

Capacitance Properties of Electrochemically Synthesised Polybithiophene-Graphene Exfoliated Composite Films

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ABSTRACT: *The graphene (GR) has attracted intensive interest due to its two-dimensional and unique physical properties. In the present study, the graphene sheets were synthesized by electrochemical exfoliation of graphite in sulfuric acid solution. The polybithiophene-graphene (PbTh-GR) composite films deposited onto indium tin oxide substrate (ITO/PbTh-GR) have been prepared by the incorporation of graphene sheets into the PbTh matrix during electropolymerization under magnetic stirring from the LiClO₄/CH₃CN electrolyte containing the bithiophene (bTh) monomer and graphene sheets. The incorporation of graphene sheets at different masses (1, 2 and 3 mg) is ensured by the effect of the stirring of the electrolyte. The characterisation of films is effected by electrochemical methods (cyclic voltammetry and impedance spectroscopy), spectroscopic technics (FT-IR, UV-Visible), X ray diffraction, thermogravimetric analysis, and scanning electron microscopy. It was observed that the electrochemical performance measurements of the ITO/PbTh-GR (3 mg) film show a specific capacity of around 65 F/g, which is six times higher than that of ITO/PbTh films, 11 F/g.*

KEYWORDS: *Graphene; Polybithiophene; Chronoamperometry; Composite film; Specific capacitance.*

INTRODUCTION

Conducting Polymers (CPs) have taken considerable attention because of their economic importance, good stability, and electrochemical properties. The Conducting organic polymers are used in sensors [1], supercapacitors [2-5], catalysis [6], batteries [7].

Derivate carbon materials as active carbon [8], carbon nanotubes [9] and graphene [10-12] are the most widely used as electrode materials in supercapacitors due to their stability and large specific area. The whole characteristics of graphene and conducting polymers attract the attention of more researchers that shows the extent of their use

in supercapacitor as electrodes. Thus, the high performance electrode materials, nano-composites conducting organic polymers and derivate carbon materials are deeply investigated because of the aforementioned properties. Within the same ideas-stream, graphene is known to be an element recently seen as the element of carbon-based materials set selected among the chief components to be applied in several electrochemical fields as supercapacitors and batteries. The supercapacitors that use conducting polymers with derivatives carbon materials form units of intermediate specific energy and high capacitance [13, 14].

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The option for graphene is extensively reasonable due to its high electrical conductivity, mechanical strength, flexibility and valuable working area [15]. Moreover, the graphene is substantially stable throughout the entire charge–discharge cycle; nevertheless, some experiences have shown bounded specific capacitance (around 100–200 F/g), unfavourable fact caused by the stored energy mechanism generated by the electric double-layer capacitance [16].

To synthesize high quality graphene, the best technique is to perform according to a direct exfoliation of graphite in solution, principally electrochemical, sonochemical, and liquid-phase exfoliation [17-19]. In conflict, the selected material required for pseudocapacitors, conducting organic polymers really allow high specific capacitance even so they poor cause stability due to the Faradic mechanism [20]. In addition, graphene might be mixed with conducting organic polymer to get graphene/conducting organic polymer compound, more electrochemically effective than pure graphene. The increase in performance of the graphene/conducting organic polymer is a direct impact of the synergistic effects of all components that improve conductivity and amplify electrochemical stability all through the discharge process [21]. Both excellent stability and high performance is subject to investigations namely with combined conducting organic polymer and pure graphene so as graphene/polyaniline [22-24], graphene/ polypyrrole [25, 26], and graphene/polythiophene composites [27, 28] predominantly stressed upon.

Due to the remarkable electrical conductivity and environmental stability of the polythiophene, which attract a large concern each year [29–31], the polythiophene and its derivatives were used positively in electrochemical capacitors. [32–34]. In fact, polythiophene allow plenty charge-store at the level of the double layer electrode/electrolyte interface and in the polymer matrix as well following to quick faradic charge transfer in the nearby of the electrode surface when suitable potential is applied. However, mechanical degradation of polymer may occur in some usual electrolytes when volume changes while the insertion/removal of ions that results in low cycle life and capacitance decay of a capacitor [35, 36]. The first experience known till now using polythiophene as supercapacitor is attributed to *Laforgue* and co-workers who succeed to obtain a specific storage level of

