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The Effect of Chemical Treatment of Reduced Graphene Oxide on NO_2 Gas Sensing

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Abstract: Graphene a two dimensional nanomaterial with extremely high surface area and highly sensitive to surface molecules adsorbates, it can be modified effectively by different chemical treatment processes. In this research, graphite flakes were converted to graphene oxide using modified Hummers procedure and then the product has been reduced by hydrazine to graphenenanosheets, this Reduced Graphene Oxide (RGO) serves as starting materials for the next chemical treatments. The effect of chemical treatment of RGO with nitric acid, sulfuric acid, boric acid and sodium hydroxide separately were studied from view of doping degree and morphological changes using SEM, AFM, EDS and FTIR. Graphite staring material, RGO and all chemical treated RGO products were tested for NO_2 gas sensing capability. RGO treated with nitric acid show the best sensitivity towards NO_2 gas at 25°C while graphite sample has the worst sensitivity towards NO_2 gas.

Key words: RGO, NO_2 gas sensor, doping, graphene, SEM, AFM, sensitivity, effect

INTRODUCTION

Geim and co-workers in 2004 at Manchester University successfully identified single layers of one atom thick sp^2-hybridized sheet of carbon atoms arranged in a honey comb lattice and the two-dimensional building block for carbon materials.

The unique features of graphene exhibits excellent electrical conductivity, mechanical flexibility, optical transparency, thermal conductivity and low coefficient of thermal expansion behavior have attracted great interest for a wide range of applications (Novoselov *et al*., 2004, 2005; Geim and Novoselov, 2007).

The absence of a semiconducting gap in pristine graphene made the electronic applications of graphene are limited but doping is regarded as one of the most feasible methods to effectively modify of graphene based electronic devices. Therefore, a lot of research has been devoted to find ways for controllable doping of graphene with electrons and holes. It has been shown that, the chemical treating with different adsorbates, either atoms or molecules, on the graphene surface can result in both n-and p-type doping (Minitha and Rajendrakumar, 2013; Guo *et al*., 2011; Kuila *et al*., 2012; Bautista-Flores *et al*., 2015).

MATERIALS AND METHODS

All chemicals were used in this research without any further purification.

Preparation of Reduced Graphene Oxide (RGO): Graphene oxide was prepared by the oxidation of graphite flakes using modified Hammer's method (Alam *et al*., 2017) in which (3.0 g) of graphite flakes (99%, Sigma Aldrich U.K) was added to concentrated H_2SO_4 (75 mL, 98%, Sigma Aldrich U.K) under stirring at room temperature, then sodium nitrate (1.5 g, 99.9%, BDH) was added in an ice bath under vigorous agitation, then $KMnO_4$ (18.0 g, 99%, BDH) was added slowly while the temperature of the suspension was kept around (1°C). Then this mixture heated to 35°C in a water bath and stirred for about 30 min, after that 150 mL DI water was added and the solution was stirred for 15 min at 95°C. Additional 510 mL of DI water was added and followed by a slow addition of 15 mL H_2O_2 (30%, BDH), turning the color of the solution from dark brown to yellow. The mixture was filtered and washed with 1:10 HCl (33%, BDH) aqueous solution (250 mL) to remove metal ions. The collected yellow-brown powder (GO) was dispersed in distilled water and reduced by adding drops of hydrazine (35% in H_2O, Sigma Aldrich UK) as shown in Fig. 1, then filtered using Millipore filtration system, the collected powder (RGO) serve as starting materials for the next chemical treatment, the following equation represents the chemical reactions of the reduction process.

Graphene Oxide (GO) Reduced Graphene Oxide (RGO)

Chemical treatment of RGO: Reaction with Sulfuric acid: (0.2 g) of the prepared RGO was mixed with (10 mL) of 66%

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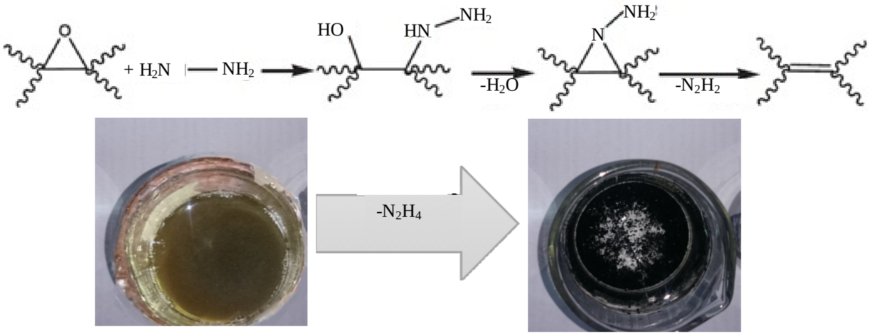


Fig. 1: Reduction of collected graphene oxide with hydrazine

H_2SO_4 solution in a beaker and stirred for 2 min and then left for 24 h after that the product was washed with DI water and filtered until neutral pH was obtained and dried at 35°C until the sample became a black powder.

