The Green Synthesized Reduced Graphene Oxide (RGO) Doped PEDOT:PSS Composite for Electrical Improvement

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Abstract

In this paper, Reduced graphene oxide (RGO) was synthesized from graphene oxide (GO) with an environment-friendly method by using polyphenol that contained a phytoextract of fresh potato as a reducing agent. Graphene oxide was prepared by modified Hummer's method. The extent of reduction was studied by varying volume reducing agent 20, 40 and 60 ml respectively. The resulting product has been characterized by Fourier transform spectroscopy, Raman spectroscopy and X-ray diffraction. Then RGO was composited with PEDOT:PSS copolymer to improve the electrical property. The electrical property was also measured by a four-point probe. From the electrical property test, the PEDOT: PSS composite with RGO has a lower electrical resistance. The above results confirm that the preparation of RGO and electrical improvement were successful.

Keywords**:** *green synthesis, graphene oxide, reduced graphene oxide, composite material, phytoextract, electrical property*

1. Introduction

PEDOT:PSS or (poly(ethylene-3,4-dioxythiophene):poly(styrene sulfonic acid)) is one of the most popular conducting transparent copolymer widely used as an electrode in optoelectronic and photovoltaic applications due to its high conductivity, transmittance and flexibility. PEDOT:PSS can be easily processed in solution and deposited on a rough surface. The electrical properties of PEDOT:PSS depend on nanostructure, that designed by a chemical method such as solvent treatment (Dimitriev et al., 2009), by a physical method such as heat treatment (Friedel et al., 2011) and by doping with conductive materials such as graphene (Yoo et al., 2014; Zhang et al., 2014) and carbon nanotube (Song et al., 2013).

Graphene is a two-dimensional sheet, it consists of a single layer of sp^2 hybridized carbon with magnificent mechanical, electrical, thermal and optical properties. Graphene was prepared by various techniques such as hydrothermal dehydration (Yong et al., 2009), photocatalytic (Williams et al., 2008), solvothermal reduction (Lin et al.,2010), chemical vapor deposition (Wei et al., 2009), catalytic and chemical reductions (Tung et al., 2009). Out of all these techniques, chemical reduction of exfoliated graphene oxide (GO) is the most popular method because it is the easy to produce high efficiency graphene in large scale. Many of chemical reducing agents has been used for the reduction of graphene oxide such as, ascorbic acid, sodium borohydride, hydrazine (Park et al., 2009) etc. The main disadvantage of using the chemical reducing agent is the irreversible aggregation of the product due to strong Vander Waals forces between reduced graphene oxide (RGO) sheets and its high toxicity (Firdhouse & Lalitha, 2013). In order to overcome this problem, organic molecules are highly considered as a reducing agent of GO to improve the dispersion property of RGO sheets in a solvent and improve the ability of adhesion on the surface and prevent reoccurrence of RGO sheet after reduction (Sadhukhan et al., 2016). Among these, use of phytoextracts as reducing agents has been explored earlier such as carrot roots (Kuila et al., 2012), green tea (Wang et al., 2011), bacteria (Gurunathan et al., 2013). Phytoextract presence of compounds like polyphenols and flavonoids which act as excellent reducing agents.

Herein, we synthesized reduced graphene oxide (RGO) by using phytoextract of fresh potato as a reducing agent and studied on the extent of reduction by varying volume of reducing agent. These phytoextracts contain many phenolic compounds, and it has a large number of hydroxyl groups, which helps

in partial removal of oxygen functionality group from graphene oxide (GO). The GO was prepared by modified Hummer's method. Furthermore, the RGO was composited with PRDOT:PSS copolymer for electrical property improvement.

2. Objectives

1. To synthesize and reduce graphene oxide using potato phytoextract.
2. To prepare RGO doped PEDOT:PSS composite to improve its electrical property.

3. Materials and Methods

3.1 Materials

Graphite fine powder extra pure was purchased from Merck Germany. Concentrate sulphuric acid (98% H_2SO_4), Potassium permanganate ($KMnO_4$), Hydrogen peroxide (30% H_2O_2), Sodium nitrate ($NaNO_3$), methanol and Pristine PEDOT:PSS aqueous solution, consisting of 1.3 wt.% of commercial PEDOT:PSS (0.5% PEDOT:0.8% PSS) dispersed in water were purchased from Sigma-Aldrich, USA. The fresh potatoes were purchased from a local market.

