



Research Article

ISSN 2320-4818

JSIR 2020; 9(2): 54-62

© 2020, All rights reserved

Received: 16-05-2020

Accepted: 13-06-2020

Salma Bilal

National Centre of Excellence in Physical Chemistry, University of Peshawar, 2512, Peshawar, Pakistan

Akhtar Ali Shah

National Centre of Excellence in Physical Chemistry, University of Peshawar, 2512, Peshawar, Pakistan

Anwar ul Haq Ali Shah

Institute of Chemical Sciences, University of Peshawar, 25120 Peshawar, Pakistan

Hajera Gul

National Centre of Excellence in Physical Chemistry, University of Peshawar, 2512, Peshawar, Pakistan

Wahid Ullah

National Centre of Excellence in Physical Chemistry, University of Peshawar, 2512, Peshawar, Pakistan

Salma Gul

Department of Chemistry, Women University Swabi, Pakistan

Correspondence:

Salma Bilal

National Centre of Excellence in Physical Chemistry, University of Peshawar, 2512, Peshawar, Pakistan

Email: dresalmabilal@gmail.com

Dodecylbenzenesulphonic Acid Doped Polypyrrole/Graphene Oxide Composite with Enhanced Electrical Conductivity

Salma Bilal*, Akhtar Ali Shah, Anwar ul Haq Ali Shah, Hajera Gul, Wahid Ullah, Salma Gul

Abstract

Polypyrrole/graphene oxide (PPyGO) composite was synthesized through in-situ emulsion oxidative polymerization method. The composite was simultaneously doped with dodecylbenzenesulphonic acid doped (DBSA). The reaction parameters were optimized in such a way to get the composite with best possible properties. Thus, the resulting composite showed enhanced conductivity that is 73 S/cm compared to DBSA doped polypyrrole (4.18 S/cm) and graphene oxide (0.57 S/cm). As, conductivity is very important characteristic for practical application of polymeric materials, so, this material with enhanced properties can be used for multiple purposes. It was further characterized through Fourier Transform infrared spectroscopy, X-Ray Diffraction Analysis, Scanning Electron Microscopy and Thermogravimetric Analysis, which showed the successful synthesis of the composite.

Keywords: Polypyrrole/graphene oxide composite, polypyrrole, graphene oxide, conductivity.

INTRODUCTION

Intrinsically conducting polymers (ICPs) have attracted attention of engineers and researchers from a variety of fields in science and technology, as important electrode materials for energy storage devices such as electrochemical batteries, supercapacitors, electrocatalysts and biosensors, artificial muscles, gas separating membranes, electromagnetic shields, anticorrosive coatings, actuators, catalysts, materials for separation [1] and electrophotography, etc [2]. Among them the most promising ICPs are polyaniline, Polypyrrole (PPy), poly(ethylenedioxythiophene), and polythiophene and their substituted derivatives. PPy has gained special importance due to its excellent properties such as excellent capacity for energy storage, facile synthesis procedures, air stability, excellent conductivity and lower cost than many other ICPs.

Combination of various ICPs with carbon based materials have been found to reinforce the stability of the polymeric composite as well as enhance other properties such as the capacitance value and conductivity [3]. Graphene oxide (GO) is found to be an excellent support material because of its high surface area and excellent mechanical stiffness when compared with other carbon fillers. GO is composed of graphene sheets containing huge amount of oxygen containing functional groups. Among these functional groups include sp^2 -hybridized carbonyl and carboxyl groups mainly exists at the edges of sheets and sp^3 -hybridized epoxide and hydroxyl groups at the top and bottom surfaces. Van der Waals interactions among various layers of GO are varied because of these functional groups, which makes them highly hydrophilic. Due to this hydrophilic nature, its exfoliation and dispersion in aqueous media is easy which leads to easy processability.

However, GO suffer from drawback, that is poor electrical conductivity of GO [4]. GO cannot be used directly due to high electrical resistance. However, the incorporation of GO in an ICP results in the formation of composites. These composites possess advantages of both the component such as good mechanical strength due to carbon matrix and excellent electrical conductivity because of the ICP.

Method of synthesis has a great influence on the properties of synthesized material [5]. Several methods are available for synthesis of composites. Some of them are in situ chemical or electrochemical polymerization, interfacial polymerization, solution mixing, pickering emulsion polymerization and the

self-assembly method. Among them in situ polymerization is preferred because it leads to uniform dispersion of sheet materials into the polymer matrix. The uniform distribution is important to achieve material with superior properties.

In this research work, we have synthesized Polypyrrole/graphene oxide (PPyGO) composites doped with DBSA. Due to DBSA, the $-SO_3H$ functional group was incorporated into the composite, which lead to hydrogen bonding and $\pi-\pi$ delocalization and results in better association among GO and PPy in the composite [6]. It results in enhanced conductivity of PPyGO composites. In-situ chemical oxidative polymerization method was used to get the composite with uniform morphology. At optimized reaction parameters the composite showed better conductivity values and can be used in many applications.

EXPERIMENTAL

Chemicals

Reagent grade pyrrole (Alfa Aeser) was distilled twice before using as a monomer, Dodecylbenzenesulphonic Acid (DBSA) (Sigma Aldrich), ammonium per Sulphate (Scharlau), sulphuric acid (Scharlau), Potassium permanganate (Scharlau), Hydrochloric acid (Scharlau), phosphoric acid (Scharlau), hydrogen peroxide (Scharlau), Graphite flakes (Sigma Aldrich), acetone (Scharlau), methanol (Scharlau) and chloroform (Scharlau) were used as received. Details of the chemicals used are given in Table 1.

