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Enhancement Cathode Electrode of PPy by GO to Applied for Supercapacitor

In this study, chemical oxidation was used to prepare polypyrrole (PPy) composites. Additionally, PPy has been treated with graphene oxide (GO) nanosheets that were produced and added in a certain ratio. The structural characteristics of the mixed polypyrrole and polypyrrole-graphene oxide were investigated. The nanocomposites were produced by adding GO to PPy in volume ratios of 10, 30, and 50%. The molecular structures of PPy, GO, and PPy-GO nanocomposites were determined. The formation of a network of polypyrrol nanofibers was confirmed. Nanocomposites were produced by doping PPy nanofibers with GO in various amounts (10%, 30%, and 50% volume ratios). According to the electrochemical experiments, the nanocomposites exhibit high pseudocapacitive activity.

Keywords: Polypyrrole (PPy); Structural properties; Supercapacitor; Capacitance
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1. Introduction

Conducting polymers (CPs) exhibit the capacity to facilitate the conduction of charge current across the polymer network in electrochemical activities, given favorable conditions [1-3]. They may be used as templates because of their enormous surface area to volume ratio, long length, consistent diameter, large surface area, and low density [4,5]. Given its ease of mixing, strong conductivity, and environmental steadiness, PPy is one of the most widely used CPs [6]. The main requirement for PPy's electrical effects is bonding. Through catalytic activities that result in the process of combining various entities, such as cations, inorganic anions, natural compounds, and so forth, the expected outcome is an enhancement in the electrical conductivity of PPy [7]. The special qualities of CPs create new opportunities for mechanical operations, such as the ability to recharge batteries or create biochemical allergies. By means of the mechanism of countercharge accumulation and release brought on by redox reactions occurring in an electric field, CPs are able to store capacitance [8-12]. Researchers from all over the world are still looking closely at the introduction of electrostatic polymers. PPy is a highly specialized polymer due to its exceptional conductivity, significant storage capacity, environmental resilience, and strong chemical current [13,14]. Capacitors are commonly built by arranging a set of parallel plates that are separated by an insulating material. When voltage is introduced in series to the plates, the opposing sign's capacitive charge begins to accumulate. Although the supercapacitors have higher capacity (F), they have lower power values (mF) than these regular capacitors [15]. The research is motivated by the unique properties of conducting polymers, like Polypyrrole (PPy), which facilitate charge conduction in electrochemical activities. These polymers offer high surface area to volume ratio, strong conductivity, and environmental stability.

Aim of the work Preparation PPy nanofiber and nanocomposites from PPy with the addition of different concentrations of GO nanosheets, studying the structural characteristics for the prepared nanocomposites, to use it in electronic device (supercapacitor device application).

2-Experimental Part

The methodology defined by Yang [16] was used to construct the combination of polypyrrole nanostructure. The first stage involved evenly dispersing 0.818 g of methyl orange in 60 mL of distilled water. 2.237 g from ferric chloride were dispersed in a fluid solution including methyl orange while being stirred slowly at 80 rpm and submerged in an ice bath with the addition of 1 milliliters of pyrrole. What was mixed turned black and stirred continuously for 1 day. The precipitate underwent multiple ethanol and distilled water washes, filtering, and drying for 60 minutes.

To create a homogeneous, ready-to-use dispersion, a suitable amount of GO was dissolved in distilled water, added to PPy at volume ratios of 10, 30 and 50% then treated to ultrasonic waves for an hour.

The production of the PPy-GO as an electrode was done on a nickel foam (1x1 cm^2) substrate. Drop casting was used to deposit PPy-GO nanocomposite on nickel foam substrate in the ratios of 10%, 30%, and 50%, respectively. The generated sample (PPy-GO/nickel foam) was tested using cyclic voltammetry (CV), galvanostatic charge-discharge analysis (GCD), and electrochemical impedance spectroscopy (EIS). In a volume of 1 mL, a concentrated solution of sulphuric acid with a concentration of 100%. The electrode (PPy-GO) weighed 0.7 mg. The supercapacitor electrode sample is schematically shown in Fig. (1).

