

# Structural and Electrochemical Analysis of Microwave-Assisted Synthesis of Graphene/Polypyrrole Nanocomposite for Supercapacitor

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A new microwave treated electrode materials have been developed for supercapacitor using graphene and polypyrrole (PPy) composite prepared by the sacrificial-template polymerization method. The prepared nanocomposites were then microwave processed with the help of the microwave oven for 10 seconds. Characterizations of the synthesized and microwave treated composite were performed by Fourier Transform Infrared Spectroscopy (FTIR), Raman Spectroscopy, and Brunauer-Emmett-Teller (BET) measurements, electrochemical measurements such as cyclic voltammetry (CV), galvanostatic charge and discharge (GCD) measurements and Electrochemical Impedance Spectroscopy (EIS). Then the electrode for electrochemical measurements is prepared by dispersing graphene/polypyrrole composite in an ordinary rubber solution and coated it on a graphite rod. From the BET analysis, microwave treated composite material exhibited the BET area of  $34.13 \text{ m}^2 \text{ g}^{-1}$ . The composite revealed a maximum specific capacitance ( $C_{sp}$ ) of  $240.4 \text{ Fg}^{-1}$  for MGP175 (mass ratio of graphene oxide to PPy is 5:1.75, microwave operated) at  $10 \text{ mV s}^{-1}$ . This simple and low-cost method is used for the development of different composites for energy storage.

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**Keywords:** graphene, polypyrrole, microwave treatment, sacrificial template polymerization, supercapacitor, electrochemical properties.

## 1. INTRODUCTION

For the past few decades, supercapacitors have attracted more researchers, due to its higher energy density and power density. Low-cost electrodes have been intensively investigated for electrode material in supercapacitor in recent periods. Amid the different electrode materials such as graphene, carbon nanotube (CNT), activated carbon, metal oxides such as  $\text{MnO}_2$ ,  $\text{RuO}_2$  and conducting polymers such as polyaniline, polypyrrole. conducting polymers considered as a promising candidate for redox

supercapacitors, due to its high conductivity and effective synthesis process. But, their specific capacitance and stability are decidedly lower than metal oxides. Similarly, specific capacitances of carbonaceous materials are limited due to its structure. Recently, graphene nanomaterials have gained more recognition in storage mechanism, owing to its distinctive properties. Based on the energy storage mechanism which happens at the interface between an electrode and electrolyte, Electrical double layer capacitance (EDLC) uses carbonaceous materials to deliver high power density and pseudocapacitance uses metal oxides or conducting polymers to achieve improved energy density [1-2]. Graphene/polypyrrole (G/PPy) composite can dispense a good number of electrochemical sites and small distances for ions and electrons transport [3]. It is a great effort to develop supercapacitor with effective specific capacitance, energy density, power density, superior conductivity, and long term stability. Conducting polymers are emerging as a promising candidate for electrodes in supercapacitor owing to their pseudocapacitance, flexibility and its cost. But, the limitations of conducting polymers are charging/discharging rate and poor stability. Different electrode materials such as graphene/activated carbon, graphene/polypyrrole, graphene/polyaniline [4-7], graphene/MnO<sub>2</sub> [8-9], graphene/ZrO<sub>2</sub> [10], graphene/Fe<sub>2</sub>O<sub>3</sub> [11], and graphene/CNT [12-14] used for energy storage related applications. Aphale [1] synthesized graphene/CNT in pyrrole monomer with  $C_{sp}$  of 453 F g<sup>-1</sup>. They fabricated supercapacitor using an electrospun nanofibrous membrane with ultrahigh energy and power density. When compared to traditional electrodes, carbonaceous material with conducting polymer electrode achieves superior supercapacitor performance. Xu [3] successfully developed novel graphene/polypyrrole composite with 318.6 F g<sup>-1</sup> of  $C_{sp}$  at 2 mV s<sup>-1</sup>.