110 F/g [37]. Subsequently, many carbon nanotubes and metal oxides combinations have been elaborated aiming to develop the quality of polythiophene [38, 39]. Thus, various works point to manifest enhancement of the thermal and electrical conductivities of the polythiophene compared to pure polythiophene ones. In the researches mainstream course aftermath, Zhao et al. produced an electromagnetic material based on GR nanosheet/polythiophene composites issued following a classic chemical polymerization process. The composite thus obtained shows marked hysteretic behaviour of a semiconductor but its use in energy storage applications has not been electrochemically characterized by the authors [40]. Following the outcome studies issued, the work published in 2011 that investigates the use of a GR/polythiophene composite as supercapacitor [41] reports an evident capacitance due to cyclic voltammograms of 176 F/g at 50 mV/s but no electrochemical characterization of composites with different ratios of GR and polythiophene have been reported.

Taking into account the advantages of the high conductivity of GR and the capacitance of polybithiophene (PbTh), the ITO/PbTh-GR composite film served as a reference for the application in supercapacitor electrode materials. In study at hand, the graphene was elaborated following an electrochemical exfoliation procedure then submitted to X-ray diffraction and FT-IR spectroscopy for characterisation. To its part, the (ITO/PbTh-GR) composite films were got through chronoamperometry technic with a working electrode (ITO) immersed in electrolyte solution (LiClO_4 0.1M/ CH_3CN) containing bithiophene (10^{-2} M) monomer and dispersed graphene by stirring at various weights (1, 2 and 3mg). The issued composite films have been characterized by scanning electron microscopy SEM, thermo gravimetric analysis TGA, UV-Visible and FT-IR spectroscopy. As additional tests, the capacitance properties were assessed through cyclic voltammetry and electrochemical impedance spectroscopy.

EXPERIMENTAL SECTION

Materials

Natural graphite was purchased from Tianjin Dengke Reagent Company, China, sulphuric acid (H_2SO_4 Sigma-Aldrich; 98%), N, N-dimethylformamide (DMF) (Sigma-Aldrich) The monomer used is bithiophene

(Sigma-Aldrich). The supporting electrolyte used for the synthesis and electrochemical characterizations is the lithium perchlorate (LiClO_4 , Fluka) which is a pure salt suitable for analysis purposes, dissolved in acetonitrile solvent CH_3CN (Sigma-Aldrich). This electrolyte was preferred than others due to its solubility in organic and aqueous solutions as well as its electrochemical stability in a large potential range.

Synthesis of Graphene

Graphene is synthesized through electrochemical exfoliation. Two high-purity graphite rods set parallel at 6 cm from each other in an ionic solution of 2.6 mL of sulphuric acid in 100 mL deionised water. The electrochemical exfoliation is performed in different potential between the graphite electrodes (5 V for 5 min). Furthermore, the graphene sheet suspension is prepared so that the exfoliated graphene sheets are collected on a 100 nm porous filter and washed under vacuum filtration with deionised water then 5 minutes dried and dispersed in N, N-dimethylformamide (DMF) solution by mild water-bath sonication for 5 minutes. The suspension thus obtained was submitted to centrifugation at 2500 rpm in order to eliminate unwanted large graphite particles. The final purified suspension is hence ready to be characterized and serve to film production. The whole electrochemical exfoliation processes were performed at normal room-temperature [42].

Characterization

The Graphene, ITO/PbTh, and ITO/PbTh-GR (1, 2 and 3 mg) films are characterized following different technics. The X-ray analysis is carried out with the Rigaku make powder X-ray diffractometer (model RINT 2100) using the $\text{CuK}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$).

For their parts, scanning electron microscopy micrographs were obtained by using a (NeoScope, JEOL, JCM-5000), TGA was carried out with a SDT Q600 thermal analyser in the temperature range ambient to 1500°C at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen flow. The UV-Visible spectrums of the different films are got from the Shimadzu UV-1800 UV-Vis spectrophotometer and finally, the Fourier Transform InfraRed (FT-IR) spectroscopy spectra are issued from the Jasco FT/IR 4200 spectrometer.

Electrochemical tests

Electrochemical tests are performed at room temperature in single compartment cell PGZ-301 Voltalab coupled connected to the computer through Voltmaster 4 software that allows appropriate electrochemical technics and required parameters. The intended technical procedure is to be performed three-electrode cell-set of an Indium Tin Oxide (ITO) glass substrate working electrode and a Saturated Calomel Electrode (SCE) and a platinum strand auxiliary electrode.