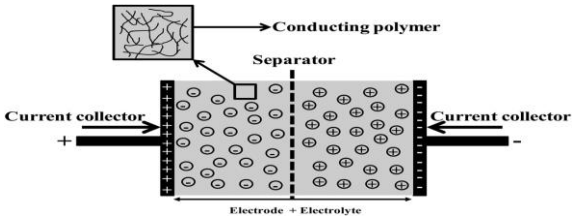


Fig. (1) A schematic of an electrochemical supercapacitor with electrodes made of a layer of conductive polymer

3-Results and Discussion

The x-ray diffraction (XRD) was employed to examine the structural characteristics of both polypyrrole (PPy) and the three different concentrations of the PPy-GO hybrid nanocomposite. XRD measurements were used to examine the composition of the composites. Figure (2) displays the PPy, PPy/GO composite's XRD patterns. The XRD pattern of pure polypyrrole (PPy) has a diffraction peak at 2θ=20.30°. This peak is characterized by poor intensity and broadness, suggesting the amorphous nature of the substance [17]. The peak intensity at 20.30° for the 10% GO composite has significantly increased and shifted to 20.80°. The increase in peak intensity may be attributed to the exfoliation of GO layers induced by ultrasonication [18].

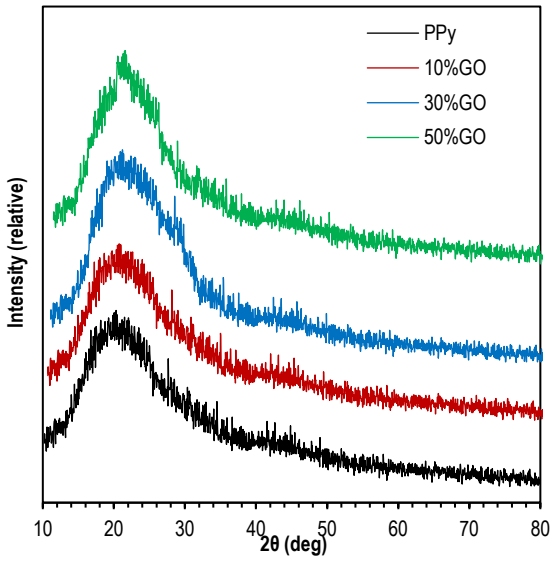


Fig. (2) XRD patterns of (a) GO, (b) PPy/GO composite and (c) Pure PPy and different percentages of PPy-GO

Polypyrrole-graphene oxide composite's active production has been confirmed using FTIR spectra. Figure (3) displays the spectra of several samples, including PPy, and PPy-GO by different percentages (10% GO, 30% GO and 50% GO). The measured signals at 3420 and 3150 cm^{-1} are attributed to PPy-GO, the hydroxyl group, and O-H bond stretching vibration [19]. The (C=O) carboxyl group is responsible for the signal at 1755 cm^{-1}. The peak at 1630 cm^{-1} is attributable to the stretching vibration of the (C-OH), the three peaks at 1090 cm^{-1}, 602 cm^{-1}, and 386 cm^{-1} are epoxide (C-O-C) [19,20]. The polypyrrole ring's N-H, C-C stretching vibration mode, and C-H deformation vibrations are each attributed to peaks in the PPy FTIR spectrum at 3630, 1540 and 1050 cm^{-1}, respectively [21,22]. The PPy-GO composite has a peak at 1090 cm^{-1}, which is a shift from the 1080 cm^{-1} peak observed in PPy-GO spectra. This shift is attributed to an interaction between PPy and GO, specifically involving the epoxide group. Additionally, the peaks at 1540 and 1680 cm^{-1} are connected to, respectively, carbonyl C=O and polypyrrole ring C=C stretching vibration. The peak previously located at 3420 cm^{-1} in PPy spectra has been shifted to 3379, 3370 and 3351 cm^{-1} at 10% GO, 30% GO, and 50% GO, respectively. This shift is a result of the interaction between PPy and GO, specifically the stretching vibration of N-H. Additionally, the peak at 3130 cm^{-1} has shifted to 3140, 3145 and 3150 cm^{-1} with different percentages of GO. This shift is attributed to the interaction between PPy and GO, specifically the stretching vibration of O-H [19,23,24].