3.2 Preparation of Graphene Oxide (GO)

To Prepare graphene oxide by modified Hummer's method, 1 g of graphite powder mixed with 0.5 g of sodium nitrate and 25ml of 98% sulfuric acid in a three-round bottom flask that stirring and placed in an ice bath. Gradually added 3 g of potassium permanganate to the mixture and stirred for 2 hours, then add 500 ml of distilled water and 20 ml of hydrogen peroxide to stop the reaction. Then the mixture is washed with distilled water and methanol several times. Finally, they are centrifuged and filtered to get the paste and dried in the oven at 60 ^{o}C for 24 hours.

3.3 Preparation of potato phytoextract

25 g of fresh potatoes were sliced into thin strips. After that, they were cleaned with distilled water and boil in 50 ml of DI water for 5 minutes before grinding to prepare a paste. Then, the mixture is centrifuged and filtered to remove sediment and store liquid.

3.4 Synthesis of reduced graphene oxide (RGO)

0.04 g of graphene oxide was mixed with 80 ml of de-ionized water and sonicate for 30 min. Then, phytoextracts with different volumes (20, 40, and 60 ml) were added to disperse a solution of GO and stirred at 95 ^{o}C for 12 hours under refluxed conditions in the oil bath. After that, the mixture is cooled at room temperature, then centrifuged and washed with distilled water before filtered and dried at 60 ^{o}C for 24 hours.

3.5 Preparation of RGO doped PEDOT:PSS composite

To prepare the RGO doped PEDOT:PSS composite, 1 g of RGO was added to 10 mL of isopropyl alcohol. The mixture was sonicated for 1 hour. Then added to 20 ml of pristine PEDOT:PSS aqueous into the mixture and stirred for three hours.

3.6 Characterization

The resulting product such as graphite, graphene oxide and different reduced graphene oxides were characterized and analyzed by using X-ray diffraction, FTIR spectroscopy and Raman spectroscopy. X-ray diffraction was performed at room temperature by LabX XRD-6100 diffractometer. The scanning rate was 2°/min. FTIR spectrum was recorded using VERTEX 70 spectrometer. Raman spectra were measured on Senterra Raman spectrometer with 532 nm laser excitation. Moreover, the electrical property was investigated by a four-point probe.

4. Results and Discussion

X-ray diffraction is used to characterize the distance of layer and crystal structure of materials. The XRD pattern of graphite, graphene oxide (GO) and reduced graphene oxide (RGO) as shown in Figure 1 The result shows that graphite had a strong and sharp peak at 2θ = 26.14° relevant to the (111) plane (d-spacing 0.34 nm). The diffraction peak of graphene oxide was observed at 2θ = 25.32° and 2θ = 10.80° (d-spacing 0.35 nm and 0.82 nm, respectively). The increase in d-spacing is attributed to the intercalated oxygen functional groups present between the layer of graphite (Sadhukhan et al., 2016). After reduction, the diffraction peak of GO at 10.80° disappeared and the broad peak appeared between 2θ = 19.64° and 2θ = 24.98° for RGO (d-spacing 0.45 nm and 0.36 nm). The result corresponding interlayer spacing of RGO decrease due to elimination of some of oxygen functional groups in GO layer. The layers of GO are separated, and formation of a few layers of RGO sheet (Liu et al., 2013), and the peak has broad due to the thickness of graphite layer was reduced because of breakdown graphite structure which causes the structure to become disorder (Lingaraju et al., 2019).

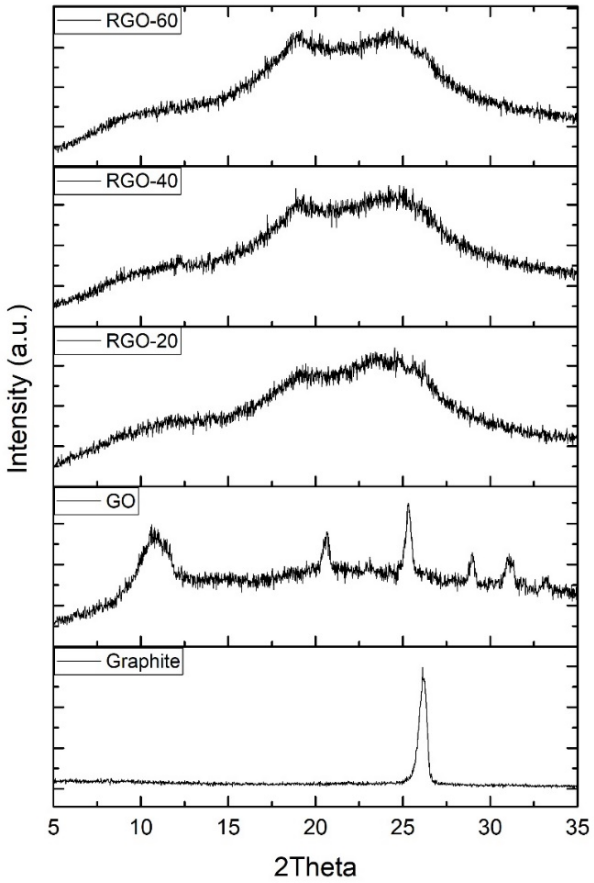

Figure 1 XRD pattern of Graphite, GO, and RGO that was synthesized from GO and using different volumes of potato phytoextract such as 20, 40 and 60 ml respectively (RGO-20, RGO-40 and RGO-60).