RESULTS AND DISCUSSION

Fig. 1 shows the XRD of graphite and graphene samples. So, the XRD graphite powder sample (Fig. 1A) points up the characteristics peaks of (002) at 26.50° , (010) at 42.31° and (004) at 54.60° with high intensity [42,43]. The graphene powder (Fig. 1B) designates a characteristic peak of (002) at 26.60° with weaker peak compared to the graphite one. The noticed intensity decrease of (002) plan peak suggests the large exfoliation of graphite to graphene nanosheets [42,44]. The size of graphene nanoparticles evaluation is quantified by the XRD in applying Debye-Scherrer's formula:

$$D = 0.9\lambda/w \cos \theta$$

While, D the size of the nanoparticle, λ the XRD wavelength, w the full-width half maxima and θ is the peak position. The size of graphene-nanoparticles formula evaluation is around 13 nm.

The bithiophene electropolymerization is carried out through chronoamperometry method from 10^{-2}M bithiophene dissolved in (LiClO_4 0.1M+ CH_3CN) at 1.2 V vs. SCE imposed potential for 2 minutes. The graphene sheets (1, 2 and 3mg) are added to the electrolyte solution then dispersed by stirring. For its part, the polybithiophene-graphene composite is deposited on the working electrode at the end-time. The whole tests were effectuated at the same conditions imposed to the electropolymerization of bithiophene in absence of the graphene particles.

Chronoamperograms of preparation films ITO/PbTh (A), ITO/PbTh-GR 1mg (B), 2mg (C) and 3mg (D) during electropolymerization were shown in Fig. 2. The chronoamperograms produced by these materials were observed to be similar. After the initially high but rapidly tailing current transient, the current increases steadily

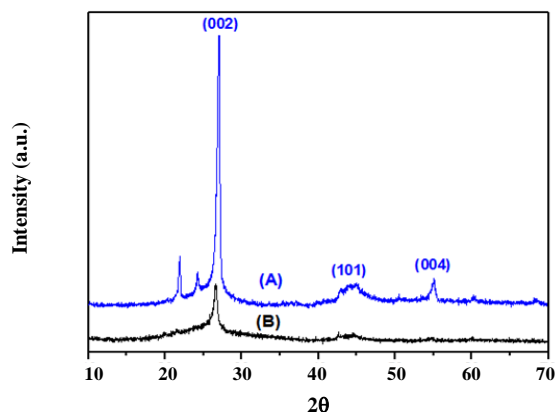


Fig. 1: XRD spectra of natural graphite (A) and graphene (B).

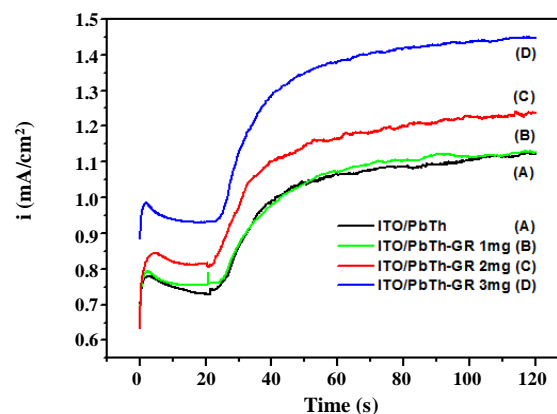


Fig. 2: Chronoamperograms of ITO/PbTh (A), ITO/PbTh-GR 1mg (B), 2mg (C) and 3mg (D).

indicating an increase in the electroactive surface area by the PbTh deposition. The potential is held steady as the current produced is measured as function of time, typical curves were obtained, the sharp current transient corresponding to the charging of the double layer, which produces a non-faradic current. The oxidation of the monomer then produces a faradic current, which increases due to the formation of a conducting polymer. The polymer growth may be limited by diffusion of monomer from the bulk solution to the vicinity of electrode [45, 46].

The SEM images of ITO / PbTh (A, B) and ITO / PbTh-GR (C, D) have been reported in Fig. 3. The ITO/PbTh film shows a porous structure. A noticeable change in the ITO/PbTh-GR image can be observed and the morphology of composite films has been significantly modified, which has shown that the presence of non-uniformly distributed graphene sheet on the surface of the polymer with different sizes.