Basnayaka [15] developed a nanocomposite material using graphene and PPy. The presence of pores in the composite has been permitted, ions diffusion through the electrolyte. The electrochemical activity of the composite increased, due to increased surface area. PPy over graphene gives the shorter diffusion path for the dissemination of ions. Eeu [16] prepared ternary nanocomposite using one pot chronoamperometry approach, to achieve electrochemical stability and enhancement. But the capacity retention ratio is small, even for less number of cycles. Graphene oxide used as an EDLC material and also good support for organic and inorganic substances. High active surface area and porous 3-dimensional structures facilitated the high electrochemical performance and penetration of an electrolyte, respectively. The specific capacitance and energy density of the graphene and polyaniline composite were respectively 466 Fg<sup>-1</sup> and 165.7 Wh kg<sup>-1</sup> [17]. Cai [18] found that the neutral electrolytes containing alkali metal ions to be very suitable for supercapacitor. The CV curves of graphene / PPy nanocomposite exhibited a rectangular shape for Na<sub>2</sub>SO<sub>4</sub>, but irregular shapes for H<sub>2</sub>SO<sub>4</sub> and NaOH electrolytes. [18] demonstrated that the nanostructures are useful for supercapacitor applications owing to its novel effects on size and improved surface area. They observed the highest  $C_{sp}$  in acidic solution, when compared to basic and neutral solution.

Li [19] developed a well-bedded microstructure, which can create a huge number of pores and provides large interfaces. The  $C_{sp}$  of 91.5 Fg<sup>-1</sup> at 0.05 V s<sup>-1</sup>, is obtained for graphene/polypyrrole/cellulose nanocomposite [20]. Molina [21] found that the increasing graphene content leads to a decrease in electroactivity of the composite. The synergistic interaction between graphene and p-type polypyrrole results in an improved storage capacity [22]. The incorporation of polypyrrole in graphene, not only provides the pseudocapacitance but also facilitate the infiltration of gel

electrolyte [23]. Kashani [24] developed hybrid graphene/polypyrrole material using electrodeposition and chemical vapor deposition. The specific capacitance obtained for this composite is  $509 \text{ F g}^{-1}$ . The high stability ternary composite (Zirconia, reduced graphene oxide, polypyrrole) developed by Alves [25] featured a 5 % increase in  $C_{\text{sp}}$  even after 1000 cycles. Devi [26] obtained  $39 \text{ Wh kg}^{-1}$  energy density and  $3105 \text{ W kg}^{-1}$  power density, by using graphene with polypyrrole spacer.

Xu [27] prepared the composite of reduced graphene oxide and polypyrrole, to prepare textile-based electrodes with high flexibility and highly conductive for supercapacitor application with flexible nature. With the help of reduced graphene oxide, shrinking and swelling of polypyrrole can be avoided. Li [28] prepared a sandwich-like composite material. Moysowicz [29] obtained  $C_{\text{sp}}$  of  $140 \text{ F g}^{-1}$  with a capacity retention ratio of 93%. He [30] found that the relatively larger size polypyrrole nanoparticles are properly utilized for the electrodes. The capacity retention ratio is 98% for nanocomposite of polypyrrole and graphene quantum dots [31]. Pattananuwat [32] prepared polypyrrole on the graphene surface. Chee [33] developed polypyrrole / graphene oxide / zinc oxide composite deposited on flexible nickel foam. Lu [34] prepared a ternary composite (graphene/polypyrrole /carbon nanotube) which exhibited large surface area and meso and macroporous system. Liu [35] prepared graphene/polypyrrole nanocomposite with the conductivity of  $1980 \text{ S m}^{-1}$ . Bora [36] developed sulfonated graphene/polypyrrole nanocomposite by interfacial polymerization.

In this report, the composites of graphene and polypyrrole are synthesized by modified hummers' method, and in situ polymerization method. And also, novel microwave treatment has been employed to prepare graphene / PPy nanostructure. The microwave treatment greatly influences the effects of the composite material. No report has been found on the synthesis of microwave-treated graphene / conducting polymer composite. The synthesized and microwave treated composites were analyzed by structural and electrochemical analysis. The electrochemical behavior of composite was investigated in  $0.5 \text{ M H}_2\text{SO}_4$  aqueous solution. The synergistic effect between graphene and polypyrrole greatly enhance the properties of the composite. With controlled morphology and microwave exposure (320 W, 10 s) of graphene/polypyrrole composite exhibited the highest energy density and power density. Thus, nanocomposites have a better performance with the use of graphene and will be an ideal electrode material for supercapacitor applications.

## 2. EXPERIMENTAL SECTION

### 2.1. Materials

Graphite was obtained from Aksharchem, sodium nitrate and potassium permanganate were from Merck, hydrogen peroxide and hydrochloric acid (HCl) were purchased from Nice chemicals private limited and concentrated sulphuric acid was obtained from RFCL limited. Without any additional purification, the chemicals were used.