FTIR spectroscopy is used to confirm the successful preparation of reduced graphene oxide by using fresh potato extract as a reducing agent. Figure 2 shows the FTIR spectra of graphene oxide (GO) and different reduce graphene oxide (RGO-20, RGO-40, RGO-60). The absorption peak corresponding to different oxygen functional groups. The peak of GO observed at 3300 cm^{-1}, 2950 cm^{-1}, 1718 cm^{-1}, 1573 cm^{-1} and 1148 cm^{-1} indicates OH stretching, CH stretching, carboxyl, carbonyl and epoxy group respectively (Phukan et al.,

2019;Roy et al., 2015). After reduction of GO, the intensity of some peaks of RGO compared to GO is decreased such as 1148 cm^{-1}. The results confirm that some of oxygen functional groups successively dispersed in RGO samples (Sadhukhan et al., 2016). Besides, The peak of RGO observed at around 2950 $cm^{-1,}$ and 3280 cm^{-1} indicates CH stretching and water absorption in the structure of RGO. In a comparison of different RGOs, the intensities of the peak at around 1530 cm^{-1} and 1160 $cm^{-1,}$ which indicates carbonyl and epoxy group in RGO-20, RGO-40, and RGO-60 are decreased, respectively. Thereby indicating the content of reducing agent increases, efficient reduction of GO will also increase.

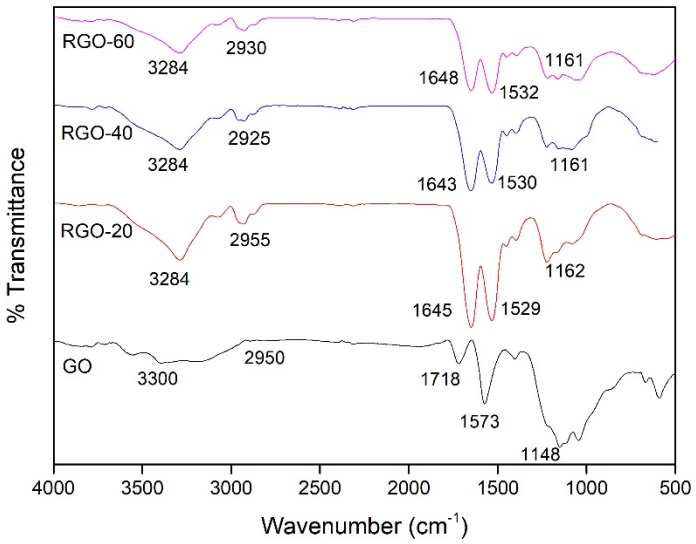

Figure 2 FTIR spectra of GO, and RGO that was synthesized from GO and using different volumes of potato phytoextract such as 20, 40 and 60 ml respectively (RGO-20, RGO-40 and RGO-60).

Raman spectroscopy is an essential tool to study the electronic structure of carbon materials. The main feature in Raman spectra is D band and G band. The D band is related to the disorder in sp^2 hybridized carbon materials, and the G band is related to common sp^2 carbon form (Roy et al., 2015; Ferrari, 2007). Figure 3. shows Raman spectra of GO, RGO-20, RGO-40 and RGO-60. The D band and G band were observed at 1339 cm^{-1} and 1578 cm^{-1} for GO, 1338 cm^{-1} and 1565 cm^{-1} for RGO-20, 1336 cm^{-1} and 1570 cm^{-1} for RGO-40 and 1329 cm^{-1} and 1565 cm^{-1} for RGO-60. The intensity ratio of D band and G band (I_D/I_G) of GO is 0.996 whereas for RGO-20, RGO-40 and RGO-60 are 0.909, 0.764 and 0.727 respectively. The decrease in I_D/I_G implies that after reduction, the intense D band of RGO has decreased and G band shifted to a higher intensity which indicates that the conjugated graphitic network (sp^2 carbon) was re-established after elimination of some of oxygen functional group from GO, and the number of layers in solid-state materials was decreased (Yaragalla et al., 2016; Coros et al., 2020).