The thermal stability of the samples was investigated using TGA technic. The TGA curves of ITO/PbTh (A) and ITO/PbTh-GR (B) composites are shown in Fig. 4. The thermogravimogram curve of ITO/PbTh, there are three discrete weight loss stages at approximately 65°C, between 150–300°C, and at more than 450°C, which correspond to the evaporation of acetonitrile, elimination of dopant LiClO₄, and degradation of PbTh chains, respectively. The thermogravimogram curve of ITO/PbTh-GR. is similar to that of pure ITO/PbTh, but the thermal stability of ITO/PbTh-GR is superior to that of ITO/PbTh. Thus from the TGA data, it is evident that both the decomposition temperature and the residual

weight increase with incorporating graphene. Hence we can say that by incorporating GR in the PbTh matrix the thermal stability of the polymer can be increased.

Fig. 5 indicates the UV–visible absorption spectra of ITO/PbTh and ITO/PbTh-GR (1, 2 and 3 mg) composite films. Every film specified by two characteristic absorption bands at 460 nm and 700 nm wavelengths. One in the visible region, which is attributed to the π - π^* transition of the main conjugated polymer chain, and another in the UV region, which is attributed to the absorption of the doped polymer [47-49]. The composite first absorption bands films ITO/PbTh-GR (1, 2 and 3 mg) declines steadily with the incorporated graphene amount that shows a hypochromic shift compared to the ITO/PbTh film one. Besides, the composite films ITO/PbTh-GR (1, 2 and 3 mg) second absorption bands steadily increase with the incorporated graphene amount. The outcome scheme may also reveal a possible increase in stability films incorporation of graphene in polybithiophene

Fig. 6 shows the graphene pure (A), ITO/PbTh (B) and ITO/PbTh-GR (C) FT-IR spectra. The pure graphene spectrum in Fig. 6A points up to C=C specific peaks within the 1340 - 1700 cm⁻¹ range. It refers to an absorption peak at 1227 cm⁻¹ that related to the C-OH stretching. The two other peaks at 2982 and 2905 cm⁻¹ refer to the well-known C-H stretching vibrations and finally the 1681 cm⁻¹ first peaks imply a carboxylic group stretching vibration and, the 1086 cm⁻¹ second peaks, C-O stretching vibrations [50]. Fig. 6B, characterize the peaks of PbTh are at 1640, 1400, 1212, 1030, 780 and 690 cm⁻¹.