## 2.2. Graphene Oxide Synthesis

Graphene oxide (GO) was prepared from natural graphite through the modified Hummers' method. Graphite powder (20 g) and sodium nitrate (5 g) were mixed and stirred. Under constant stirring 230 ml of concentrated sulphuric acid were added with the above-prepared solution. After 1 h, 15 g of potassium permanganate ( $\text{KMnO}_4$ ) was added slowly to the prepared solution, maintaining  $5^\circ\text{C}$ . Then, the solution was stirred at  $6^\circ\text{C}$  for 14 h. Finally, under vigorous stirring, 250 ml of water was added for dilution. Fortify the reaction with  $\text{KMnO}_4$ ; the prepared solution was mixed with 30 ml of hydrogen peroxide. The obtained solution was repeatedly scoured with hydrochloric acid, ethanol, and distilled water respectively. Then filtered and dried at  $100^\circ\text{C}$  for 24 h and got the desired graphene oxide sheets.

## 2.3. Synthesis of $\text{MnO}_2$ / Graphene Oxide nanocomposites

For the preparation of  $\text{MnO}_2/\text{GO}$  composites, 90 mg of GO was dissolved in 78 ml  $\text{H}_2\text{O}$  and stirred it by ultrasonication for 3 minutes. Then 5 ml of  $\text{H}_2\text{SO}_4$  were mixed with the above-prepared solution by ultrasonication. Then, the prepared solution was heated at  $80^\circ\text{C}$  for five minutes, and 450 mg of  $\text{KMnO}_4$  was added under stirring. After 20 minutes vigorous stirring, the composites were obtained by centrifugation and cleansed with water for 3 times and kept at room temperature for 24 h.

## 2.4. Synthesis of Polypyrrole / Graphene Oxide nanocomposites

Polypyrrole / GO composites were prepared through sacrificial-template polymerization method. The mass ratio of graphene oxide to polypyrrole is maintained at 5:0.25, 5:0.75 and 5:1.75 and labeled as GP025, GP075, and GP175, respectively. 0.25 g of  $\text{MnO}_2/\text{GO}$  composites was dissolved in 15 ml distilled water by 5-minute ultrasonication, and then 5 ml of pyrrole monomer was mixed into the resultant solution and then sonicated it for 5 minutes. Concentrated HCl of 3 ml was added into the final solution under constant stirring. After 1 hour 40 minutes, with the help of centrifugation and cleanse 3 times with water, the composites were obtained.

## 2.5. Microwave treatment of Polypyrrole / Graphene Oxide nanocomposites

Polypyrrole / Graphene Oxide nanocomposites were treated in a microwave oven (LG/MH3948WB). The microwave oven had a maximum power of 640 Watts with four different power values such as 160 W, 320 W, 480 W, and 640 W. The different combinations were placed in a Petri dish, which was kept in the oven. Microwave irradiation on the composite GP025 for 30 seconds led to smell and resulting explosion. To avoid such a pressurized situation, time period for microwave radiation is limited for 10 seconds only. After microwave irradiation, the volume expansion of the composite observed at 320 W. Finally the composites were treated in a microwave oven, named as MGP025, MGP075, and MGP175.