Table 1: Details of the chemicals used.

| S. No. | Chemical name | Molecular formula | Molecular weight | Density g/cm ³ | % Purity |
|--------|------------------------|---------------------------------------------------------------|------------------|---------------------------|----------|
| 1 | Pyrrole | C ₄ H ₄ NH | 67.09 | 0.966 | 96 |
| 2 | DBSA | C ₁₈ H ₃₀ O ₃ S | 326 | 1.06 | 95 |
| 3 | Chloroform | CHCl ₃ | 119.38 | 1.48 | 99 |
| 4 | Acetone | C ₃ H ₆ O | 58.08 | 0.79 | 99 |
| 5 | Hydrochloric acid | HCL | 36.46 | 1.18 | 37 |
| 6 | Phosphoric acid | H ₃ PO ₄ | 97.99 | 1.88 | 85 |
| 7 | Potassium permanganate | KMnO ₄ | 158.034 | 2.7 | 97 |
| 8 | Methanol | CH ₃ OH | 32.04 | 0.79 | 99.8 |
| 9 | Ammonium per Sulphate | (NH ₄) ₂ S ₂ O ₈ | 228.18 | 1.98 | 98 |
| 10 | Sulphuric acid | H ₂ SO ₄ | 98.079 | 1.84 | 98 |
| 11 | Hydrogen peroxide | H ₂ O ₂ | 34.01 | 1.45 | 30 |

METHODOLOGY

Synthesis of Polypyrrole

Polypyrrole (PPy) was synthesized using in-situ chemical oxidative polymerization method [20]. A typical experiment was performed by taking 0.37 mol of Pyrrole in a flask containing 100 ml of water. The mixture was stirred for few minutes and 0.015 mol of dodecylbenzenesulphuric acid (DBSA) was added to the mixture. To initiate the reaction, 0.29 molar solution of ammonium per sulphate (APS) was added drop wise to the reaction mixture. The PPy: DBSA: APS ratio was maintained as 2.58: 5.13: 1.7. A change of color from greenish to black was observed when the reaction was completed after being kept on a stirrer for 24 hours. The black powder of PPy obtained was washed several times with water, methanol and acetone and dried at room temperature. The sample was named as PPy.

Synthesis of Graphene Oxide

Graphene oxide (GO) was synthesized by improved Hummer's method [20]. 1.5 g of graphite flakes were taken in a flask already put on a stirrer,

containing a mixture of sulphuric acid (36 ml) and phosphoric acid (4 ml). The flask was put in an ice bath to proceed the reaction at low temperature. The above mixture was stirred for 30 minutes and then 3 g of potassium permanganate (KMnO₄) was added gradually. Thereafter, the ice bath was removed and 50 ml and 100 ml of distilled water, with the gap of 15 minutes, were added and the reaction mixture was stirred for another 2 hours. 10 ml of hydrogen peroxide (H₂O₂) was added which ultimately completed the reaction and color was changed from brown to yellow which confirmed the formation of graphene oxide. The product was dried in oven at 60 °C and stored. The sample of graphene oxide was named as GO.

Synthesis of Polypyrrole/Graphene Oxide Composites

The composites of Polypyrrole/graphene oxide (PPy/GO) were synthesized through in-situ polymerization. The experiment was performed by taking 0.37 mol of Pyrrole in a flask containing 100 ml of water. The mixture was stirred for few minutes and 0.015 mol of DBSA was added to the mixture. Graphene oxide (5 weight %) synthesized by improved hummer's method was added to the reaction mixture. To initiate thereaction, 0.29 Molar solution of APS was added drop wise to the reaction mixture. A change of color from greenish to dark black was observed when the reaction was completed after being kept on a stirrer for 24 hours. The black product powder of the composite obtained was washed several times with water, methanol and acetone and dried at room temperature.

The same procedure was followed and all other parameters were kept constant but the amount of the APS was varied. Samples of varying concentration of APS were named as PPyGO1, PPyGO2, PPyGO3, PPyGO4 and PPyGO5 where the concentration of APS was 0.0024 mol, 0.0049 mol, 0.007 mol, 0.009 mol and 0.12 mol, respectively. Samples containing various concentration of GO and keeping all other parameters constant were synthesized. The samples were named as PPyGO5%, PPyGO10% and PPyGO15% where the concentration of graphene oxide was 5 weight %, 10 weight %, and 15 weight %.

INSTRUMENTATION

Effect of oxidant on the percent yield of the composites was studied by synthesizing PPGO composites containing various amount of oxidant. To elucidate the structural information, the samples were characterized by Fourier Transform infrared (FTIR) spectroscopy using Shimadzu (IR Prestige-21) spectrometer (Japan). The samples were further characterized by X-ray diffraction (XRD) techniques using JDX-3532 (JEOL JAPAN). Scanning electron microscopy (SEM) of the samples was done using JEOL Scanning Electron Microscope Model JSM-5910 (Japan) to study surface morphologies of the samples. To study the thermal stability of the samples, Thermogravimetricanalysis (TGA) was made using Diamond TG/DTA (Perkin Elmer USA) analyzer. Electrical Conductivity measurements of the samples were measured using a collinear 4 probe apparatus (CMT-SR2000N, Chang Min Co. Ltd., South Korea). For this round shaped pellets having thickness of 5 mm of the samples under study were made using a compression molding machine at room temperature (298 K). The sheet resistance of the samples were recorded through which the resistivity was derived using the following equation.

$$\text{Resistivity } (\rho, \text{ ohm.cm}) = (V/I) 2\pi S$$

Where V is the applied voltage, I is the measured current passed through the sample and S is the distance between the probes.

The conductivities of the samples were measured using the following equation.

$$\text{Conductivity } (\sigma, \text{ S/cm}) = 1/\rho$$

RESULTS AND DISCUSSION

Effect of Oxidant on Percent Yield

To study the effect of oxidant on the percent yield of composites, PPyGO composites of various amounts of APS were synthesized. The amount of pyrrole (0.37mol), GO (5 mg) and DBSA (0.015 mol) was kept constant and the amount of APS varied i.e., 0.0024 mol, 0.0049 mol, 0.007 mol, 0.009 mol and 0.012 mol for samples PPyGO1, PPyGO2, PPyGO3, PPyGO4 and PPyGO5, respectively (Table 2). It was found that with increasing amount of APS the product was increased manifold. This is because that at high amount of oxidant more cations of pyrrole are formed and thus there is promotion of chain propagation reaction which subsequently results in high chain length and yield of polymer. There should be favorable conditions for promoting chain propagation reaction which occurs if high amount of oxidant is present which create

polymerized active centers. While on the contrary, if there is less amount of oxidant present, then there is less creation of polymerized active centers, though the chain propagation reaction proceeds but produces less yield. Also, the polymer yield was decreased after PPyGO4, this might be due to over oxidation [7]. The following formula was used for calculating % yield of PPyGO composites.