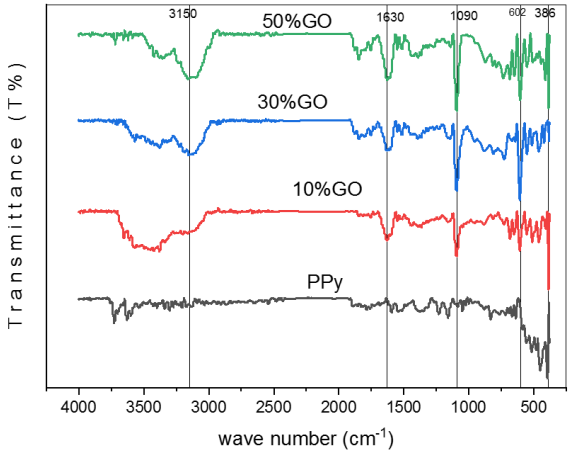
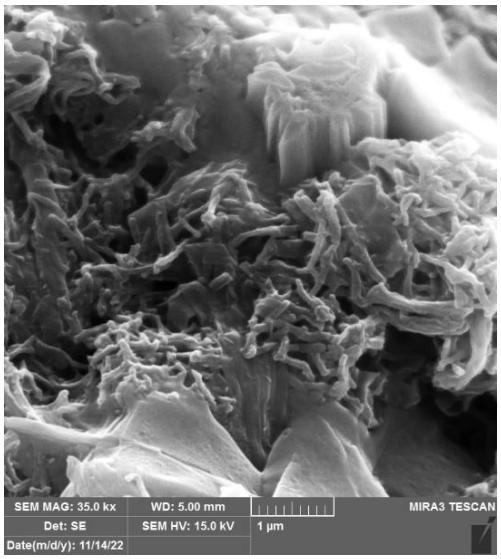
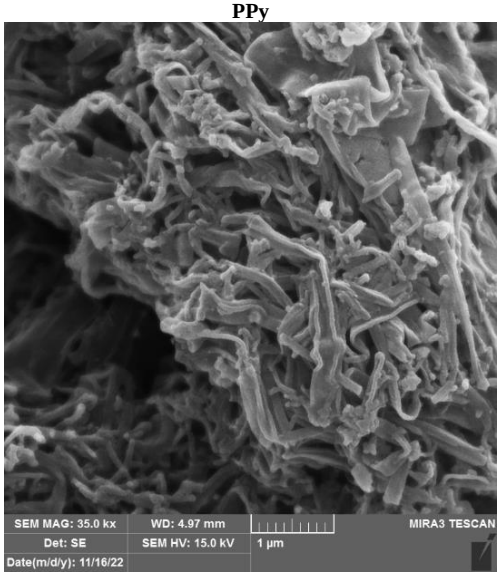