Reaction with nitric acid: the same above procedure was used for the reaction of RGO with 66% nitic acid.

Reaction with boric acid: About 0.2 g of the prepared RGO was doped with boron by mixing (3 g) of boric acid (H_3BO_3) and 100 mL of ethanol. The solution was sonicated for 10 min for homogenization. The solution was then transferred into a sealed Teflon-lined 100 mL stainless steel cell and the reaction (Hydrothermal reaction) was conducted at 150°C for 11 h.

Reaction with sodium hydroxide: Abour 0.2 g of the prepared RGO was mixed with (10 mL) of 2M NaOH solution in a beaker and stirred for 5 min and then left for 24 h after that the graphene sample was washed with DI water and filtered until neutral pH was obtained and dried at 350°C until the sample became a black powder.

Characterization of RGO and chemically treated RGO: The morphology of the prepared RGO and chemically treated RGO were examined using SEM (S-4160, Hitachi, Japan) and AFM (SPM-AA300, Angstrom Advanced Inc., USA) and the doping and degree of doping establishment were followed by EDS and FTIR (8300, Schimadzou, Japan) while other electronic properties were checked using Raman spectroscopy (Bruker, Germany).

Fabrication RGO sensors and testing for NO_2 gas sensing: Two integrated aluminum electrodes deposited by evaporation on a piece of glass previously coated with the produced RGO or chemical treated RGO, Fig. 2 in order fabricate gas sensor to determine the sensitivity, response time and recovery time of the fabricated gas sensor when exposed to NO_2 gas.

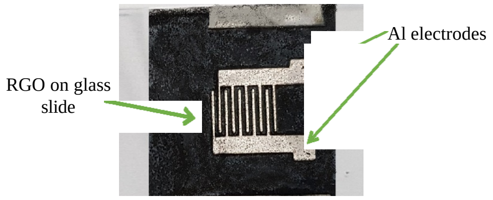


Fig. 2: Integrated aluminum electrodes deposited by evaporation on a piece of glass coated previously with RGO

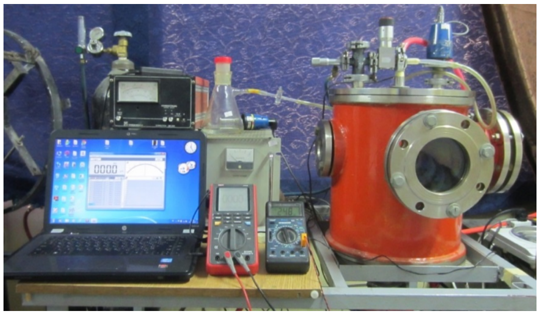


Fig. 3: Gas sensor testing homemade apparatus

The gas sensor testing system (homemade) is shown in Fig. 3 the system consists of: A cylindrical shaped chamber made of stainless steel with a diameter of 30 cm, height of 35 cm and the effective volume is 6594 cc with an inlet to allow the NO_2 gas to flow into the chamber, an air valve to control and allow the flow of atmospheric air after evacuation.

The sensor body mounted on electric controlled heater to reach the desired test temperature. A PC-interfaced digital multi meter and a laptop PC was used to record the variation of the sensor current or resistance when exposed to air/NO_2 gas mixing ratio. The mixture of gases were fed through needle valve to flow meter before entering the test vessel. The sensitivity, response time and recover time were calculated using the following equations (Varghese *et al*., 2015).

$$\text{Sensitivity} = \frac{R_2\text{-}R_1}{R_2}*100\% \qquad (1)$$

$$\text{Response time} = |\,t_2\text{-}t_1|*9\% \qquad (2)$$

$$\text{Recover time} = |\,t_3\text{-}t_2 *90\% \qquad (3)$$

Where:

R_1, R_2 = The resistances of RGO film in air and in NO_2 gas respectively
t_1 and t_2 = The time to record R_1 and R_2
t_3 = The time to return back to the steady stat after exposure to NO_2 gas

RESULTS AND DISCUSSION

Figure 4 presnts the SEM images of all produced RGO types, these images visualy reflucted a larg area plate like structures for all RGO types, the lowest number of graphene sheets are seen in the untreated RGO (a) and H_2SO_4 traeted RGO (c) while more thick grahene sheets appeared for HNO_3 treated RGO (b), H_3BO_3 treated RGO (d) and NaOH treated RGO (e).