## 2.6. Material Characterization methods

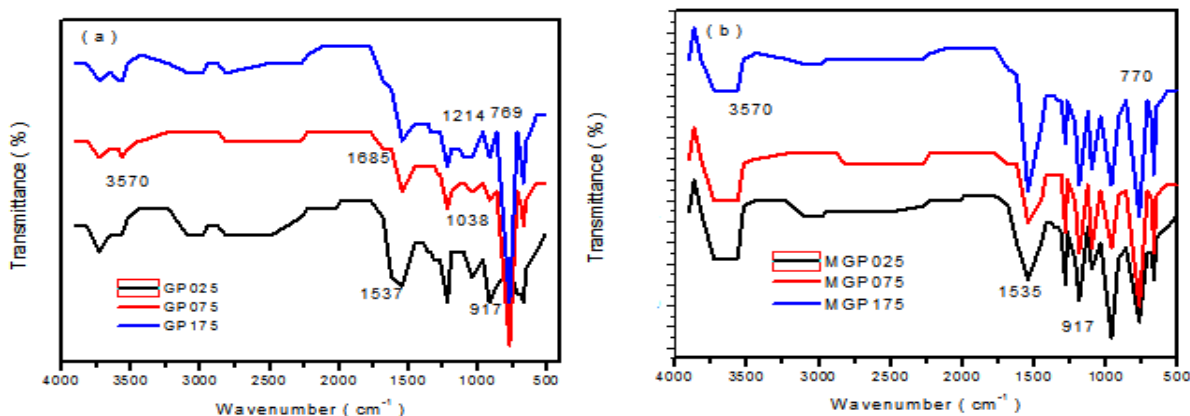
FTIR spectroscopy measurements of (G/PPy) nanocomposite and microwave treated (G/PPy) nanocomposite were measured by the KBr method recorded on Shimadzu spectrometer over a range from 400 to 4000  $\text{cm}^{-1}$ . Raman spectra were recorded on EZRaman-N analyzer employing 532 nm excitation length frequency stabilized, narrow linewidth diode Laser beam. For an electrochemical analysis, the working electrode was assembled into a 3 electrode system. The following steps are used for the preparation of the working electrode. To evaluate electrochemical performance in an aqueous solution, prepared the electrode using the composite material, mixed with an ordinary rubber solution in the weight ratio (60:40). The mixture was made as a slurry and coated on graphite rod with the help of the brush. The pasted graphite lead electrodes were dried at room temperature for 30 minutes. The loading amount of active material is approximately 200  $\mu\text{g}$ . The electrolyte used was 0.5 M  $\text{H}_2\text{SO}_4$ . The electrochemical nature of composite was tested within a range of -1.5 to 2 V. Ag / AgCl electrode, and a platinum wire was used as reference and counter electrode, respectively. CV, GCD, and EIS were carried out in an electrochemical workstation (metrohm, Netherlands, potentiostat - galvanostat).

## 3. RESULTS AND DISCUSSION

### 3.1. FTIR measurement

FTIR analysis of graphene / PPy composite and its microwave version measured by the KBr method recorded on Shimadzu spectrometer over a range from 400 to 4000  $\text{cm}^{-1}$  to understand the chemical structure of the composite. Fig. 1 shows the FTIR spectra of graphene / PPy composite and its microwave treated version. For an ordinary sample, the band at 1537  $\text{cm}^{-1}$  confirms the presence of PPy in the nanocomposite. The sharp peak observed at 1535  $\text{cm}^{-1}$  for microwave treated composite assigned to the antisymmetric ring stretching modes. The peak at 1214  $\text{cm}^{-1}$  is assigned to the N-C stretching vibration and the sharp peak observed at 769  $\text{cm}^{-1}$  indicates the presence of polymerized pyrrole. The peak at 917  $\text{cm}^{-1}$  assigned to =C-H out of plane vibration. The composite shows a broader peak at 3570  $\text{cm}^{-1}$  corresponds to the O-H stretching vibration [17]. From the FTIR spectra, an interaction between PPy and graphene confirmed, which is responsible for the development of the composite. When compared with the graphene / PPy composite, a good number of firm peaks observed in microwave treated composite and also most of the peaks are shifted to lower wavenumbers [18]. In the FTIR of the nanocomposite, it is possible to identify characteristics of PPy at 3570 and 1537  $\text{cm}^{-1}$  [22]. The composite exhibited the C-H in-plane vibration at 1214  $\text{cm}^{-1}$ , the C=C stretching vibration peaks at 1535  $\text{cm}^{-1}$ , the ring deformation at 917  $\text{cm}^{-1}$  and C-H in-plane bending at 1038  $\text{cm}^{-1}$  attributed to the characteristics of PPy [23]. FTIR spectrum exhibited characteristic absorption band at 1537  $\text{cm}^{-1}$  assigned to C=C stretching vibrations. The vibrations observed at 1038  $\text{cm}^{-1}$  assigned to C-H in-plane deformation [26]. The band at 1038  $\text{cm}^{-1}$  is considered as C-H bond in-plane vibration [37]. The peak at 1214  $\text{cm}^{-1}$  attributed to epoxy C-O stretching vibration [27]. All samples exhibited a broad band in the range of 3400 – 3800  $\text{cm}^{-1}$ , ascribed to O-H and N-H stretching vibrations [28, 35-36]. The broad