$$\text{Percentage yield} = \frac{\text{Weight of the composite}}{M \times \text{weight of monomer} + M \times \text{weight of dopant}}$$

Table 2: Effect of APS amount on % yield of PPyGO composites

| S. No. | Sample | Pyrrole Conc. (mol) | APS conc. (mol) | % yield |
|--------|--------|---------------------|-----------------|---------|
| 1 | PPyGO1 | 0.37 | 0.0024 | 0.0054 |
| 2 | PPyGO2 | 0.37 | 0.0049 | 0.0270 |
| 3 | PPyGO3 | 0.37 | 0.007 | 0.0704 |
| 4 | PPyGO4 | 0.37 | 0.009 | 0.975 |
| 5 | PPyGO5 | 0.37 | 0.012 | 0.1354 |

FTIR Spectroscopy

FTIR analyses of PPy, GO, PPyGO composites were carried out in the range of 500-4500 cm^{-1} using KBR pellet method. Figure 1, show FTIR spectrum of DBSA-doped PPy, GO and PPyGO composites. DBSA-doped PPy (Figure 1 (a)) shows characteristic peak at 3437 cm^{-1} which is due to N-H symmetric stretching. The peaks at 2900-2859 cm^{-1} are attributed to C-H and S=O stretching modes clearly indicating the presence of benzenoid ring in DBSA molecule. DBSA in PPy sample shows characteristic peak at 660 cm^{-1} . The peak present at 1454 cm^{-1} and 1543 cm^{-1} are reported to be because of C-C and C-N symmetric and asymmetric stretching vibrations, respectively. The peaks at 1028 and 560 cm^{-1} are due to N-H and C-H deformation, and C-S stretching

vibration [8]. These investigation shows that DBSA were successfully incorporated in the polymer matrix. FTIR of GO (Figure 1 (b)) shows two distinctive broad peaks at 3435 cm^{-1} and 1631 cm^{-1} are attributed to O-H stretching and C=O stretching vibrations, respectively. The broad peak at 1074 cm^{-1} and a small wide peak at 1369 correspond to C-O stretching and C-OH stretching vibrations. The peak at 1074 cm^{-1} clearly showing that epoxide group is present in GO layers [9].

While in the case of PPyGO composites (Figure 1 (c-h)), the characteristic absorption peaks are downshifted. This is because of the π - π interaction involved between the PPy rings and GO layers in the composite [10].

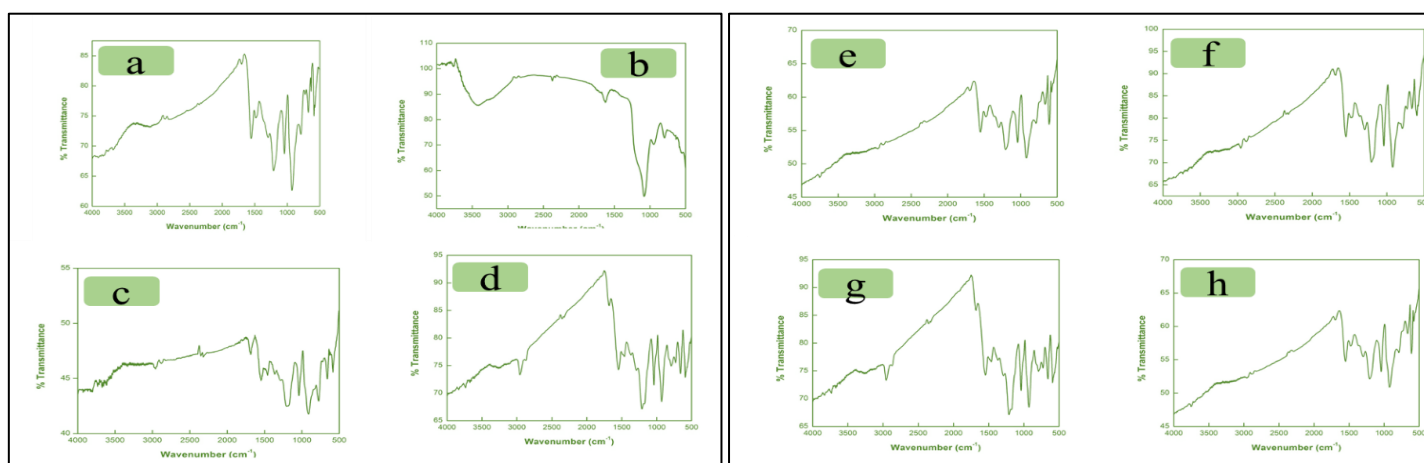


Figure 1: (a) FTIR spectrum of DBSA-doped PPy. (b) FTIR spectrum of GO. (c) FTIR spectrum of PPyGO1. (d) FTIR spectrum of PPyGO2. (e) FTIR spectrum of PPyGO3. (f) FTIR spectrum of PPyGO5 wt. %. (g) FTIR spectrum of PPyGO10 wt. %. (h) FTIR spectrum of PPyGO15 wt. %

The strong peaks in the 540-680 cm^{-1} region in the composites show that PPy is in bipolaron state in the PPyGO composites. The peaks at 1548 cm^{-1} and 1467 cm^{-1} are the characteristic peaks of PPy which are present in the PPyGO composites suggesting that PPy is present in the PPyGO composites. DBSA in PPyGO composites shows characteristic peak at 660 cm^{-1} confirming its incorporation in the PPyGO backbone.

The red shift in the spectrum of PPyGO composites was observed for π - π^* transitions on increasing percentage of GO which might be the extended conjugation length of polymer (PPy) chains [11]. This extension

in the conjugation length of the PPyGO composites corresponds to the π - π stacking between GO sheets and the polymer (PPy) backbone. Moreover, there might be some coupling present in between conjugation length of the polymer (PPy) and GO sheets.

X-Ray Diffraction (XRD) Analysis

The structure and the nature of a particular material can be best described by XRD. It is a fast analytical technique applied primarily for the

identification of crystalline materials and gives valuable information about unit cell dimensions. In XRD, a crystal is bombarded with X-rays.