More accurate estimation about the morphology of RGO'S structures deduced from AFM examinations, untreated RGO reflucted a pieces of planner layers of Graphene with length exceeded 2.5 µm and roughness of 1.95 nm while the thickness seems to be around 12 nm as shown in Fig 5. AFM images in Fig. 6 shows a clear changes in the morphologies of the different chemical treated RGO.

In a similar way presented in Fig. 5, the section lines of AFM analysis for area, thicknesses and roughness measurements for other treated RGO are summerized in Table 1.

The variation in surface roughnesses did not follow a usefull manner to explain the doping process. The elemental analysis derived from EDS for untreated RGO reflected only the existence of carbon atoms as shown in Fig. 7 it consisted of about 100% carbon.

For the other treated RGO the EDS tests gave a very good indication that the doping were successful and also, gives the approximate percentage of sulfur, nitrogen, boron and sodium in RGO samples as shown in Fig. 8. Depending on these EDS analysis the doping degree of graphene to S, N, B, Na can follow the order:

$$B > N > S > Na$$

The effect of doping elements on the graphene thickness follow the electronic properties of the dopant, boron which suffer from deficiency of electrons (Kawai *et al*., 2015) easily replaced the carbon atom inside the hexagonal rings and led to less thickness of graphene sheet while nitrogen and sulfur have pair of electrons show less percentages of doping and higher thicknesses (Panchakarla *et al*., 2009; Ma *et al*., 2015).

The low percentage of Na doping is attributed to the big differences of the electronegativity between carbon and sodium atom. The existence of dopant-carbon bonds were checked by FTIR spectrums for H_2SO_4 treated RGO (C = S) stretch clearly recorded at exactly 1501 cm^{-1} (Fig. 9a) (Zhao *et al*., 2010).

Table 1: Data of AFM section lines analysis for area, thickness and roughness measurements for all treated RGO

RGO types	Thickness/nm	Area/µm	Roughness/nm
Untreated RGO	12	2.5	1.98
H_2SO_4 traeted RGO	28	2.2	25.50
HNO_3 treated RGO	52	1.8	9.08
H_3BO_3 treated RGO	15	2.1	0.23
NaOH treated RGO	38	2.8	1.34

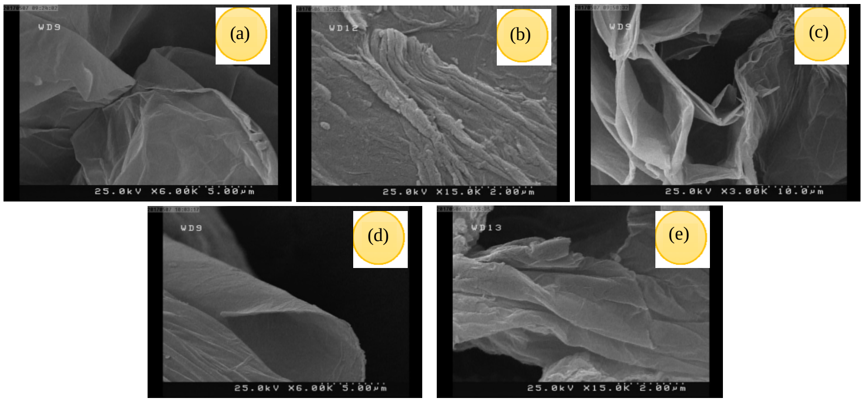


Fig. 4: SEM images of: a) Untreated RGO; b) HNO_3 treated RGO; c) H_2SO_4 traeted RGO; d) H_3BO_3 treated RGO and e) NaOH treated RGO