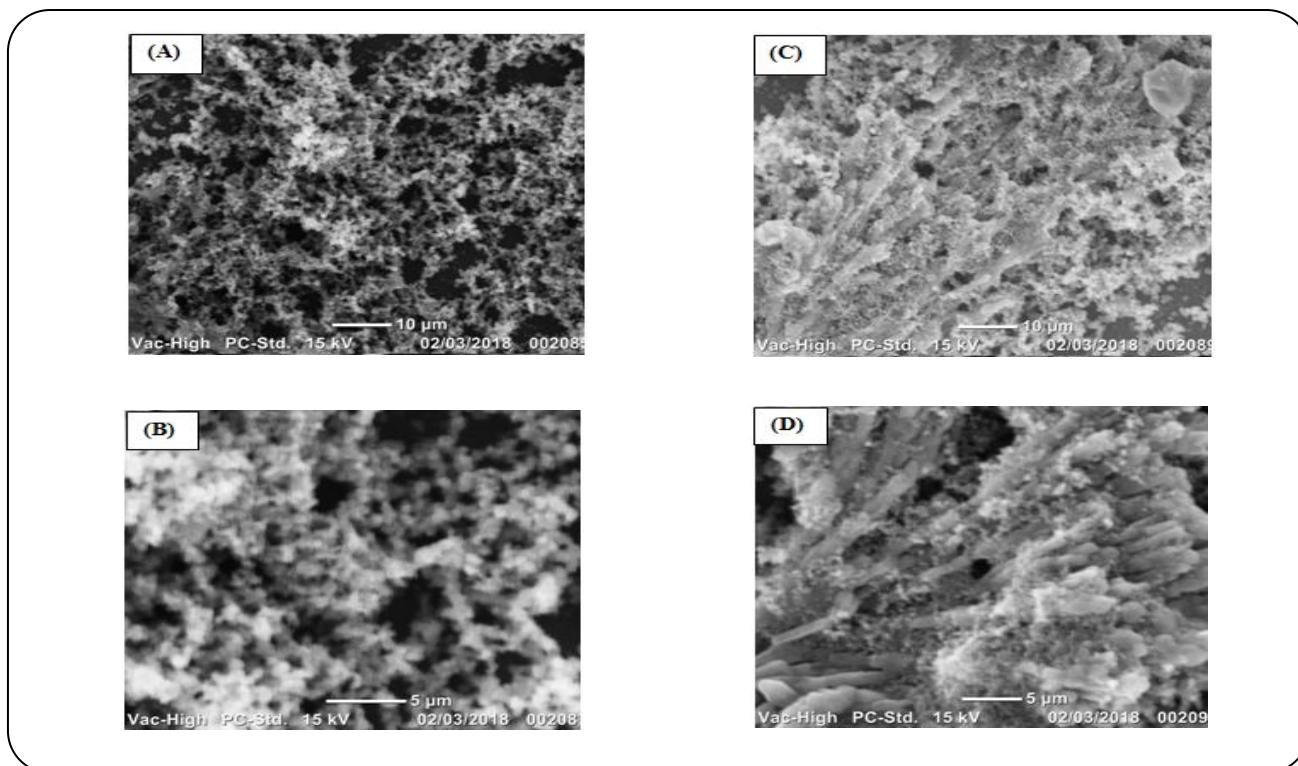


Fig. 3: FESEM images of ITO/PbTh (A, B), ITO/PbTh-GR (C, D)..

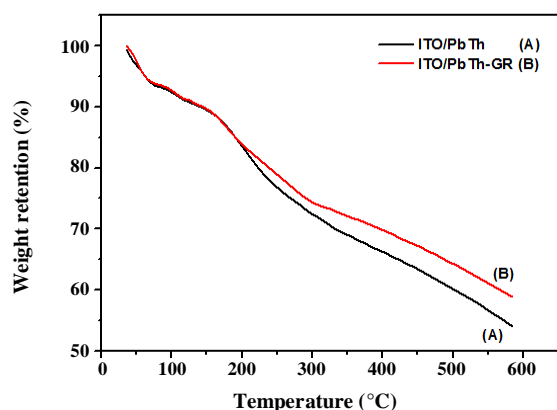


Fig. 4: TGA curves of ITO/PbTh (A) and ITO/PbTh-GR (B).

The peaks at 1640 and 1400 cm^{-1} match with the C=C asymmetric and symmetric stretching vibrations of the thiophene ring, respectively [51, 52]. The band at 1212 cm^{-1} related to C-C stretching vibrations, mentioning the C-H in-plane bending band located at 1030 cm^{-1} [53]. The band at 780 cm^{-1} belong to the C-H out-of-plane vibration of the 2, 5 substituted thiophene monomer [54], while the peak at 690 cm^{-1} is related to the C-S stretching

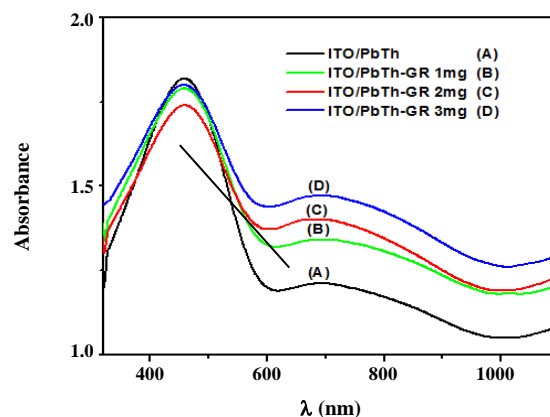


Fig. 5: UV-Visible spectra of ITO/PbTh (A), ITO/PbTh-GR 1mg (B), 2mg (C) and 3mg (D).

in the thiophene ring [55,56]. As for the PbTh/GR composite (Fig. 6C), the spectra include a mixture of GR and PbTh characteristic absorption bands. Some peaks assigned to PbTh are slightly shifted, such as the C-C vibration at 1203 cm^{-1} , the C-H in-plane bending band at 1028 cm^{-1} and the C-S stretching that refer to the thiophene ring at 690 cm^{-1} , which both indicate the GR interact to some extent with PbTh.

