

# Influence of deposition temperature as a reducing agent on synthesis of reduced graphene oxide (RGO) nanosheets

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## Abstract

In this paper we have investigated the physical properties of reduced graphene oxide (RGO) thin films prepared at various substrate temperatures of 230, 260, 290, 320 and 350 °C using spray pyrolysis technique. We have compared these films from various viewpoints, including structural, morphological, optical, electrical and thermos-electrical properties. XRD analysis showed a phase shift from graphene oxide (GO) to RGO due to elevate the substrate temperature from 200 °C to higher temperatures, in agreement with the FTIR spectra of the layers. FESEM images of RGO thin films reveal that a stacked image of irregular and folding nanosheets, and rod-like features at temperatures below and above 290 °C; respectively. Optical studies showed that the layers have a relatively high absorption coefficient ( $\sim 0.8 \times 10^4$  to  $1.7 \times 10^4$   $\text{cm}^{-1}$ ) in the visible range, with an optical band gap of 1.67–1.88 eV. The Hall effect data showed that all samples have a *p*-type conductivity with a hole concentration of  $\sim 10^{15}$   $\text{cm}^{-3}$ , and sheet resistance values of about  $10^6$   $\Omega/\text{square}$ , in agreement with previous reports. The thermoelectric measurements revealed that with increasing applied temperature gradient between the two ends of the samples, the thermoelectric electromotive force (emf) of the prepared RGO thin films increases.

**Keywords:** Reduced graphene oxide (RGO); Nanosheets; Optical properties; Electrical properties;

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## 1. INTRODUCTION

Graphene, as a 2D material, has attracted increasing attention due to its unique mechanical, thermal, electrical and optical properties [1-8]. This material has a zero-band gap and ‘minimum’ conductivity of  $\sim 4 e^2/h$  even when the carrier concentration tends to be zero [9]. However, the zero-band gap of graphene limits its use in field-effect transistors in nano-electronics. Oxygen functionalization is known to tune the band gap of graphene. A gradual reduction of oxygen concentration of GO also

tailors the band gap of the material as an alternative route.

There are several approaches to produce and modify reduced graphene oxide (RGO). These are: (1) fabrication of GO thin film from GO aqueous dispersion and subsequent reduction of GO films using a hot vapor of reducing agent [10-13]; (2) thermal treatment of GO to obtain “RGO”; (3) direct surface coating of GO for composites followed by a thermal or hydrothermal treatment through simultaneous

reactions; and (4) chemical reduction in combination with thermal annealing to eliminate the chemical residuals and clear the patches of RGO [14]. Reducing GO at elevated temperatures (above 500 °C) was shown to reduce the oxygen concentration, but introduces defects in RGO. For these reasons, the main focus of this research is production of high quality RGO thin films mainly by thermal treatments via oxygen removal from GO thin films.

In our previous report, since the non-reduced GO thin films at substrate temperature below 200 °C showed insulating behavior as usual, chemical reduction was then applied to make the layers conductive for different opto-electronic applications [15]. In this regards, we report preparation of reduced graphene oxide (RGO) thin films by increasing substrate temperature above 200 °C (230–350 °C) without further chemical reduction in toxic atmosphere such as hydrazine vapor. We have investigated and compared the corresponding reduced samples from various viewpoints, including structural (crystallinity and surface morphology), optical (UV–Vis–near-IR absorption coefficient spectra and optical band gap estimation), electrical (carrier density and resistivity) and thermo-electrical properties.

## **2. EXPERIMENTAL DETAILS**

### **2.1. Materials**

Graphite (99.99%), Ethanol (99.99 %) and hydrochloric acid (37%) were supplied by

Merck (Germany); Deionized water (10 MΩ cm) was used for all processing.