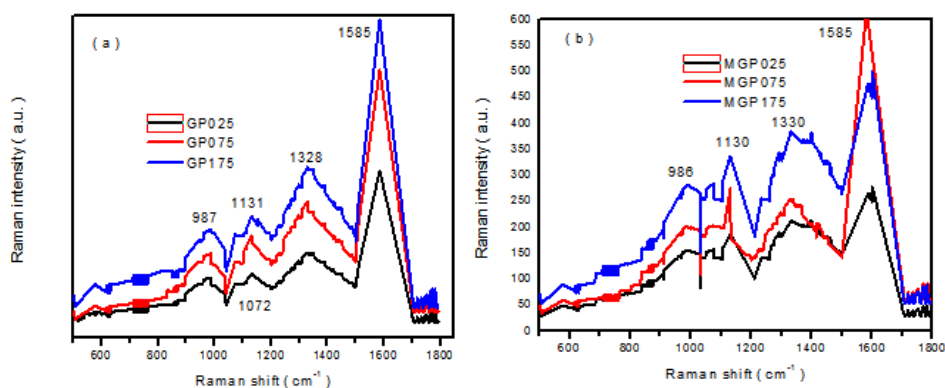
center peak obtained at  $3570\text{ cm}^{-1}$ , of composite attributed to OH vibration and structural OH groups [32].



**Figure 1.** FTIR spectra of (a) graphene/polypyrrole composite and (b) microwave treated graphene/polypyrrole composite

3.2. Raman spectroscopy

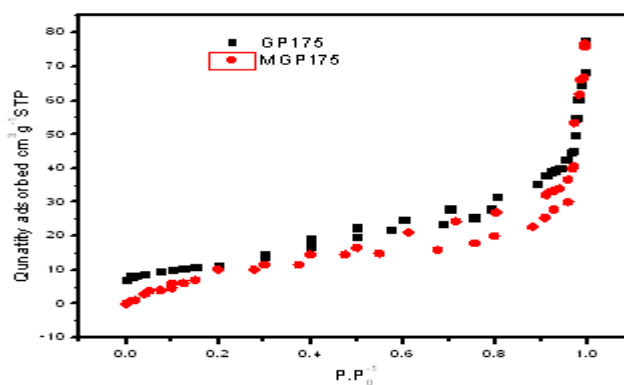
Fig. 2 demonstrates the Raman spectra of graphene/PPy composite and its microwave treated version. In the Raman spectra, the peaks at  $987\text{ cm}^{-1}$  and  $1072\text{ cm}^{-1}$  confirms the presence of PPy in composite [36]. The two peaks at  $1585$  and  $1328\text{ cm}^{-1}$ , corresponding to the G and D band respectively [38-39]. The peak at  $1585\text{ cm}^{-1}$  is due to C=C backbone stretching. The peak at  $987\text{ cm}^{-1}$  is due to ring vibration of PPy. Also, the peaks at  $1072$  and  $1131\text{ cm}^{-1}$  are due to C-H stretching [15]. Intercalation of PPy with graphene forms graphene/PPy composite [35]. The peaks around  $1072$  and  $987\text{ cm}^{-1}$  are ascribed to in and out of plane vibrations of N-H and C-H modes, respectively [23, 38]. D band appearance in the spectra indicated that during the synthesis there is a formation in the presence of structural defects and disordered structures. The small peak observed at  $937\text{ cm}^{-1}$  due to the symmetric C-H in-plane bending [24-26].



**Figure 2.** Raman spectra of (a) graphene/PPy composite and (b) microwave treated graphene/PPy composite

### 3.3. BET surface area measurement

Fig. 3 shows the nitrogen adsorption and desorption isotherms of the graphene/PPy composite, and microwave treated graphene/PPy composite at 76.44 K. According to the IUPAC classification, the isotherms of the composite can be identified as type IVa isotherm. There is an observation of the hysteresis loop in the range of 0.3 to 0.9  $P/P_0^{-1}$  for GP175 and 0.2 to 0.9  $P/P_0^{-1}$  for MGP175 suggested that the availability of mesopores in the composite.



**Figure 3.** Nitrogen adsorption / Desorption isotherms of graphene/polypyrrole composite and microwave treated graphene/polypyrrole composite