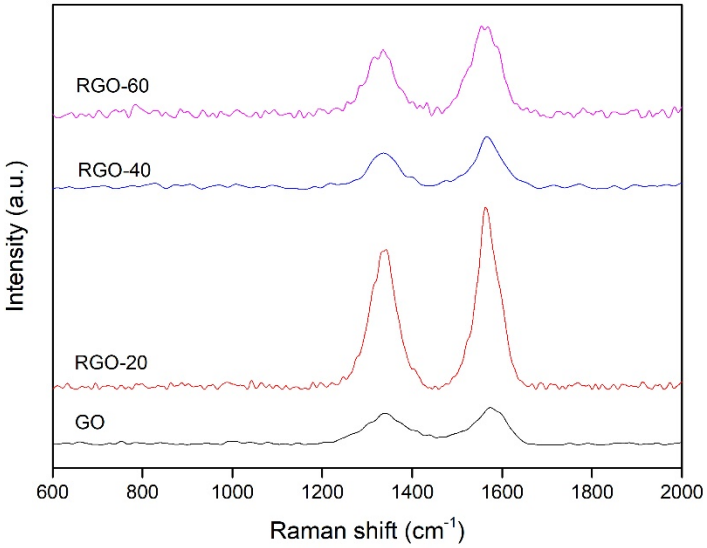

Figure 3 Raman spectra of GO, and RGO that was synthesized from GO and using different volumes of potato phytoextracts such as 20, 40 and 60 ml respectively (RGO-20, RGO-40 and RGO-60).

RGO was composited with PEDOT:PSS copolymer to improve the electrical property. The electrical property was also measured by a four-point probe. Figure 4 show resistivity of PEDOT:PSS copolymer and composite materials such as PEDOT:PSS/RGO-20, PEDOT:PSS/RGO-40 and PEDOT:PSS/RGO-60. The result shows PEDOT:PSS has resistivity value of 8.04 MΩ/sq whereas all of RGO composite with PEDOT:PSS show slightly lower resistivities of 6.61 MΩ/sq, 4.33 MΩ/sq and 3.04 MΩ/sq for PEDOT:PSS/RGO-20, PEDOT:PSS/RGO-40 and PEDOT:PSS/RGO-60, respectively, which implies that RGO can improve the electrical property of copolymer. In the comparison of different RGOs in composite materials, it can be observed lower resistivity in order that of PEDOT:PSS/RGO-60 < PEDOT:PSS/RGO-40 < PEDOT:PSS/RGO-20 because the RGO-60 has higher efficiency in partial reduction of oxygen-containing functionality from GO and more restoration of conjugated sp^2 hybridized structure in RGO.

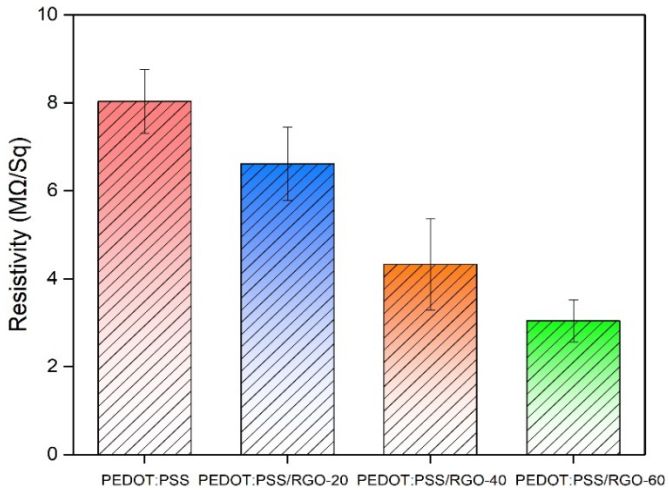

Figure 4 Resistivity of PEDOT:PSS/RGO-20, PEDOT:PSS/RGO-40 and PEDOT:PSS/RGO-60

5. Conclusion

In this paper, the reduced graphene oxide (RGO) was synthesized by a green route. We used phytoextract of fresh potato as a reducing agent. The RGO was characterized by X-ray diffraction, Fourier Transform spectroscopy and Raman spectroscopy. The results show that oxygen functionality was removed from the structure of GO, and the conjugated graphitic network was restoration. The extent of reduction was studied by varying volume of reducing agent 20, 40 and 60 ml. It can be observed that the efficiency of reduction is increased when adding more reducing agent. Then different RGOs were composited with PEDOT:PSS copolymer to improve the electrical property. The composite materials (PEDOT:PSS/RGO-20, PEDOT:PSS/RGO-40 and PEDOT:PSS/RGO-60) were characterized by the four-point probe for measure resistivity. The result shows all the composite materials have lower resistivity than PEDOT:PSS copolymer, which is indicated succession of electrical improvement.

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