Fig. (3) FTIR spectra of PPy, 10% GO, 30% GO and 50% GO

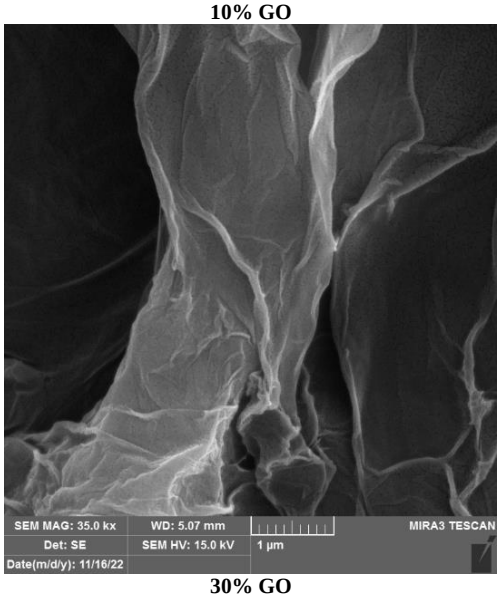
As-made PPy and PPy-GO hybrid nanocomposite films were examined for surface morphology using the field emission scanning electron microscopy (FE-SEM) method, as shown in Fig. (4). The nanofiber shapes in the microstructure images of pure PPy in figures (4a) and (4b) are depicted at different magnifications of 350000X and 135000X, respectively. When PPy was chemically created in the method of chemical oxidation and the ice bath as previously described, it was discovered through the examination of the morphology of the material that the substance was nanofibers by the photographs.