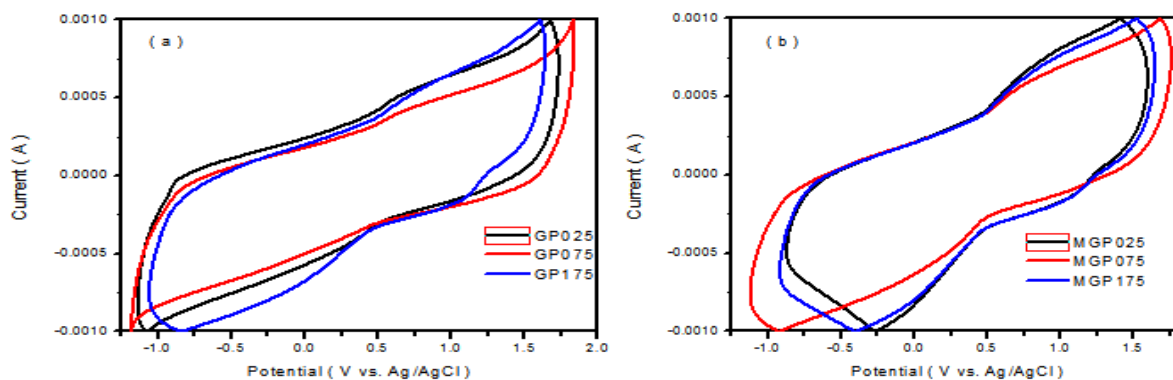
During the charging/discharging process, the mesopores facilitated the quicker transport and migration of ions, which is required for high rate supercapacitor. Also, the composite exhibited the BET area of  $24.34 \text{ m}^2 \text{ g}^{-1}$ . The microwave treated composite exhibited the BET area of  $34.13 \text{ m}^2 \text{ g}^{-1}$ .

### 3.4. Electrochemical measurements

Cyclic voltammetry (CV) tests of the graphene/PPy nanocomposite and its microwave version in a three-electrode system using  $0.5 \text{ M H}_2\text{SO}_4$  solution as an electrolyte is shown in Fig. 4 (a) with the range of  $-1.2 \text{ V}$  to  $+2 \text{ V}$ . Fig. 4 (b) shows the CV curves of microwave-treated graphene/PPy nanocomposite. The different working potential window can be observed for the different composite ratio.

Rectangular CV curve is the response of an ideal capacitor. The presence of graphene nanoparticles in polypyrrole exhibited quasi-rectangular curve and also obtained EDLC contribution from graphene and pseudocapacitance from the polypyrrole. The movement of redox peaks towards more positive voltage attributed, due to the optimized ratios of graphene and polypyrrole. Due to this redox peak movement, the electronic conductivity increases. Thus, the charge transport mechanism and redox process of the composite has been improved. The specific capacitances are  $219.7$ ,  $198.6$ ,  $230.8$ ,  $237.6$ ,  $227.4$ , and  $240.4 \text{ F g}^{-1}$  for samples GP025, GP075, GP175, MGP025, MGP125, and MGP175 at  $10 \text{ mV s}^{-1}$ . GP075 has relatively low specific capacitance compared with GP025. The graphene/PPy composite and its microwave version have excellent electrochemical nature owing to the synergistic effects between graphene and PPy. In general, electrochemical stability of the double layer

capacitor is better than that of pseudocapacitor. PPy is mostly related to redox a reaction which is in favor of pseudocapacitance. Graphene possesses excellent electrochemical performance and electron transport, which provide enough electrons for reactions with PPy. Based on intrinsic electrochemical properties of microwave-treated graphene/PPy composite, the composite exhibited excellent electrochemical stability. This graphene/PPy composite can be useful for high energy and power density supercapacitor. Table 1 summarizes the electrochemical performances of graphene/PPy composite analysis.



**Figure 4.** ( a ) Cyclic voltammograms of graphene/polypyrrole composite at 10 mVs<sup>-1</sup> and ( b ) Microwave treated graphene/polypyrrole composite at 10 mVs<sup>-1</sup>