### **2.2. Preparation of Go suspension and deposition of their thin films**

We started from GO produced by the modified Hummers method [16]. The resulting graphene oxide suspension was washed by repeated centrifugation (4000 rpm) with a hydrochloric acid (HCl, 37%) and then with deionized water and ethanol. The final suspension of graphene oxide in ethanol was rigorously sonicated using a bath sonicator for 2 min, in order to more exfoliation of the graphene oxide and prevention of the breakage of GO sheets. Then GO dispersed in ethanol with concentration of 0.2 mg/mL and was sprayed onto preheated glass substrates by spray pyrolysis instrument (Modern Technology Development Institute, Iran). Here the substrate temperature was varied from 230 to 260, 290, 320 and 350 °C with an accuracy of  $\pm 5$  °C using a digital temperature controller. Other deposition parameters such as spray solution volume, spray deposition rate, nozzle to substrate distance and hot plate rotation speed were maintained at: 100 ml, 10 ml/min, 30 cm and 50 rpm, respectively. The samples are labelled as ‘RGO–230’, ‘RGO–260’, ‘RGO–290’, ‘RGO–320’ and ‘RGO–350’. An X-ray diffractometer (D8 Advance Bruker, Germany) was used to record X-ray diffraction (XRD) patterns using Cu–K alpha radiation ( $\lambda = 0.15406$  nm) in the  $2\theta$  range of 10–70deg. Spectral transmittance was recorded in the wavelength range 400–1100 nm by a

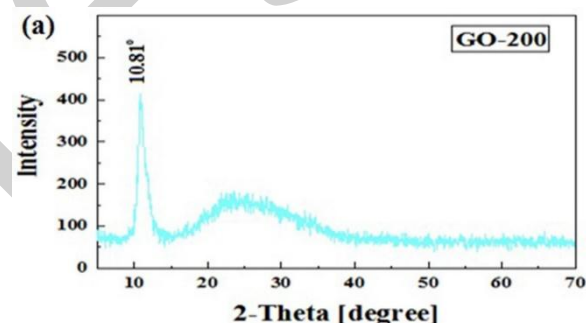
Shimadzu UV1800 (Japan) spectrophotometer. The surface morphology was observed using a HITACHI S-4160 Field (Japan) Emission Scanning Electron Microscope (FESEM). The film thickness was measured using a Taly step profilometer (roughness detector with a stylus-Taylor Hobson model, UK). This apparatus is able to find the height of the films in a step-like configuration with a precision of about 10 nm. The electrical resistivity and Hall effect data (magnetic field strength = 200 mT) of the samples were measured in the Van der Pauw configuration [17]. Finally, by applying a temperature gradient between the two ends of the samples, the thermoelectric electromotive force (emf) of the prepared films was measured, and then the Seebeck coefficients were determined by calculating the slope of the thermoelectric emf versus temperature difference.

### 3. RESULTS AND DESCUSSIONS

#### 3.1. Structural studies

The XRD patterns of GO and RGO thin films are presented in Fig.1. As shown in the Fig. 1(a), the pattern of GO thin film fabricated at substrate temperature of 200 °C has a high-intensity peak centered at  $2\theta$  about  $10.81^\circ$ . Also the d-spacing of GO is 1.38 times larger than that of graphite, increased to 0.819 nm. The larger interlayer distance of GO than that of graphite might be due to the formation of oxygen-containing functional groups, such as hydroxyl, epoxy and carboxyl [18]. After increase 30 °C of substrate temperature, as seen

in the XRD patterns in Fig. 1(b), it could be inferred that the typical sharp peak at  $2\theta$  about  $10.81^\circ$  of GO thin films disappears, indicating the transformation of GO to RGO. It is worth to mention that after increasing substrate temperature, RGO230–350 samples show a broad diffraction peak at about  $23.32^\circ$ , corresponding to the interlayer spacing of 3.82 Å. The interlayer spacing of RGO thin films were slightly larger than that of graphite, which was resulted from the small amount of residual oxygen-containing functional groups or other structural defects [19].