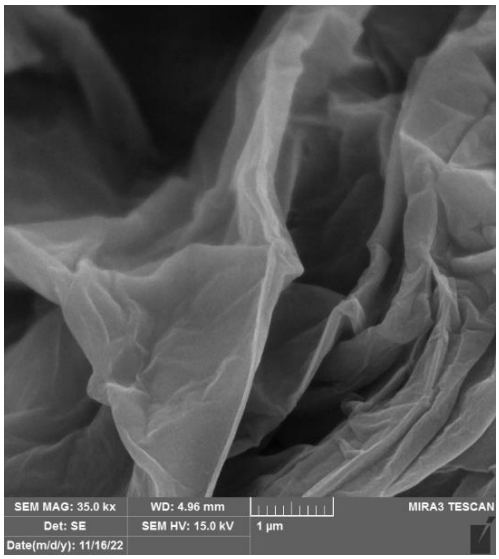
PPy



10% GO

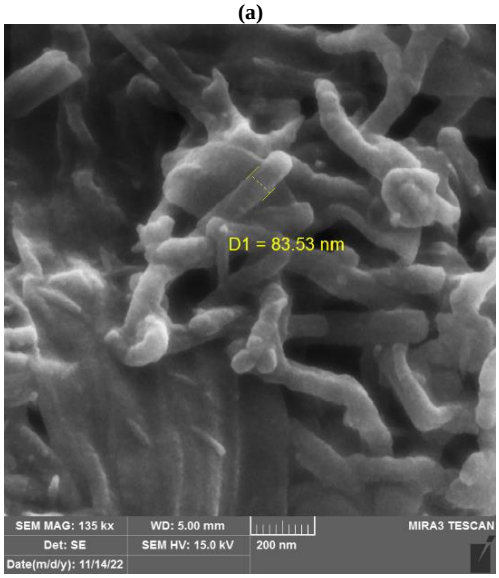


30% GO

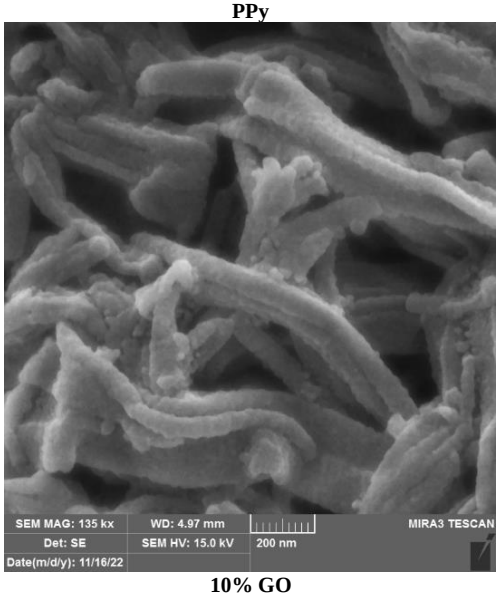


50% GO

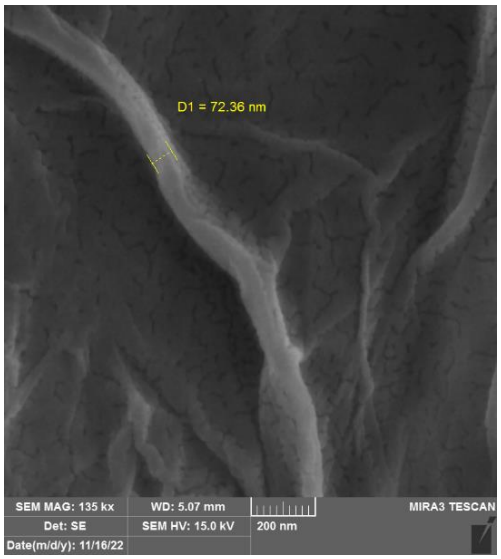
(a)



PPy



10% GO



30% GO

50% GO

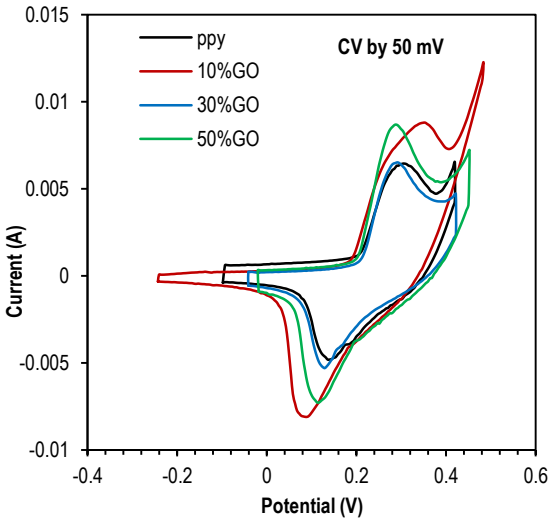
(b)

Fig. (4) FE-SEM images of PPy, 10% GO, 30% GO and 50% GO at (a) 35000X magnification, and (b) 135000X magnification

The shape of the PPy-GO nanocomposites, which displayed a homogeneity between PPy nanofibers and GO nanosheet morphology, is depicted in figures (4a) and (4b) at 10, 30 and 50% GO by different magnifications. The PPy constructed scaffold provides interconnected, 3D-conductive fibers/sheets in the matrix, with the majority of these nanofibers having widths between 50 and 100 nm. The PPy-GO hybrid nanocomposites exhibit the formation and aggregation of PPy fibers on the surface, due to the interactions between the fibers and GO sheets, as observed in the FE-SEM images. The outcomes of these images are nearly identical to those of the subsequent study [25,26].

Figure (5a-c) shows the results of the cyclic voltammetry examination of the PPy and PPy-GO films. We can see the anode and cathode peaks at (6.37, 8.72, 6.47, 8.67mA), (13.2, 16.4, 12.9, 16.9mA), and (19.1, 24.1, 19.9, 25.6mA), respectively, by repeatedly applying the scan rate (150, 100, 50mV). The materials exhibit electrochemical dynamism within the specified potential range, according to CV results. The electrochemical functions of both PPy and GO are incorporated into the PPy-GO combination film. The nanocomposites PPy-GO membrane has an apparent electrochemical activity observed when the voltage is set under a positive value of 0.6 V, as shown in Fig. (5). The anode electrode functions as the emitter of positive charges, The cathode electrode functions as the location where positive charge carriers are stored in the PPy and PPy-GO materials, During the discharge process, this mechanism operates. The cathode side turns black when CV forms, while the anode stays white. Unlike pure PPy, the Gaussian distribution seen in Fig. (5) highlights the notable importance of the electrochemical interaction within PPy-GO composites. The elucidation of this phenomenon may be achieved due to the synergistic effects of PPy and GO. The presence of two distinct and prominent redox peaks on each curve depicted in Fig. (5a-c) indicates the occurrence of a pseudo-capacitative characteristic in the supercapacitor. This feature is a result of the Faradaic redox reactions. The polyaniline-GO composite membrane was reported to have comparable characteristics [16,27].