XRD analysis of the synthesized showed that the DBSA-doped PPy was semicrystalline in nature. DBSA-doped PPy shows a broad peak in region between $2\theta=10^\circ$ to 30° having shoulders at $2\theta= 13^\circ, 15^\circ, 23^\circ$ and 26° (Figure 2) [12]. The small shoulders are supposed to be because of the close packing between benzene rings which is an indication of the crystalline domain of amorphous PPy powder.

The shoulder at $2\theta=17^\circ$ shows the spacing exist among the ring planes of benzene rings lie next to PPy chains [13]. ICPs usually show broad peaks which is a clear indication that ICPs are semicrystalline in nature. That is why the broad observed in the plots may be assigned to the semicrystallinity of DBSA-doped PPy. GO shows a strong peak in the region $2\theta= 11.43^\circ$ which is attributed to the interlayer spacing between the GO sheets and corresponds to reflection peak, and similar to that reported before. This indicated the formation of GO sheets [14].

The shifting of peak from $2\theta= 11.43^\circ$ to $2\theta= 11.63^\circ$ and the remarkable decrease in the intensity may be assigned to the ultrasonication of GO which resulted in its exfoliation. The broad peak at $2\theta= 26.43^\circ$ is attributed to PPy which is the characteristic peak of PPy and confirms its presence in the composite [15].

The peaks at $2\theta= 11.63^\circ$ and $2\theta= 26.43^\circ$ in all PPyGO composites indicate the successful synthesis and development of the composite. That shifting upon increasing concentration of GO can be observed clearly. That shows the interaction between DBSA-doped PPy and GO and mostly because of the involvement of π - π stacking between them [16].

PPyGO composites show the characteristic peaks of PPy and GO in its XRD findings which confirm the formation of composites. From the above findings of XRD it can be said that GO was well exfoliated in all the samples and PPy matrix allowed its uniform dispersion, though the semicrystallinity of PPy somewhat affected upon its incorporation.

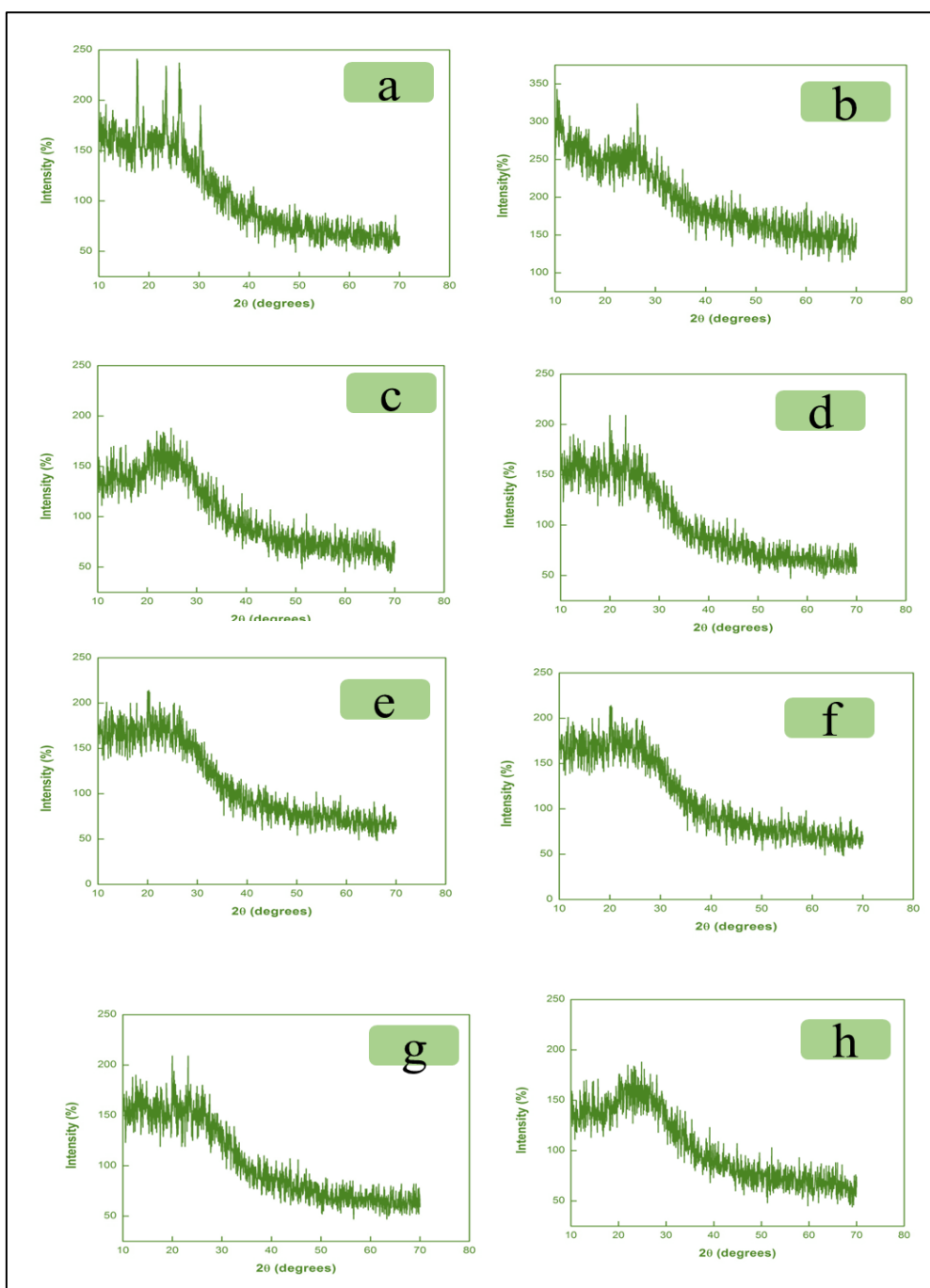


Figure 2: (a) XRD pattern of DBSA-doped PPy. (b) XRD pattern of GO. (c) XRD pattern of PPyGO1. (d) XRD pattern of PPyGO2. (e) XRD pattern of PPyGO3. (f) XRD pattern of PPyGO5 wt%. (g) XRD pattern of PPyGO10 wt%. (h) XRD pattern of PPyGO15 wt%.