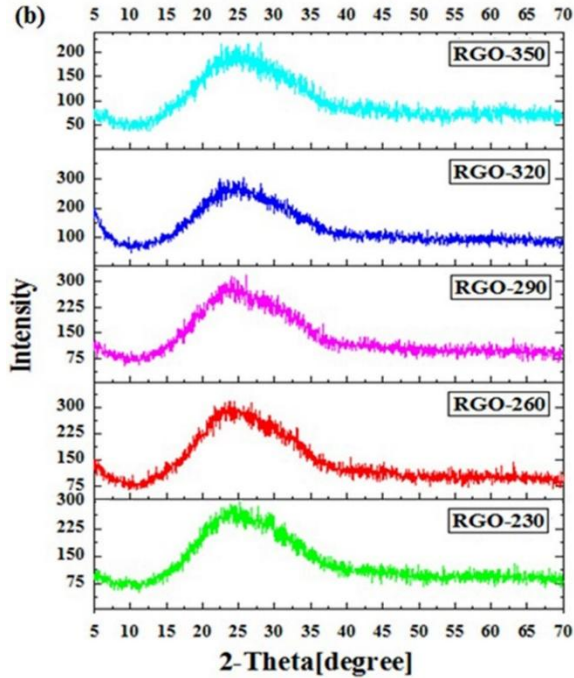


Fig. 1: XRD pattern of (a) GO and (b) RGO thin films prepared at various substrate temperatures.

### 3.2. Morphological studies

FESEM images of the spray-coated RGO thin film fabricated at various substrate temperatures are seen in Fig. 2 (a-e). Electronic Microscopic images reveal that a stacked image of irregular and folding nanosheets at temperatures below 290 °C. Samples RGO-320 and RGO-350 doesn't demonstrate any fluffy features, rather exhibit rod-like features in addition to the sheets.

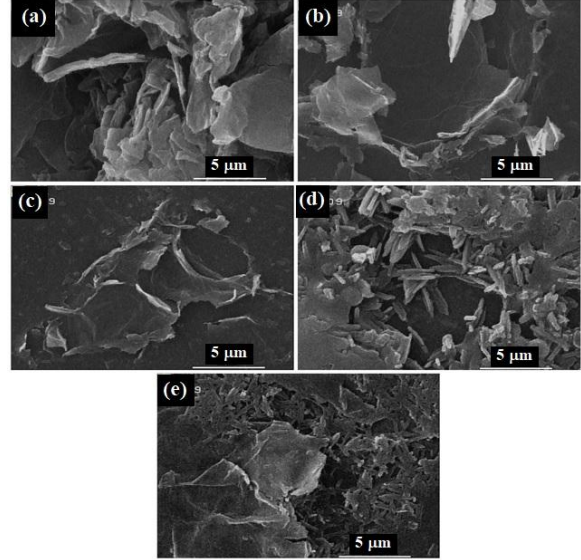


Fig. 2: FESEM images of the studied RGO thin films (a) RGO-230, (b) RGO-260, (c) RGO-290, (d) RGO-320 and (e) RGO-350.

### 3.3. Optical studies

Fig. 3 shows the spectral transmittance curves for reduced graphene oxide films. It is seen that after increasing substrate temperature the absolute transmittance of the films is increased by an amount of about 20-30%. This increment trend might be attributed to the difference in their morphological properties as examined by FESEM, and/or due to the increase in the density of free charge carriers which results in more absorption of light. This result agrees with the discussion of the electrical properties, section 3.4.

It is also mentioned that, independent of thickness, our films have a flat optical transmittance profile across the visible and near infrared region of the spectrum, making them potentially desirable for solar cell, display, and optical communication applications.

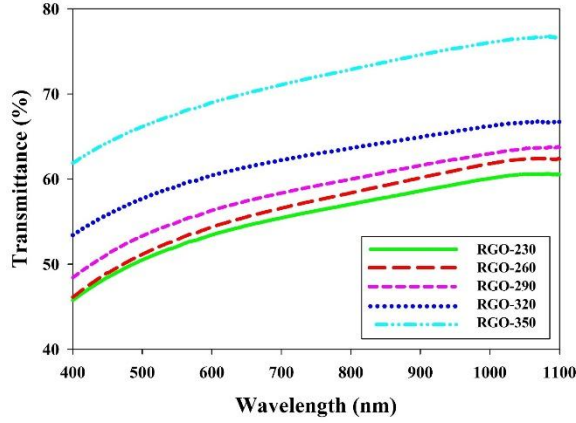


Fig. 3: Results of transmittance measurement of the RGO thin films.