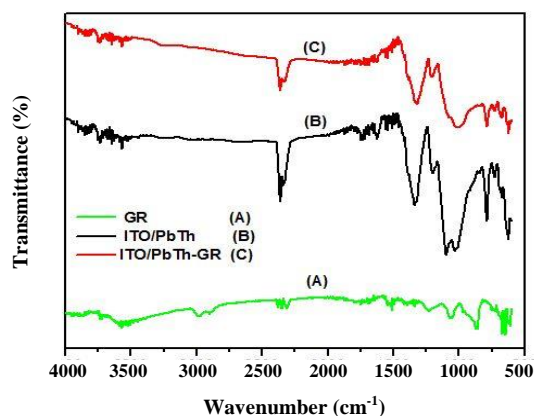


Fig. 6: FT-IR spectrum of GR (A), ITO/PbTh (B), ITO/PbTh-GR (C).

The Fig. 7 illustrates the of ITO/PbTh and ITO/PbTh-GR (1, 2 and 3 mg) cyclic voltammetry curves composite films measured in a potential range of 0.2 to 1.8 V vs.SCE at 50 mV/s scan rate in (LiClO_4 0.1M/ CH_3CN). What is worth mentioning is that in the whole potential investigated range there is no evident peak on both positive and negative sweep of every electrode with almost rectangular curves. The observed aspect proves the patent behavior of double-layer capacitance in the fast charging–discharging process. Besides, compared to the ITO/PbTh film, the entire ITO/PbTh-GR composite films markan important increase in the charge and discharge curves in the cyclic voltammetry plots areas with incorporated mass graphene in polymer matrix that result in a patent improvement in the specific capacitance. This might be related to the fact that the high surface area and high electrical conductivity of the GR improves the PbTh capacitance. In conclusion, the use of electrochemical capacitors of PbTh/GR composite as electrode materials is a promising approach to allow the maximization and utilization of the electrochemical performance [57].

The impedance spectra of ITO/PbTh (A) and ITO/PbTh-GR 1mg (B), 2mg (C) and 3mg (D) composite films measured at open circuit potential (0.230 V vs.SCE) are shown as Nyquist diagrams in Fig. 8. The films were analysed (LiClO_4 0.1M/ CH_3CN). All measurements were plotted on a frequency band ranging between 100 KHz and 100 mHz, with an alternative current voltage of 10 mV.

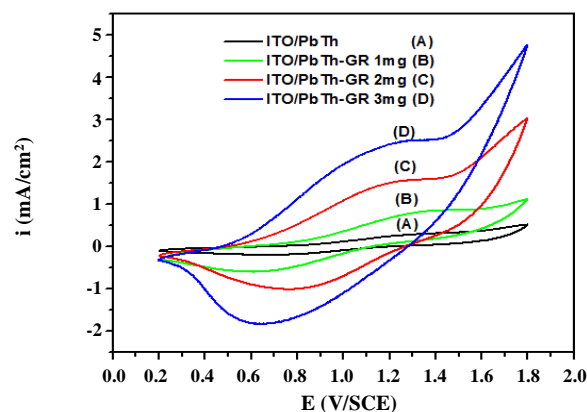


Fig. 7: Cyclic voltammograms of ITO/PbTh (A), ITO/PbTh-GR 1, 2 and 3mg scan rate 50 mV/s in (LiClO_4 0.1M+ CH_3CN).

The EIS measurements are interpreted in terms of an equivalent electric circuit (Randles), the electrode/solution interface is modelled as a circuit composed of a Constant Phase Element (CPE) in parallel of charge transfer resistance (R_2) and Warburg impedance (Z_w); this circuit is preceded by an electrolyte resistance (R_1). The fitting of the a.c. impedance data was done using electrochemical software the EC-Lab Z fitting. The impedance parameters listed in Table 1 confirm the incorporation of graphene particles in PbTh film, which decreases the electrical resistance of the composite film. The calculated value of R_{ct} of ITO/PbTh is $91.68\Omega\cdot\text{cm}^2$, and it decreases until $4.57\Omega\cdot\text{cm}^2$ for ITO/PbTh-GR 3 mg. The fitting results indicate that the ITO/PbTh-GR composite materials are much more conductive than ITO/PbTh.

