduction potentials are 1.6 and 0.5 V, respectively.

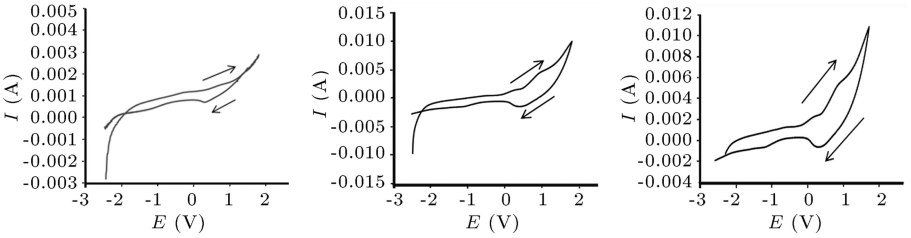
Then, cyclic voltammetry of PTh/EG composite layers was carried out. As it is depicted in Figure 7(b), the result of cyclic voltammetry for nanocomposites with 0.25 percent of graphite nanosheets is completely different from pure polythiophene results. As displacement of the oxidation and reduction peaks takes place, the oxidation and reduction potentials are shifted in the positive and negative direction by 1 V and 0.4 V, respectively. Figure 7(c) shows the cyclic voltammetry of polythiophene nanocomposites in the presence of 0.5 percent graphite nanosheets. The electrochemical behavior of these two composites is approximately similar.

3.4. Charge capacity

The area under CV peak is proportional to the redox charge passing within this wave, which provides information about the electrochemical properties of nanocomposites. The area under CV peak which was proportional to the redox charge passing was plotted. Integration (area under the plot) equals to potential (Volts) * current (mA) which is power (mW). This quantity divided by the scan rate (50 mV/s) is the charge (mC) transferred in the redox process. These nanocomposites may be feasible for polymer batteries owing to their specific properties. The use of cyclic voltammetry enabled us to evaluate the prospect of these materials for battery applications. Figure 8(a) shows the cyclic voltammetry of polythiophene in several cycles. Figure 8(b) and (c) show the cyclic voltammetry of polythiophene nanocomposites in presence of 0.25 and 0.5 percent graphite nanosheets. The stability of oxidation and reduction peaks of nanocomposites in cyclic voltammetry up to 100 cycles shows that the obtained nanocomposites are very appropriate to be used in rechargeable batteries [21,22]. As is evident from Figure 8(d), the electrode coated with PTh/EG 0.25% shows a rather satisfactory stability even after 100 charge/discharge cycles.

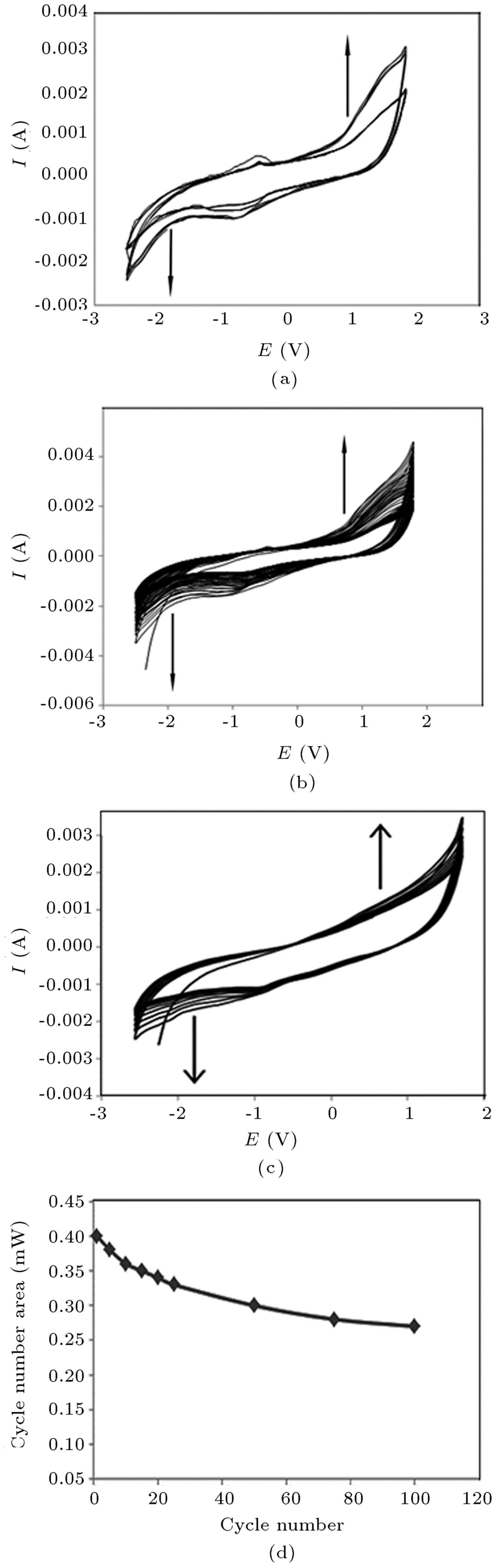
4. Conclusion

In this paper, the PTh/EG composites have been successfully synthesized by incorporation of EG via polymerization of thiophene in presence of dispersed EG. Nanocomposites were characterized by Fourier transform infrared spectroscopy (FT-IR), Scanning Electron Microscopy (SEM), Scanning Tunneling Microscopy (STM), and X-Ray Diffraction (XRD) which show the success in the nanocomposites' synthesis. The DC electrical conductivity of PTh/EG nanocomposites dramatically increases from 45 Scm^{-1} to 125 Scm^{-1} with increase in EG. The composite film shows favorable reversible electrochemical response, which retains



(a) (b) (c)

Figure 7. Cyclic voltammograms of a) polythiophene, b) PTh/EG 0.25%, and c) PTh/EG 0.5%.



(a)

(b)

(c)

(d)

Figure 8. Cyclic voltammograms of a) polythiophene, b) PTh/EG 0.25%, c) PTh/EG 0.5% up to 100th cycles, and d) cycle number area vs. cycle numbers for PTh/EG 0.25%.

its charge capacity even up to 100 cycles. Ultimately, all evaluations corroborate that these nanocomposites are capable to be used in rechargeable batteries and solar cells.

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