Scanning Electron Microscopy (SEM)

Figure 3, show the SEM of PPy, GO and PPyGO composites synthesized at various concentrations. Porous, granular, and uniform surface morphology is shown in the case of DBSA-doped PPy. This irregular sphere-like and a continuous chain structure of PPy is observed which is consistent with reported literature [17]. Such type of morphology is preferred for gas sensing applications which promote the adsorption of gas molecules through the surface. SEM image of GO shows a flat and multilayered morphology having stacked GO sheets. Furthermore, it shows that it is well exfoliated with a uniform and clean surface. GO shows layer-by-layer network structure and the same morphology of GO has been reported in the literature [18].

Presence of DBSA and GO in the PPy-GO composites greatly influenced the morphology of PPy which confirmed that PPy was successfully polymerized on GO sheets surface [19]. The sphere-like or hemispherical morphology of PPy observed before was not in the case of PPy-GO composites. A flaky and rough morphology of composites was observed which may because of the presence of GO in polymer matrix. As DBSA was used as a dopant in all the composites, the composites morphology was strongly affected by it. The agglomeration in PPy and PPy-GO composites are thought to be because of the DBSA. Thus if high amount of DBSA was used it may lead to lowering of the conductivity of the polymer and conducting polymer composites [20]. A change in morphology of the composites was observed on for composites of varying concentration of GO in the composites. This change of the composites from individual polymer might be attributed to the polymerization of PPy on the GO surface.

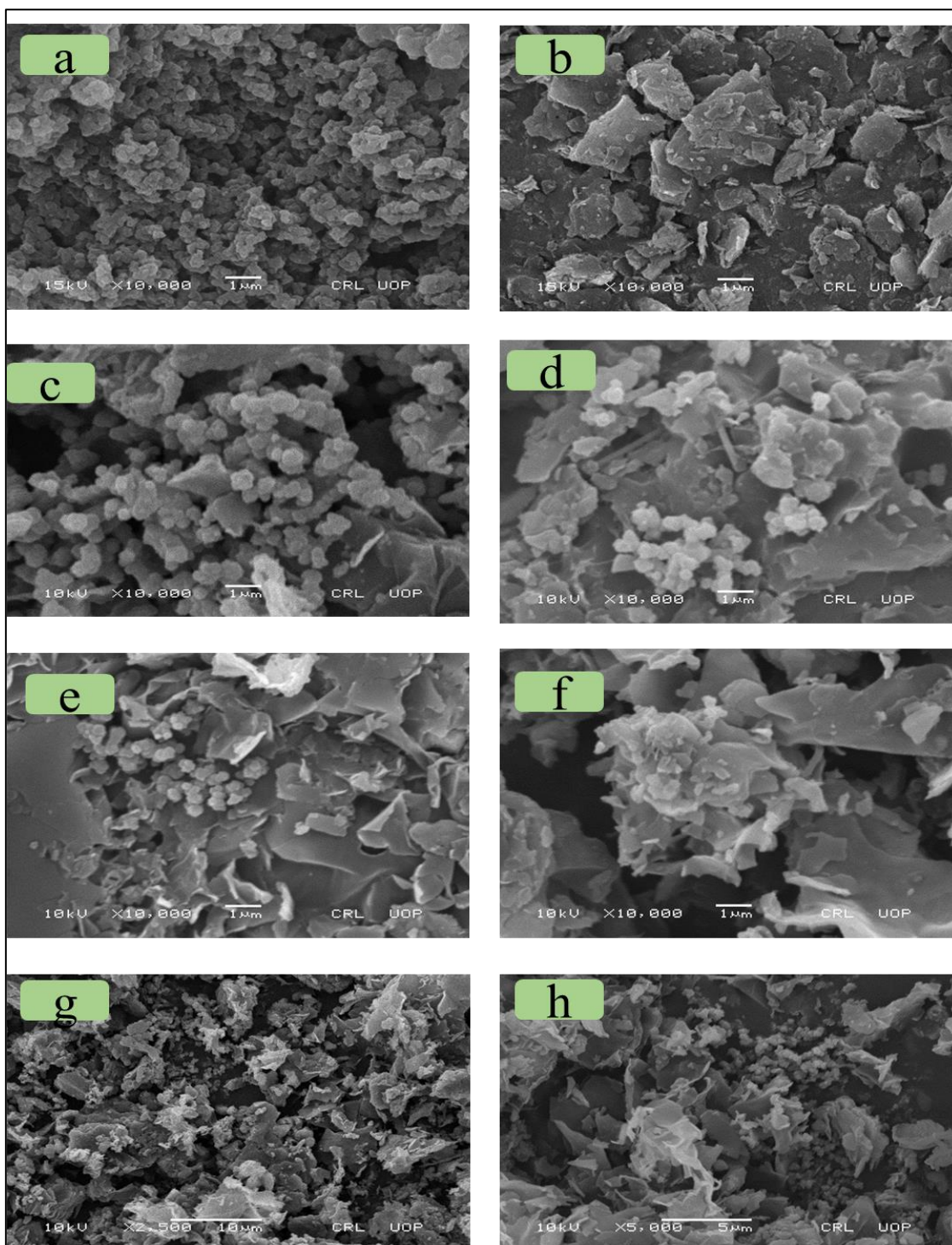


Figure 3: (a) SEM of PPy. (b) SEM of GO. (c) SEM of PPyGO1. (d) SEM of PPyGO2. (e) SEM of PPyGO3. (f) SEM of PPyGO5wt%. (g) SEM of PPyGO10wt%. (h) SEM of PPyGO15wt%.

Thermogravimetric Analysis (TGA)

A balance of thermal stability, processibility and conductivity is important for various applications. Among other techniques, TGA is a wonderful technique used to study how the synthesized polymer and composites are thermally stable and what their thermal decomposition temperatures are. TGA measures the effect of temperature as a function of change or weight loss, or time, in the sample under controlled atmosphere.

