The Optical Properties of Thin Film Reduced Graphene Oxide/Poly (3,4 Ethylenedioxytriophene):Poly (Styrene Sulfonate)(PEDOT:PSS) Fabricated by Spin Coating

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Abstract. Reduced Graphene Oxide (rGO) has been successfully synthesized from Graphite powder through chemical process using modified Hummers method by removing NaNO₃ from reaction formula. Hydrazine hydrate 80 wt% has been chosen as reductor to eliminate the epoxy group in GO. FTIR and Uv-Vis spectroscopy result showed that Graphene Oxide (GO) and rGO were formed. Our produced rGO then used to fabricated the composite thin film rGO/PEDOT:PSS by spin coating at room temperature. The optical constant of thin film rGO/PEDOT:PSS were calculated from the absorbance spectrum of Uv-Visible spectra. The result showed that the value of coefficient absorbance of rGO dropped from $4.7 \times 10^6 \text{ m}^{-1}$ to $1.3 \times 10^6 \text{ m}^{-1}$ after doped with 0.02 mL PEDOT:PSS, then increase with the addition volume concentration of PEDOT:PSS. The value of extinction coefficient decrease from 0.31 to 0.08 after rGO doped with 0.02 ml PEDOT:PSS and then increase with the addition concentration of PEDOT:PSS. Our result show that thin film rGO/PEDOT:PSS was more transparent than that of thin film rGO.

Keywords: Thin film, Graphene Oxide, reduced Graphene Oxide, PEDOT:PSS, Optical properties.

1. Introduction

Graphene, a novel and an exciting material composed of sp² bonded carbon atoms densely packed in a honeycomb crystal lattice have received significant attention in recent years, due to its excellent properties like high electron mobility, high thermal conductivity, extraordinary elasticity and stiffnes. The electron mobility graphene will be up to 150,000 cm²/Vs at a temperature of 300 K and 6,000 cm²/Vs at a temperature of 4K [1]. Universal conductance of graphene is about $6.08 \times 10^{-5} \ \Omega^{-1}$ at 0.1
eV to 0.6 eV [2]. Near the Fermi energy, graphene has linear band energy [3,4,5] which make graphene has semimetal and very high conducting and mobility properties.

Optical properties of graphene also have unique properties with transparency up to 97.7% [5] in the visible range. Universal of optical conductivity graphene ($\sigma_0 = \pi e^2/2h$) at infrared to visible range [6,7,8], also calculation of graphene absorbance in infrared to visible range spectrum showed that graphene absorbance is constant ini $\pi a = 2.93\%$ [9]. These features have made graphene has wide range of application in various industries such as photovoltaic cells. Due to its high electron mobility and transparency properties have made graphene potentially to be applied as an alternative transparent electrode in photovoltaic device.

Besides its application as transparent electrode, graphene can be applied as donor/acceptor material in hetero junction solar cell. However, to be applied as donor/acceptor material graphene should have doped with conductive polymer. Doping can be a feasible method to open band gap in graphene also in controlling electron or hole. Zahibi et al. [10] report that thin film graphene doped with P3HT can be applied as donor material in solar cell and it has a power conversion efficiency up to 5.17%.

On the other hand, PEDOT:PSS is conducting transparent co-polymer widely used in photovoltaic device as the hole transporting layer and even as a transparent electrode [11, 12]. Blending graphene with PEDOT:PSS can be controlling its hole transport due to hole majority charge at conductive polimer PEDOT:PSS. Also doped graphene with PEDOT:PSS could be improved electrical and mechanical properties as reported by Chen et al. [13]. Chen reported that optical thin film graphene doped with PEDOT:PSS up to 720 S/cm.

The investigation of optical properties of rGO doped with PEDOT:PSS is very important to utilize graphene as transparent electronic devices. In this work, we use reduced graphene oxide (rGO) which obtained by chemical reduction of GO. GO was synthesized using modified Hummer’s method [14]. We were focused on the optical properties of thin film rGO/PEDOT:PSS.

2. Experimental

2.1. Synthesis of graphene oxide

Graphite oxide was synthesized using a modification Hummer’s method by removing NaNO₃ from reaction formula. Firstly, 3 mg of graphite powder was added to 70 ml of concentrate H₂SO₄ under stirring for 1 h in ice bath. Then 9 gr of solid KMnO₄ were subsequently added to the mixture and stirred for 3 h while the temperature was kept below 20 °C. Successively, the mixture was vigorously stirred for about 20 h while the temperature was kept at 40 °C using oil bath. Then, 150 ml of distilled water was added to mixture and stirred for 15 min at 95 °C. After 15 min, the heat was turning off and additional 500 ml distilled water was added then followed by a slow addition of 15 ml H₂O₂ (30%) until the color of mixture changed from dark brown to yellow. To remove ions, the mixture was washed with HCl (10%). Next the mixture was washed with distilled water and then centrifuged at 4000 rpm for 30 min to remove the acid. At last, the resulting filter cake was dried in oven (100 °C) during 4 h.

2.2. Reduction of graphene oxide by hydrazine

rGO was obtained by reducing GO with hydrazine hydrate as reducing agent. A homogeneous GO aqueous suspension was achieved by dispersing 300 mg of graphite oxide in 100 ml of distilled water using ultra sonication. Then 100 µL of hydrazine hydrate was added and the mixture stirred for 3 h in oil bath to kept the temperature at 70 °C. Finally, a black rGO dispersion was obtained. The resulting filter cake was washed using distilled water and then dried in oven (80 °C) during 4 h.