Using GCD test, this electrochemical characteristic of the composite PPy-GO electrode were determined. In order to ensure optimal performance of the hybrid system, potential fluctuations for individual electrodes were recorded independently when a Ni-foam reference anode was introduced. With one and two stages for the negative and positive electrodes, respectively (protrusions present when charging and discharging), the potential variations are nearly slanting, identical to the CV data given in Fig. (5). This is due to redox reactions' possible dependent nature. A polymer that inserts anions, PPy is p-doped.



(a)

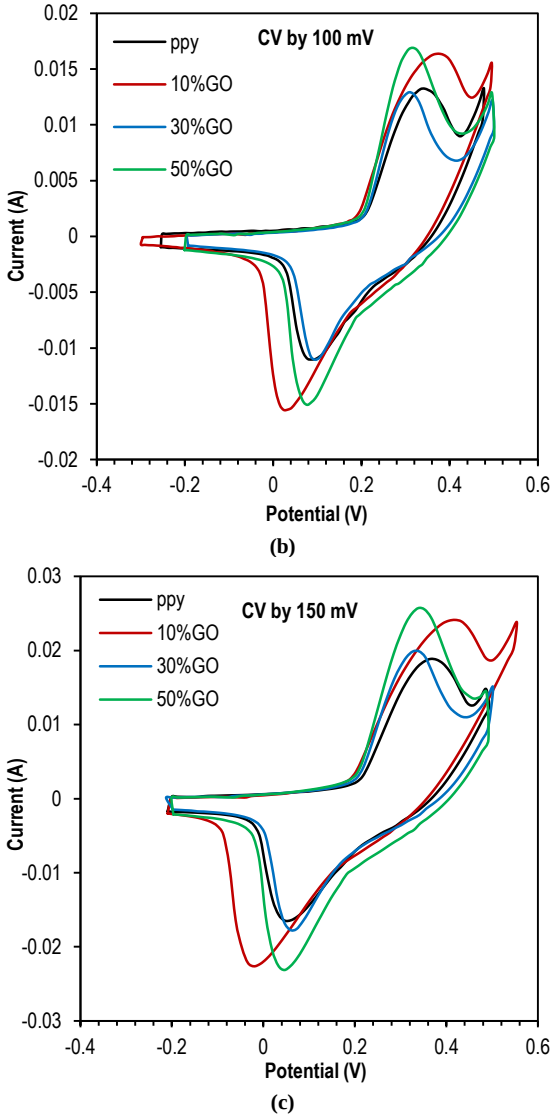


Fig. (5) C-V curves of PPy and PPy-GO nanocomposite with various GO concentrations at (a) 50 mV, (b) 100 mV, and (c) 150 mV

A polaron emerges as a consequence of the continuous movement of electrons within a neutral region of their quinoid structure chains causes a localized distortion of the positive charge. The PPy and PPy-GO electrodes exhibit reasonable performance over the typical potential ranges during the charge and discharge processes, as depicted in Fig. (6). Additionally, the PPy-GO hybrid composite electrode can function within the 0.2 V working potential window [28].

The following equation can be used to determine the specific capacitance from the CD curve. The specific capacitance (C) can be calculated using the formula $C=I\Delta t/m\Delta V$, where C represents the specific capacitance (in F/g), ΔV represents the potential window (V) (in this case, it is 0.2 V), I represents the discharge current (A) (in this case, it is 0.5 mA), Δt represents the discharge time (s) (5 s for pure PPy, 6 s for 10% GO, 5.7 s for 30% GO, and 4 s for 50% GO), and m represents the electrode's mass (PPY or PPY-GO) (g) (in this case, it is 0.1 mg) [16]. We were able to increase the capacity of pure PPy from 125 F/g to 142.5 F/g by adding 30% GO, and we were able to increase it to 150 F/g by adding up to 10% GO while the capacity decreased to 100 F/g at 50% GO. The higher capacitance observed may be attributed to the attractive forces between polypyrrol nanofibers and graphene oxide, leading to an increase in surface area. The oxidative polymerization process in PPy-GO nanocomposites and 1 M H_2SO_4 electrolysis achieved a maximum capacity value of 150 F/g [29].