Using the transmittance data, the absorption coefficient ( $\alpha$ ) could be determined by the following equation [20]:

$$\alpha = \frac{1}{d} \ln\left(\frac{1}{T}\right) \quad (1)$$

Where  $d$ , the thickness of the layers measured and found  $\sim 400 \pm 40$  nm. The variations of the absorption coefficient  $\alpha$ , as a function wavelength are presented in Fig. 4. As seen, the deposited layers have a relatively high absorption coefficient ( $\sim 0.8 \times 10^4$  to  $1.7 \times 10^4$   $\text{cm}^{-1}$ ) in the visible range.

The absorption coefficient ( $\alpha$ ) is related to the incident photon energy ( $h\nu$ ) by the following equation [21]:

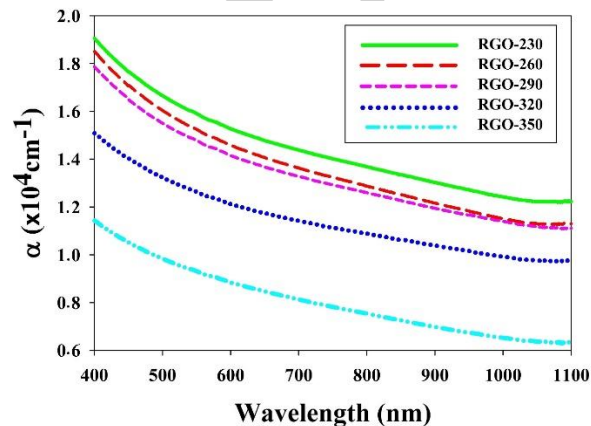


Fig. 4: The optical absorption coefficient,  $\alpha(\lambda)$ , for RGO thin films.

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (2)$$

where  $E_g$  is the energy band gap and  $h\nu$  the incident photon's energy.

Fig. 5 shows the variation of  $(\alpha h\nu)^2$  versus  $h\nu$  of reduced graphene oxide thin films prepared at different substrate temperatures and their values are presented in Table 1. The values of  $E_g$  were estimated from the intersection of the extrapolated linear part of the  $(\alpha h\nu)^2$  curves with the energy axis. A glance on Table 1 and Fig. 5 shows that in contrast to the GO film (Fig. 5 (a)), the RGO films prepared at substrate temperature above  $200^\circ\text{C}$  exhibit the lower band gap values, so that the values of band gap significantly decrease from about 3.46 eV in the GO film to the range of 1.67 – 1.88 eV in the RGO films. The decrease of band gap may be attributed to the change in phase (see Fig. 1); and also more oxygen vacancies by removing the oxygen-containing groups by applying higher substrate temperature, which increase the density of localized states in the band gap and consequently decrease the energy.

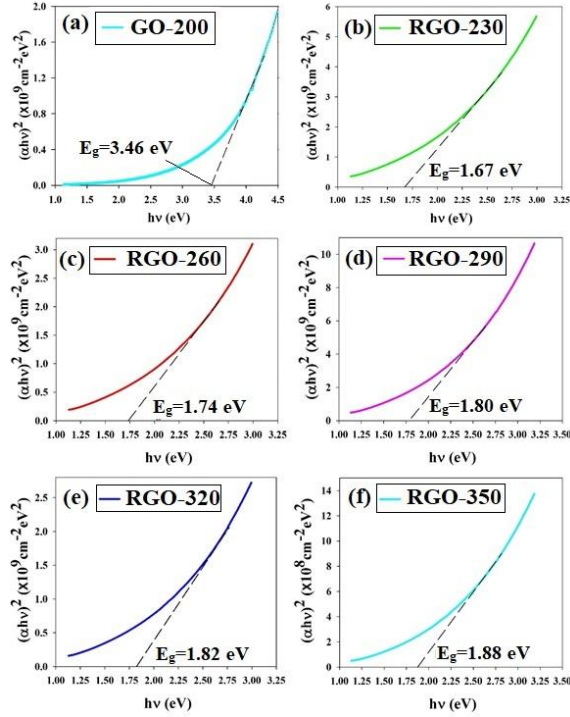


Fig. 5: The detail analysis for the optical band gap determinations in our samples (a) GO-200, (b) RGO-230, (c) RGO-260, (d) RGO-290, (e) RGO-320 and (f) RGO-350.