**Table 1.** Electrochemical performance of graphene / PPy

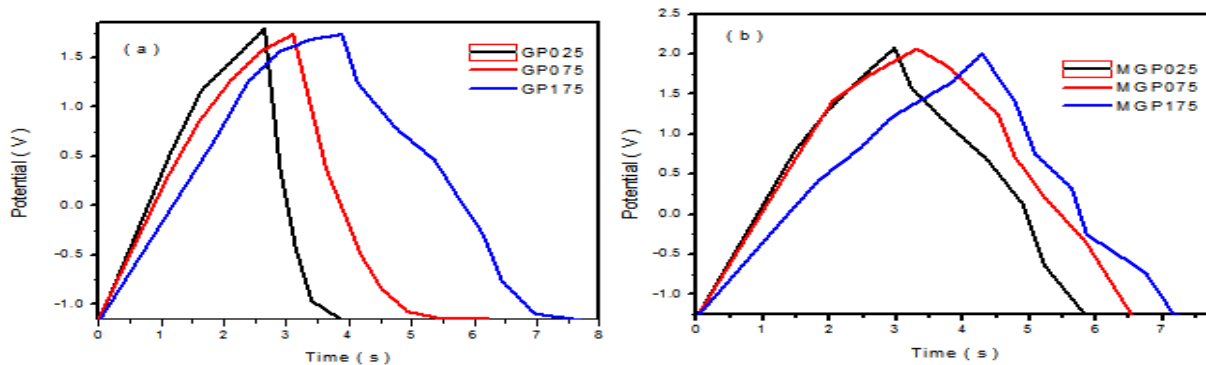
Electrode	Synthesis methods	Electrolyte	Specific Capacitance	SSA (m <sup>2</sup> g <sup>-1</sup> )	ESR (Ω)	Ref no.
Graphene / CNT/ PPy	In-situ polymerization	1 M H <sub>2</sub> SO <sub>4</sub>	453 F g <sup>-1</sup> (5 mV s <sup>-1</sup> )	----	----	1
Graphene / PPy	Modified Hummers' method, In situ chemical polymerization	1 M H <sub>2</sub> SO <sub>4</sub>	318.6 F g <sup>-1</sup> (2 mV s <sup>-1</sup> )	----	----	3
Graphene / PPy	Facile method	1 M KCl	466 F g <sup>-1</sup> (10mV s <sup>-1</sup> )	----	0.78 6	17
Graphene / PPy	Modified Hummers' method, In situ chemical oxidation polymerization	0.1 M Na <sub>2</sub> SO <sub>4</sub>	231 F g <sup>-1</sup> (1mV s <sup>-1</sup> )	----	3.8	18
Graphene / PPy	Modified Hummers' method, In situ polymerization, Vacuum filtration	Phosphate Acid/ polyvinyl alcohol	345 F g <sup>-1</sup> (1 A g <sup>-1</sup> )	157	----	19
Graphene / PPy	In situ polymerization	1 M NaCl	91.5 F g <sup>-1</sup> (50mV s <sup>-1</sup> )	----	----	20
PPy/ Graphene	Modified Hummers' method, In situ oxidative, Interfacial polymerization	1 M KCl	277.8 F g <sup>-1</sup>	33.5	----	22
PPy/	Nanoporous nickel-based CVD,	PVA –	509 F g <sup>-1</sup>	258	35	24



Graphene	Electrochemical deposition	H <sub>2</sub> SO <sub>4</sub>	(0.5 A g <sup>-1</sup> )			
PPy/ Graphene	Modified Hummers' method, reactive self-degrade methyl orange (MO)-FeCl <sub>3</sub> template method.	1 M KCl	281 F g <sup>-1</sup>	----	6.94	26
PPy /RGO	Modified Hummers' method, Chemical polymerization	1 M KOH	336 F g <sup>-1</sup>	----	119. 7	27
PPy/ Graphene / hydroxid e nanowire s	Improved Hummers method, In situ polymerization, Hydrothermal method	1 M KOH	845 F g <sup>-1</sup> (2mV s <sup>-1</sup> )	----	0.42	28
PPy/ Graphene	Modified Hummers' method, Modified oxidative polymerization	1 M KOH	418 F g <sup>-1</sup> (0.5A g <sup>-1</sup> )	----	----	30
PPy/ Graphene	Photo- Fenton reaction, In situ chemical oxidative polymerization	2 M H <sub>2</sub> SO <sub>4</sub>	485 F g <sup>-1</sup> (5mV s <sup>-1</sup> )	----	1.62	31
PPy/ Graphene	Modified Hummers' method, Electrochemical anodizing polymerization	0.5 M H <sub>2</sub> SO <sub>4</sub>	640.8 F g <sup>-1</sup> (1A g <sup>-1</sup> )	----	----	32
PPy/ Graphene	Modified Hummers' method, In situ polymerization	1 M Na <sub>2</sub> NO <sub>3</sub>	235.2 F g <sup>-1</sup>	----	----	37
PPy/ Graphene	Modified Hummers' method, electrochemical deposition	1 M KCl	310 F g <sup>-1</sup> (0.3 A g <sup>-1</sup> )	----	0.6	39
PPy/ Graphene	Modified Hummers' method, Sacrificial polymerization method, Microwave treatment	0.5 M H <sub>2</sub> SO <sub>4</sub>	240.4 F g <sup>-1</sup> (10 mV s <sup>-1</sup> )	34.13	1.34	This work