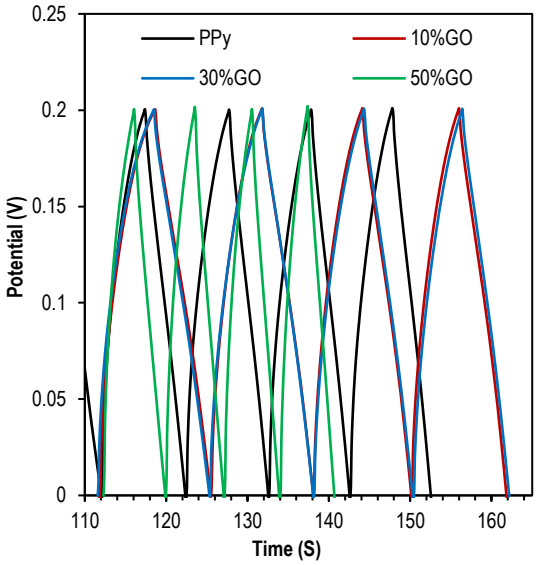


Fig. (6) GCD for pure PPy and PPy-GO at a different percentages

The Nyquist plot was examined by applying a sinusoidal AC voltage with an amplitude of 5 mV at the open circuit potential. The frequency range used for the test ranged from 1 Hz to 1000 kHz, as shown in Fig. (7). In order to get insight into the charge transfer behavior of the PPy/GO electrode material, an electrochemical impedance spectroscopy (EIS) plot was conducted on both PPy samples and PPy/GO composites (Fig. 7). The measurement of ohmic resistance can be obtained by determining the high-frequency intercept of the semicircle within the impedance.

At elevated frequencies, the diminutive semi-circle indicates a diminished transfer resistance of the charge accompanied by a less pronounced diffusion at lower frequencies. If the straight line showed a 45° angle in the low-frequency band, it suggests that the mechanism was affected by diffusion. Conversely, if the slope was 90°, it indicates that the behavior was purely capacitive. The impedance map displays a semi-circular pattern, indicating a highly efficient passage of electric charge. The aforementioned discovery provides additional evidence supporting the remarkable durability of the PPy/GO nanocomposite during electrochemical cycling. This material exhibits promising prospects as an electrode

material for electrochemical supercapacitors [30] [31].

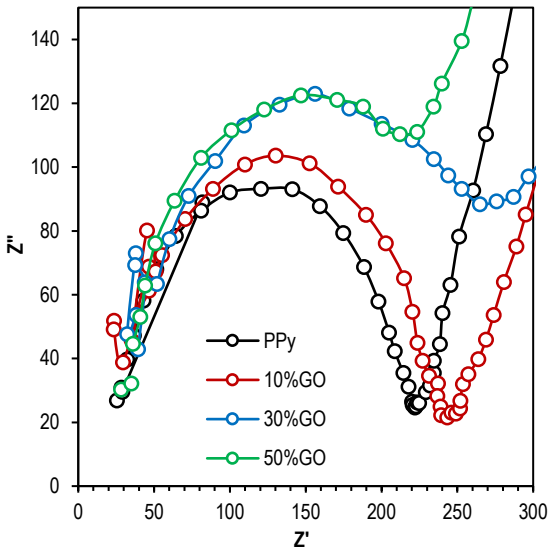


Fig. (7) The Nyquist plots obtained from the electrochemical impedance spectroscopy measurements conducted on the samples of PPy and PPy/GO

4. Conclusions

In summary, PPy nanofiber and nanocomposite of PPy/GO have been prepared by simple method. The composite film of PPy and GO is a good electrode material for electrochemical supercapacitor. The maximum capacitance values (153 F/g) that determined by GCD curves were obtained from PPy nanofibers doped with 30% GO, but for pure PPy the capacitance is very small compared to PPy doping with GO. Therefore, doping plays a very important role in improving the capacitance of supercapacitor.

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