### 3.4. Electrical studies

In our experiments, the thin film prepared at substrate temperature of 200 °C (GO-200) and below it, showed insulating behavior as usual [15]. Since a reduction process can dramatically improve the electrical conductivity of GO thin films, thermal (increasing substrate temperature) approach to produce conductive RGO thin films was applied. In the following, the effect of increasing substrate temperature on the electrical properties of the studied samples was evaluated by the Hall effect and sheet resistance measurements in the Van der Pauw configuration. We found all the studied samples are exhibited p-type conductivity. The room

temperature values of carrier density ( $p$ ) and sheet resistance ( $R_s$ ) against the substrate temperature (and/ or sample) are given in Table 1.

Table 1: optical and electrical measurement results of the RGO thin films.

Sample	Band gap energy (eV)	Sheet resistance ( $\times 10^6 \Omega/\text{square}$ )	Carrier concentration ( $\times 10^{15} \text{cm}^{-3}$ )
RGO230	1.67	10.24	0.65
RGO260	1.74	6.58	1.04
RGO290	1.80	5.37	2.18
RGO320	1.82	4.13	3.99
RGO350	1.88	1.96	4.74

It is evident that: while the substrate temperature of thin films increases: (1) the degenerate hole density gradually increases from  $\sim 6.5 \times 10^{14} \text{cm}^{-3}$  in RGO-230 to about  $4.775 \times 10^{15} \text{cm}^{-3}$  in RGO-350. (2) The estimated sheet resistances value decreases from  $10.24 \times 10^6 \Omega/\text{square}$  in RGO-230 to about  $1.96 \times 10^6 \Omega/\text{sq}$  in RGO-350. The exact reason for this behavior of ' $p$ ' is not known but this could be understood as follows. It is a well-known fact that the various factors, such as crystallinity, morphology, roughness, porosity, stress, composition, film-substrate interface, etc., play a crucial role in determining the electrical properties of the films. Hence, the variation in the electrical parameters of the films reported in the present study, with respect to substrate temperature and Ag to S molar ratio, can be attributed to the difference in their

morphological properties as examined by FESEM. The  $R_s$  values of our RGO thin films are in agreement with previous reports on the electrical resistance of reduced graphene oxide thin films with chemical process [22-24].

### 3.5. Thermo-electrical studies

Fig. 6 presents the variation of the thermoelectric e.m.f versus temperature difference ( $\delta T$ ) for RGO thin films. It can be seen that thermoelectric e.m.f. of films is increased with increasing the temperature difference between the hot and cold sides. The explanation for increasing thermoelectric behavior is through increased majority carrier concentration with increasing temperature [25].

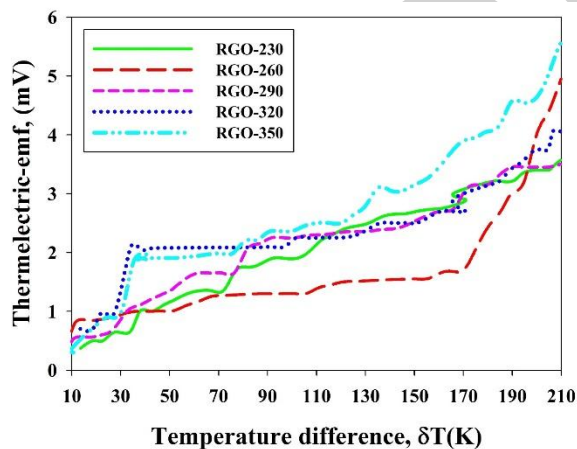


Fig. 6: Thermoelectric e.m.f versus temperature difference for the RGO thin films.