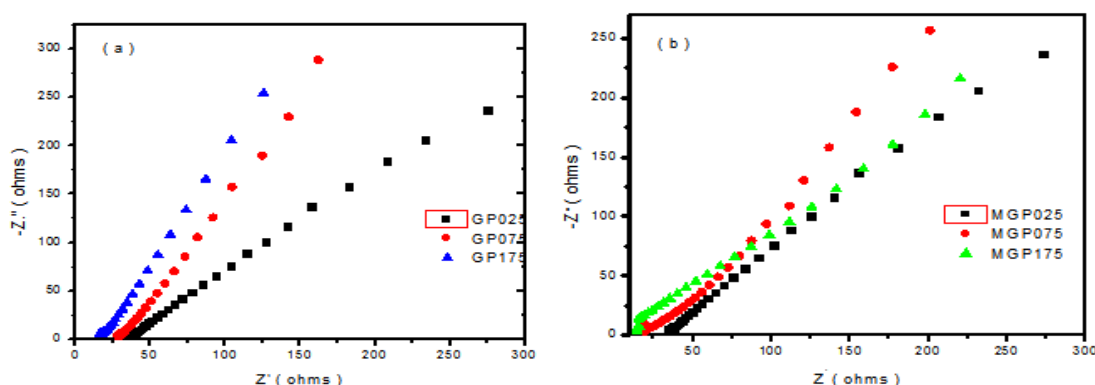
It is observed from the table that, the specific capacitance of 240.4 F g<sup>-1</sup> has been obtained from CV spectra, at 10 mV s<sup>-1</sup>. This indicates that the proposed method gives better results than the other related works. Similarly, ESR value is comparatively smaller than few reported work.

GCD curves of graphene/PPy composite and its microwave version are demonstrated in Fig. 5 (a) and (b) with a voltage window of -1.3 V to + 1.8 V at current density of 0.05 A g<sup>-1</sup>. The composites exhibited a close approximation of triangular shape, which implies that the EDLC of graphene and pseudocapacitance of PPy. The charge curve is symmetric nature to the discharge curve with a small curvature, indicated pseudocapacitance nature. Highest specific capacitance is observed for MGP175, due to the enhancement of oxidation-reduction reaction of PPy. The major limitations of conducting polymer are its lack of stability. The specific capacitance is due to the synergistic effects between graphene and PPy. The specific surface area of the electrode and efficient communication between graphene and PPy are used to improve the specific capacitance. The synergistic effects between graphene and PPy played an effective role in enhancing the nature of the composite.



**Figure 5.**GCD curves of (a) graphene / PPy composite and (b) microwave treated graphene / PPy composite

Impedance spectra of graphene/PPy composite and its microwave version are shown in Fig. 6 (a) and (b). The curve intercepted with the real axis in the high-frequency area of the Nyquist plot gives the equivalent series resistance (ESR) [36]. All samples exhibited low  $R_s$  value. The charge transfer resistance is  $1.34 \Omega$  for MGP175. The  $45^\circ$  slope in the low-frequency area indicated the Warburg resistance caused by ion diffusion in the electrolyte. Charge transfer resistance ( $R_{ct}$ ) is increased with the system’s poor conductivity, which can be identified from the diameter of semicircle. Among the different composite materials, GP175 indicated the low diffusion resistance and high capacitance. The lower ESR of GP175 is attributed to  $\pi$ - $\pi$  stacking and doping concentration level in the composite. The lower  $R_{ct}$  of GP175 nanocomposite attributed to high conductivity. The results obtained from CV, GCD and EIS are consistent. To make faster electron transfer, graphene and polypyrrole were formed an excellent conductive network.



**Figure 6.** Nyquist impedance plots of ( a ) graphene/polypyrrole composite and ( b ) microwave treated graphene/polypyrrole composite

#### 4. CONCLUSION

In this work, the graphene/PPy composite was prepared via the sacrificial template polymerization method. This composite can enhance the EDLC and pseudocapacitance, which can be ascribed to minimize the migration and diffusion paths of electrolyte ions. By varying the mass ratio of

graphene and PPy, graphene / PPy nanocomposites with a variety of combinations were synthesized and then each of the prepared composite treated with microwave oven for 10 seconds. The graphene/PPy composite and its microwave version were found to be an active material for electrodes of the supercapacitor. Among the variants, GP175 and MGP175 showed good conductivity and improved electrochemical performance. The obtained equivalent series resistance value is small. CV study revealed a specific capacitance of  $240.4 \text{ F g}^{-1}$  for MGP175 at  $10 \text{ mV s}^{-1}$ . This simple method is suitable for fabrication and microwave treatment of other composites for energy storage applications.

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