The TGA graphs of PPy, GO, and composites are shown in Figure 4. Various weight loss steps are given in Table 3. PPy showed three distinct losses. The first loss is reported to have been because of the removal and elimination of moisture from the samples. The second loss is owing to the removal of DBSA from PPy. The third weight loss of the PPy at high temperature shows the breaking of polymer chain which results in the formation of highly volatile gases. PPy shows thermal stability up to 600 °C which is much higher than the thermal stability reported for PPy earlier i.e. 450 °C [21]. GO shows major weight loss at 215 °C to 310 °C which reveals that functional groups are present on its surface. During this weight loss, functional groups containing oxygen are removed from GO and the material left behind is graphene and graphite oxide. The residual weight of GO is 60 wt. %, showing 40 wt. % functional groups were present on GO before it was thermally treated by TGA [22].

Table 3: Showing weight loss of PPy, GO, and PPyGO composites

| Sample | Temperature range (°C) | % Weight loss |
|------------|------------------------|---------------|
| PPy | 30-66 | 4 |
| | 284-510 | 55 |
| GO | 215-310 | 25 |
| | 400-500 | 35 |
| PPyGO1 | 200-300 | 20 |
| | 400-500 | 80 |
| PPyGO2 | 200-300 | 20 |
| | 400-500 | 70 |
| PPyGO3 | 200-300 | 25 |
| | 400-500 | 75 |
| PPyGO5wt% | 200-300 | 20 |
| | 400-500 | 70 |
| PPyGO10wt% | 200-300 | 25 |
| | 400-500 | 80 |
| PPyGO15wt% | 200-300 | 25 |
| | 400-500 | 75 |

The thermal stability of the composites is found to be increased upon the incorporation of GO in the polymer matrix, though the degradation of composites is nearly the same. However, the major degradation of the composites starts at higher temperatures when it is compared with PPy. In TGA curve of composites, the weight loss near 200 °C might be of the pyrolysis of labile functional groups containing oxygen [23].

After 200 °C, the major loss shown in Figure 4, is reported to be because of the decomposition of PPy from the composites. The residual value in case of composites is found to be increased and enhanced comparatively. PPyGO composites show 16-32 % weight retention at 620 °C. This might be because of the presence of carbon net structure in the PPyGO composites [24]. PPy and PPyGO composites synthesized here are found to be thermally stable up to 650 °C. The residual weight loss of PPy and PPyGO are comparatively higher. So the synthesized PPy and PPyGO composites can be applied where high thermal stability of the material is required.

Electrical Conductivity

The electrical conductivities of the PPy, Go and PPyGO composites were measured and the values are mentioned in the Table 4. The electrical conductivity of GO was recorded 0.5 S/cm which was same as reported before in the literature [25]. The conductivity of DBSA-doped PPy found to be increased. This increase in the conductivity is attributed to the incorporation of the bulky DBSA in the polymer matrix. Omastova et al. [26] reported that anionic surfactant form an ionic bond with polycation

of PPy which then adsorbed on the PPy and causes enhancement in the conductivity and yield of the PPy. Omastova et al prepared samples of PPy in the presence of DBSA which show enhanced conductivities when compared to PPy prepared without DBSA surfactant. The conductivity of the PPy synthesized in the presence of surfactant was much higher. PPy chain has got different types of structural disorders which greatly alter the charge-carrier transport, and mainly the conductivity of the polymer [27]. There is possibility to make changes in the parameters responsible for conducting network in PPy chains and chains regularity by introducing anionic surfactants during polymerization.

PPyGO1, PPyGO2 and PPyGO3 showed enhanced conductivities. The enhanced conductivities are attributed due to the presence of DBSA in the composite matrix and GO. PPyGO 5 wt. % , PPyGO 10 wt. % , and PPyGO 15 wt. % contained various amount of GO and showed increasing trend in conductivity. This increasing trend can be attributed to different reasons. Firstly, it may be because of extended hydrogen bonding between DBSA-doped PPy and GO which allows high extended π -conjugation in the former case [28]. Secondly, the polymerization of DBSA-doped PPy on GO surface restricts and prevents the twisting of the former backbone away from planarity, which seems to play an important role in increasing conductivity. Thirdly, at higher GO content there may have been π - π stacking between the polymer backbone and GO which increase the electron movement in the composite [29]. And, lastly, GO owing to its high aspect ratio and greater surface area act as effective conducting bridges and thus even increase the conductivity of the composite even if it is present in low amount.

Moreover, pressing pressure also plays a greater role in enhancing the conductivity of the samples. When the pressing pressure is increased from 2 ton to 4 ton the voids and entrapped air in the polymer and composite matrix can be cleared and GO can come in contact with the polymer and makes a conductive path, reducing the resistance in the composite structure [30-35]. When the pressing pressure is increased manifold, it then does not show dramatic increase in the conductivity which may be due to the fact that at 4 ton pressure the entrapped air and voids have already been removed. In order to conclude, from the above discussion it can be concluded that the nature of dopant, synthetic method and pressing pressure can collectively be the instrumental factors in enhancing the conductivities of the polymer. The conductivities of the prepared materials are remarkably high and can be more increased if the GO is used in reduced form.

Table 4: Showing the conductivities of DBSA-doped PPy, GO, and PPyGO composites

| S.no | Samples | Conductivity (S/cm) |
|------|----------------|---------------------|
| 1 | DBSA-doped PPy | 4.18 |
| 2 | GO | 0.57 |
| 3 | PPyGO1 | 42.2 |
| 4 | PPyGO2 | 44 |
| 5 | PPyGO3 | 46 |
| 6 | PPyGO 5 wt. % | 48 |
| 7 | PPyGO 10 wt. % | 65 |
| 8 | PPyGO 15 wt. % | 73 |