So the specific capacitance is calculated accurately on the basis of the following equation

$$SC = \frac{\int_{E_1}^{E_2} i(E) dE}{2(E_2 - E_1)mv}$$

SC: Specific capacitance

E_2-E_1 : Potential window in cyclic voltammetry

$\int_{E_1}^{E_2} i(E) dE$: Voltammetric charge obtained by

integration of curve in CV.

m : the weight of deposited material on working electrode, we used a balance with an accuracy of 0.01 mg
 v : Scan rate.

Our results in the present work for ITO/PbTh shows a specific capacitance of 11 F/g, after the incorporation of the graphene nanosheets a significant increase of specific

capacitance was observed for ITO/PbTh-GR (1, 2 and 3 mg) composite films electrodes 18.32, 29.74, and 65 F/g.

Table 1: Impedance electrical parameter values corresponding to ITO/PbTh (A), ITO/PbTh-GR 1mg (B), 2mg (C) and 3mg(D).

Films	R_1 ($\Omega \cdot \text{cm}^2$)	R_2 ($\Omega \cdot \text{cm}^2$)	Q_{CPE} ($\mu\text{F} \cdot \text{cm}^2$)
ITO/PbTh	93.26	91.68	11.78
ITO/PbTh-GR 1mg	74.61	15.13	6.41
ITO/PbTh-GR 2mg	75.12	4.27	4.76
ITO/PbTh-GR 3mg	83.31	4.57	2.38

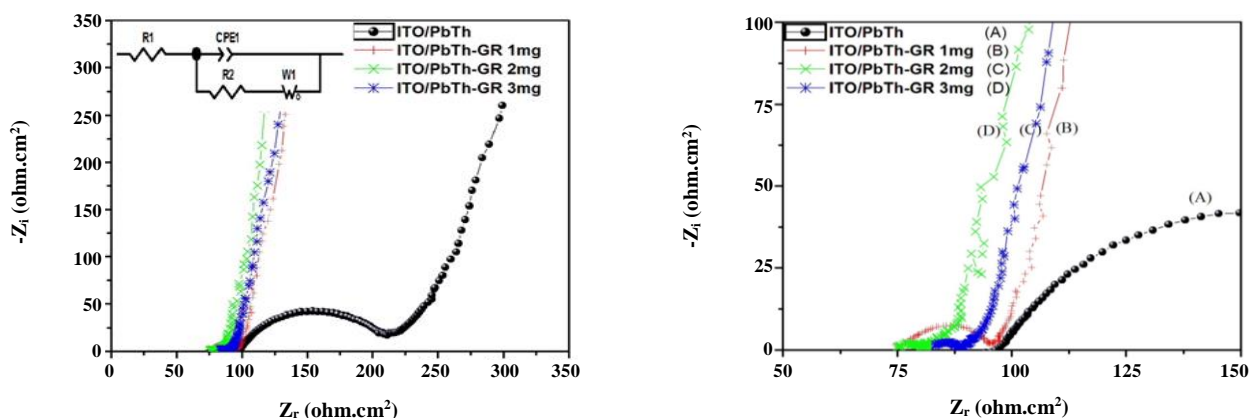


Fig. 8: Nyquist plots of ITO/PbTh (A), ITO/PbTh-GR 1mg (B), 2mg (C) and 3mg (D) in (LiClO_4 0.1M+ CH_3CN) electrolyte

CONCLUSIONS

The (ITO/PbTh-GR) composite films are prepared by chronoamperometry tests on a working electrode (ITO) immersed in an electrolyte solution (LiClO_4 0.1M/ CH_3CN) containing bithiophene monomer (10^{-2} M) and dispersed graphene by stirring at various weights (1, 2 and 3mg). The synthesized ITO/PbTh-GR composite films serve as reference for ulterior application in supercapacitor electrode materials. The specific capacity of obtained ITO/PbTh material alone is around 11 F/g that is increased up to 65 F/g with regard to the composite film ITO/PbTh-GR (3 mg). The noticed high capacitance of the polybithiophene and graphene is due to the positive effect of the added electronic conductivity graphene. The strategy at hand i.e. composite films synthesis could be extended to other conducting polymers such polypyrrole, polyaniline and poly (3-hexylthiophene).

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