The variations of Seebeck coefficients as a function of temperature for RGO thin films are shown in Fig. 7. Variation of Seebeck coefficient at low temperatures is nearly nonlinear, which decreases very slow with a linear behavior with increasing temperature higher than 370 K. The nonlinear manner in

temperatures below 370 K is related to the electron-phonon and phonon-phonon interactions, while slow linear variations are related to free electron model which are temperature dependent phenomena [26].

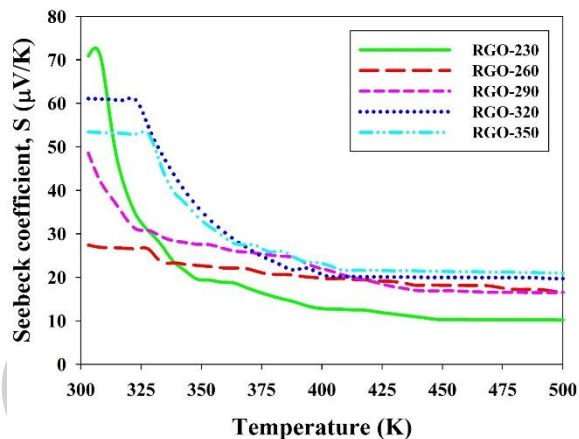


Fig. 7: Seebeck coefficient versus temperature for the RGO thin films.

### 3.6. FTIR studies

The FTIR spectra obtained for the graphene oxide (GO) and reduced graphene oxide (RGO) are shown in Fig. 8. The existence of oxygen groups in graphene oxide FTIR spectrum was affirmed by the peaks observed at 1053, 1230, 1734 and 3407  $\text{cm}^{-1}$  corresponds to C–O (vibrational mode), C–O–C (breathing vibrations from epoxy groups), C=O (stretching vibration band from carbonyl and carboxyl groups), and C–O–H (stretching vibration. Also, a narrow peak with the maximum at 2870  $\text{cm}^{-1}$  in the upper spectrum was identified to be due to the C–H bonding from hydroxyls and trapped water molecules in the GO sample. For reduced graphene oxide, lower spectrum, this peaks is disappeared due to the partial removal of hydroxyl groups and water molecules by chemical reduction. On the other hands, the

increased peak intensity of C=C stretching upon reduction suggests the recovery of sp<sup>2</sup> lattice, while the markedly weaker bands of adsorbed water and oxygen groups confirm their removal. Nevertheless, the O–H bending mode from hydroxyl groups was still observed in reduced material. The removal of oxygen functionalities after reduction is confirmed by the corresponding weaker bands in reduced materials.

#### 4. CONCLUSIONS

Reduced graphene oxide thin films were prepared by spray-coated GO dispersion at various substrate temperatures from 230 to 350 °C. X-ray analysis showed that with increasing substrate temperature from 200 °C to higher substrate temperatures, typical sharp peak at 2θ about 10.81° of GO thin film disappears, indicating the transformation of GO to RGO. FESEM images of the spray-coated RGO thin film reveal that a stacked image of irregular and folding nanosheets at temperatures below 290 °C; and rod-like features in addition to the sheets at temperatures above it. Optical measurements showed that absorption coefficient values as high as ~10<sup>4</sup> cm<sup>-1</sup>, and the direct optical band gap in average increases from 1.67 eV to 1.88 eV. Finally, the Hall experiment data showed that all the reduced thin films have a *p*-type conductivity with a carrier density of about 10<sup>15</sup> cm<sup>-3</sup>, and sheet resistance values of about 10<sup>6</sup> Ω/sq, in agreement with previous reports on the electrical resistance of chemically reduced graphene oxide thin films. The thermoelectric

measurements showed that while variation of Seebeck coefficient at low temperatures is nearly nonlinear, it changes to linear manner at temperatures above 370 K.

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