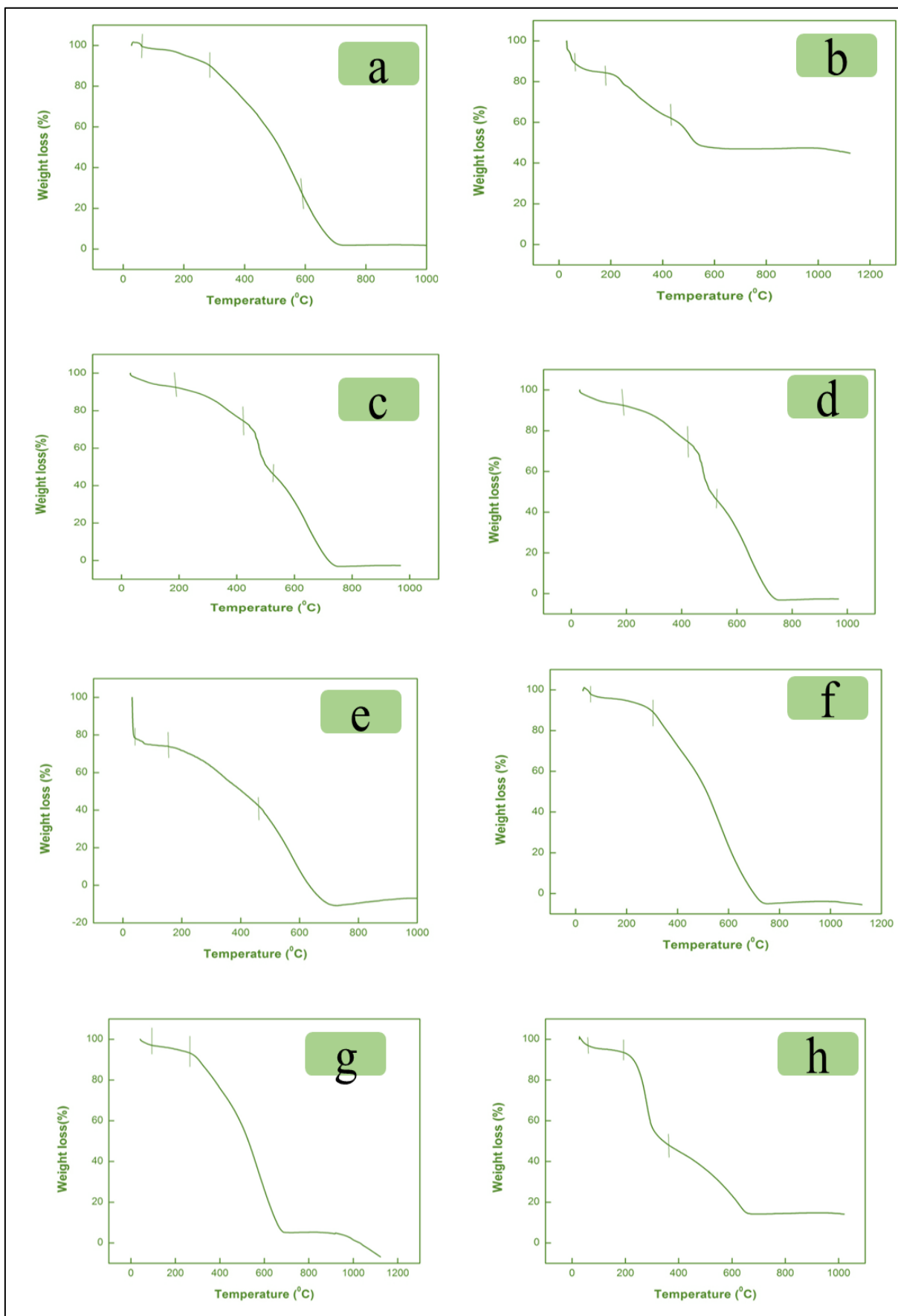


Figure 4: (a) TGA of PPy. (b) TGA of GO. (c) TGA of PPyGO1. (d) TGA of PPyGO2. (e) TGA of PPyGO3. (f) TGA of PPyGO 5wt. %. (g) TGA of PPyGO10 wt. %. (h) TGA of PPyGO15 wt. %

CONCLUSION

In conclusion, highly conductive DBSA-doped PPyGO composites were synthesized via in situ chemical oxidative polymerization pathway by using Pyrrole as a monomer, DBSA a dopant and APS an oxidant in the presence of GO. The most important outcome of the method is obtaining PPy and PPyGO composites in very high yield with very good conductance value of 73 S/cm, a thermal stability of 650 °C. The properties of the composites mostly show dependence on the amount of the oxidant. FTIR spectra of DBSA-doped PPy and PPyGO composites reveal the presence of respective functional groups confirming the formation of composites. SEM images of the DBSA-doped PPy and PPyGO composites showed granular, porous, and rough and flaky morphology, respectively. The morphology was found to be greatly affected in the presence of DBSA and increasing amounts of GO. XRD findings suggest semicrystalline nature of the PPy and PPyGO composites.