2.3. Preparation of thin film rGO/PEDOT:PSS

PEDOT:PSS solution was mixed with rGO dispersion (5 mg mL⁻¹) in various volume concentration (0.02 mL; 0.04 mL; 0.06 mL; 0.08 mL) and sonicated for 30 min to form a stable mixture. The
mixture was then spin coated using vacuum spin coater VTC-100 on clean quartz substrate at 1000 rpm for 60 s. Then the resulted film then dried at 100 °C for 5 min.

2.4. Characterization
Uv-Visible (Uv-Vis) absorption spectra of powder of GO and rGO also thin film GO, rGO, and rGO/PEDOT:PSS were obtained on Shimadzu UV-1700 spectrophotometer in the spectrum range of 200-800 nm in ambient condition and at room temperature. FTIR ABB MB was used for Fourier Transform Infra Red (FTIR) characterization. GO and rGO powders were pulverized and pressed into pellets. Their spectra were measured in the range 1000-4000 cm⁻¹.

2.5. Optical Constant Calculation
By using Uv-Vis absorbances data, we could calculate imaginary part of refractive index of rGO and rGO/PEDOT:PSS by using following equation:

\[
\alpha = \frac{\text{absorbance value} \times 2.3026}{d}
\]

with \( \alpha \) is coefficient of absorbance and \( d \) is a thin film thickness. From equation above we could get imaginary part of refractive index \( (k) \) as write by following equation:

\[
k = \frac{\alpha d}{4\pi}
\]

3. Results and discussion

3.1. The characterization of GO and rGO
GO was synthesized from natural graphite using the modified Hummers method. The resulting product of GO powder is light brown in color and water dispersible. The GO was reduced by hydrazine hydrate. When hydrazine hydrate was added to the GO suspension, the color of GO suspension gradually changed from light brown to black, this change indicate that the GO was reduced by hydrazine hydrate. The reduction of synthesis Graphene Oxide (GO) and reduced Graphene Oxide (rGO) was characterized with Uv-Visible and FTIR spectroscopy. Absorbance spectrum of GO and rGO result by using Uv-Visible spectrophotometer was shown in Fig. 1. The absorbance result for GO showed two peaks at 230 and 300 nm that can be correlated to the electronic transition from \( \pi \rightarrow \pi^* \) and \( n \rightarrow \pi^* \) orbitals, respectively. These two peaks are characteristics in GO absorbance. Uv-Vis spectroscopy at Fig. 1 also showed the absorbance spectrum of rGO, which only one peak at a wavelength of 268 nm appears. This peak can be correlated to the \( \pi \rightarrow \pi^* \) orbital transition. This peak is the characteristic for rGO absorbance spectra. At longer wavelength, the absorbance has constant value that similar to pristine monolayer graphene.

Fig. 2 shows the FTIR spectroscopy result of GO and rGO. The GO spectra shows wide peak at 3433 cm⁻¹ (O-H stretching) which shows that GO has hydrophilic properties. It can be mentioned that the reducing FTIR spectra at 1000 cm⁻¹ and 1700 cm⁻¹ as GO is reduced to rGO inferring that C=O and C-O bounding is decreased. As it seen from FTR spectra, there were reducing of C=C bounding which shows at 1600 cm⁻¹. It can be happened due to the presence of energetic Hydrazine.

![Figure 1. The absorbance of GO and rGO](image1.png)

![Figure 2. FTIR spectrum of GO and rGO](image2.png)
3.2. The optical constant of thin film rGO/PEDOT:PSS

Fig. 3 and 4 is show absorbance and coefficient absorbance of thin film rGO and rGO/PEDOT:PSS, respectively. Its shows that the coefficient absorbance value decreased from dropped from $4.7 \times 10^6$ m$^{-1}$ to $1.3 \times 10^6$ m$^{-1}$ after doped with 0.02 mL PEDOT:PSS. The addition concentration of PEDOT:PSS (0.4 mL, 0.6 mL, 0.8 mL) increase the coefficient absorbance value.

Fig. 5 shows coefficient extinction ($k$) of thin film rGO and rGO/PEDOT:PSS that shows the decreased $k$ value of rGO after doped with 0.02 mL PEDOT:PSS from 0.31 to 0.08, as volume concentration of PEDOT:PSS increased the value of $k$ also increased. It could be mention that transparency of rGO increased after doped with 0.02 mL PEDOT:PSS, and after increasing the volume concentration into 0.4 mL, 0.6 mL, and 0.8 mL the transparency of thin film rGO/PEDOT:PSS was decreased. But the $k$ value of rGO/PEDOT:PSS was lower than the $k$ value of rGO, it indicate that thin film rGO/PEDOT:PSS more transparent than thin film rGO. The dropped $k$ value of thin film rGO after doped with 0.02, 0.04, 0.06 and 0.08 mL PEDOT:PSS shows that thin film rGO/PEDOT:PSS was more transparent from thin film rGO. At low energy as indicated by increasing of $k$ values, the carrier is increased as PEDOT:PSS added, inferring that more carriers responds the photon at lower photon energy.

Figure 3. The absorbance of thin film rGO and rGO/PEDOT:PSS in various concentration of PEDOT:PSS

Figure 4. Coefficient of absorbance of thin film rGO and rGO/PEDOT:PSS in various concentration of PEDOT:PSS

Figure 5. Coefficient extinction of thin film rGO and rGO/PEDOT:PSS in various concentration of PEDOT:PSS
4. Conclusion
From $k$ value data, we got to know that thin film rGO/PEDOT:PSS was more transparent from thin film rGO. So its shows that thin film rGO/PEDOT can be applied as transparent electrode in photovoltaic device.

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