REFERENCES

1. Wu J, Pawliszyn J. Preparation and applications of polypyrrole films in solid-phase microextraction. *Journal of Chromatography A*. 2001; 909 (1):37-52.
2. Tat'yana VV, Efimov ON. Polypyrrole: a conducting polymer; its synthesis, properties and applications. *Russian chemical reviews*. 1997;66 (5):443.
3. Konwer S, Boruah R, Dolui SK. Studies on conducting polypyrrole/graphene oxide composites as supercapacitor electrode. *Journal of electronic materials*. 2011 Nov 1;40 (11):2248.
4. Bora C, Dolui SK. Fabrication of polypyrrole/graphene oxide nanocomposites by liquid/liquid interfacial polymerization and evaluation of their optical, electrical and electrochemical properties. *Polymer*. 2012 Feb 17;53 (4):923-32.
5. Gul H, Shah AU, Krewer U, Bilal S. Study on Direct Synthesis of Energy Efficient Multifunctional Polyaniline-Graphene Oxide Nanocomposite and Its Application in Aqueous Symmetric Supercapacitor Devices. *Nanomaterials*. 2020 Jan;10 (1):118.
6. Gul H, Shah AU, Bilal S. Fabrication of Eco-Friendly Solid-State Symmetric Ultracapacitor Device Based on Co-Doped PANI/GO Composite. *Polymers*. 2019 Aug;11(8):1315.
7. Bilal S, Gul H, Gul S. One Pot Synthesis of Highly Thermally Stable Poly (2-Methylaniline) for Corrosion Protection of Stainless Steel. *Iranian Journal of Science and Technology, Transactions A: Science*. 2018 Dec 1;42(4):1915-22.
8. Hsu FH, Wu TM. In situ synthesis and characterization of conductive polypyrrole/graphene composites with improved solubility and conductivity. *Synthetic metals*. 2012 May 1;162(7-8):682-7.
9. Deshpande PP, Jadhav NG, Gelling VJ, Sazou D. Conducting polymers for corrosion protection: a review. *Journal of Coatings Technology and Research*. 2014 Jul 1;11(4):473-94.
10. Liesa F, Ocampo C, Alemán C, Armelin E, Oliver R, Estrany F. Application of electrochemically produced and oxidized poly (3, 4-ethylenedioxythiophene) as anticorrosive additive for paints: Influence of the doping level. *Journal of applied polymer science*. 2006 Oct 15;102(2):1592-9.
11. Hermelin E, Petitjean J, Lacroix JC, Chane-Ching KI, Tanguy J, Lacaze PC. Ultrafast electrosynthesis of high hydrophobic polypyrrole coatings on a zinc electrode: Applications to the protection against corrosion. *Chemistry of Materials*. 2008 Jul 8;20(13):4447-56.
12. Ahuja T, Mir IA, Kumar D. Biomolecular immobilization on conducting polymers for biosensing applications. *Biomaterials*. 2007 Feb 1;28(5):791-805.
13. Lv Z, Chen Y, Wei H, Li F, Hu Y, Wei C, Feng C. One-step electrosynthesis of polypyrrole/graphene oxide composites for microbial fuel cell application. *Electrochimica Acta*. 2013 Nov 30;111:366-73.
14. Ruhi G, Bhandari H, Dhawan SK. Corrosion resistant polypyrrole/flyash composite coatings designed for mild steel substrate. *American Journal of Polymer Science*. 2015;5(1A):18-27.
15. Wang LX, Li XG, Yang YL. Preparation, properties and applications of polypyrroles. *Reactive and Functional Polymers*. 2001 Mar 1;47(2):125-39.
16. Omastova M, Trchová M, Kovářová J, Stejskal J. Synthesis and structural study of polypyrroles prepared in the presence of surfactants. *Synthetic Metals*. 2003 Jul 4;138(3):447-55.
17. Chen GZ, Shaffer MS, Coleby D, Dixon G, Zhou W, Fray DJ, Windle AH. Carbon nanotube and polypyrrole composites: coating and doping. *Advanced Materials*. 2000 Apr;12(7):522-6.
18. Wang Z, Yuan TB, Hou ZY, Zhou WD, Lu JD, Ding HB, Zeng XY. Laser-induced breakdown spectroscopy in China. *Frontiers of Physics*. 2014 Aug 1;9(4):419-38.
19. Amaike M, Yamamoto H. Preparation of polypyrrole by emulsion polymerization using hydroxypropyl cellulose. *Polymer journal*. 2006 Jul;38(7):703-9.
20. Ateh DD, Navsaria HA, Vadgama P. Polypyrrole-based conducting polymers and interactions with biological tissues. *Journal of the royal society interface*. 2006 Dec 22;3(11):741-52.
21. Bredas JL, Street GB. Polarons, bipolarons, and solitons in conducting polymers. *Accounts of Chemical Research*. 1985 Oct 1;18(10):309-15.
22. Jayamurgan P, Ponnuswamy V, Ashokan S, Mahalingam T. The effect of dopant on structural, thermal and morphological properties of DBSA-doped polypyrrole. *Iranian Polymer Journal*. 2013 Mar 1;22(3):219-25.
23. Hatchett DW, Josowicz M. Composites of intrinsically conducting polymers as sensing nanomaterials. *Chemical reviews*. 2008 Feb 13;108(2):746-69.
24. Imran SM, Kim Y, Shao GN, Hussain M, Choa YH, Kim HT. Enhancement of electroconductivity of polyaniline/graphene oxide nanocomposites through in situ emulsion polymerization. *Journal of materials science*. 2014 Feb 1;49(3):1328-35.
25. Kang H, Geckeler KE. Enhanced electrical conductivity of polypyrrole prepared by chemical oxidative polymerization: effect of the preparation technique and polymer additive. *Polymer*. 2000 Aug 1;41(18):6931-4.
26. Liu J, Bai H, Wang Y, Liu Z, Zhang X, Sun DD. Self-assembling TiO₂ nanorods on large graphene oxide sheets at a two-phase interface and their anti-recombination in photocatalytic applications. *Advanced Functional Materials*. 2010 Dec 8;20(23):4175-81.
27. Li S, Lu X, Xue Y, Lei J, Zheng T, Wang C. Fabrication of polypyrrole/graphene oxide composite nanosheets and their applications for Cr (VI) removal in aqueous solution. *PLoS One*. 2012;7(8).
28. Dai L, Lu J, Matthews B, Mau AW. Doping of conducting polymers by sulfonated fullerene derivatives and dendrimers. *The Journal of Physical Chemistry B*. 1998 May 21;102(21):4049-53.
29. Saville P. Polypyrrole Formation and Use. *DRDC Atl. TM 2005, 4 (January), 1-33*
30. Zhu Y, Murali S, Cai W, Li X, Suk JW, Potts JR, Ruoff RS. Graphene and graphene oxide: synthesis, properties, and applications. *Advanced materials*. 2010 Sep 15;22(35):3906-24.
31. Deng M, Yang X, Silke M, Qiu W, Xu M, Borghs G, Chen H. Electrochemical deposition of polypyrrole/graphene oxide composite on microelectrodes towards tuning the electrochemical properties of neural probes. *Sensors and Actuators B: Chemical*. 2011 Nov 15;158(1):176-84.
32. Shukla N, Thakur AK, Shukla A, Marx DT. Ion conduction mechanism in solid polymer electrolyte: an applicability of almond-west formalism. *Int J Electrochem Sci*. 2014 Dec 1;9(12):7644-59.
33. Yang Y, Liu T. Fabrication and characterization of graphene oxide/zinc oxide nanorods hybrid. *Applied Surface Science*. 2011 Aug 15;257(21):8950-4.

34. Stejskal J, Omastova M, Fedorova S, Prokeš J, Trchová M. Polyaniline and polypyrrole prepared in the presence of surfactants: a comparative conductivity study. *Polymer*. 2003 Mar 1;44(5):1353-8.
35. Imran SM, Shao GN, Haider MS, Abbas N, Hussain M, Kim HT. Electroconductive performance of polypyrrole/graphene nanocomposites synthesized through in situ emulsion polymerization. *Journal of Applied Polymer Science*. 2015 Apr 15;132(15)