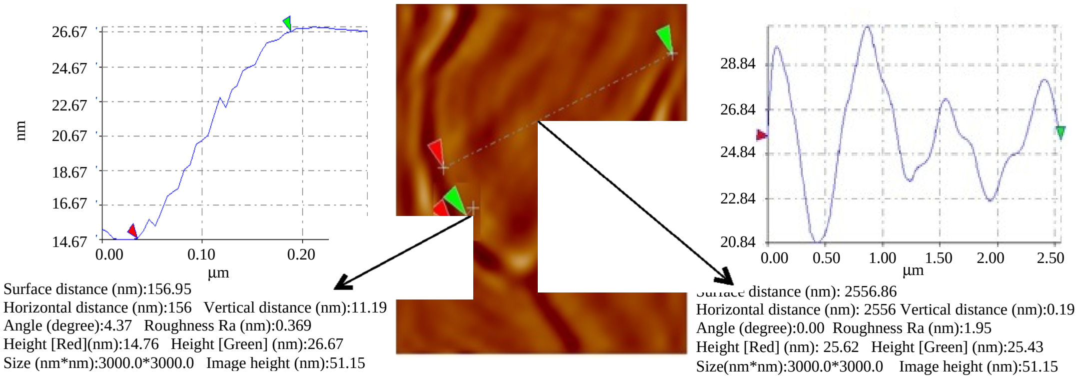


Fig. 5: AFM image with section line analysis for thickness and area of untreated RGO

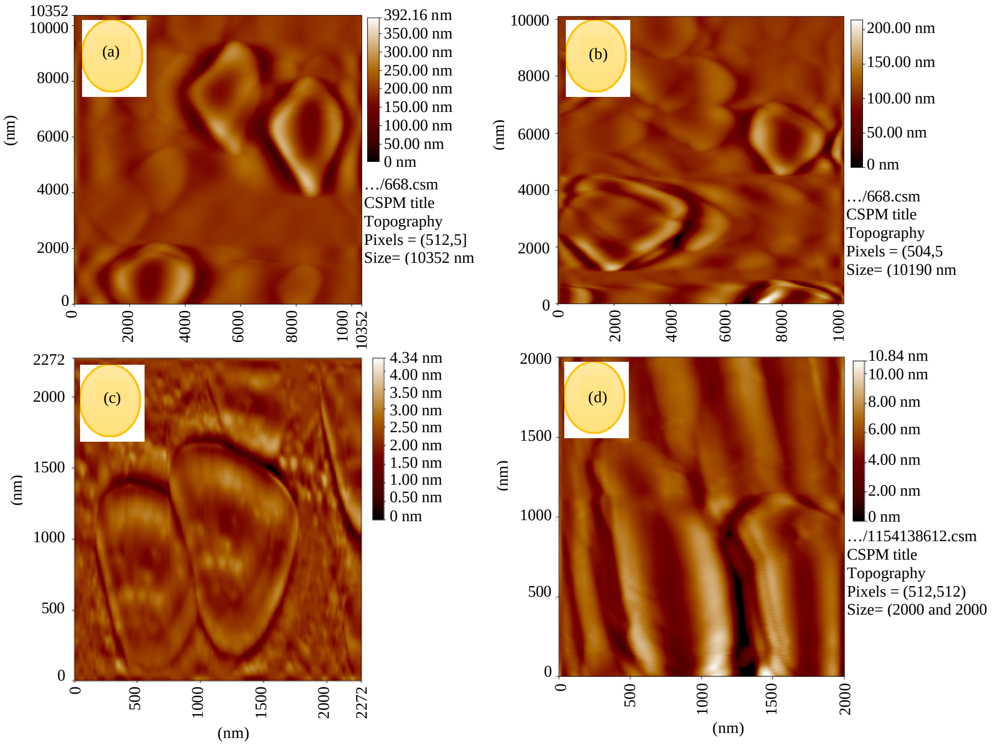


Fig. 6: AFM images of: a) H_2SO_4 treated RGO; b) HNO_3 traeted RGO; c) H_3BO_3 treated RGO and d) NaOH treated RGO

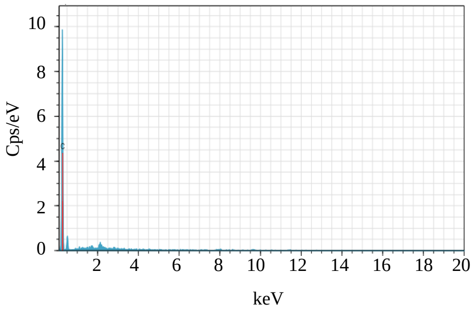
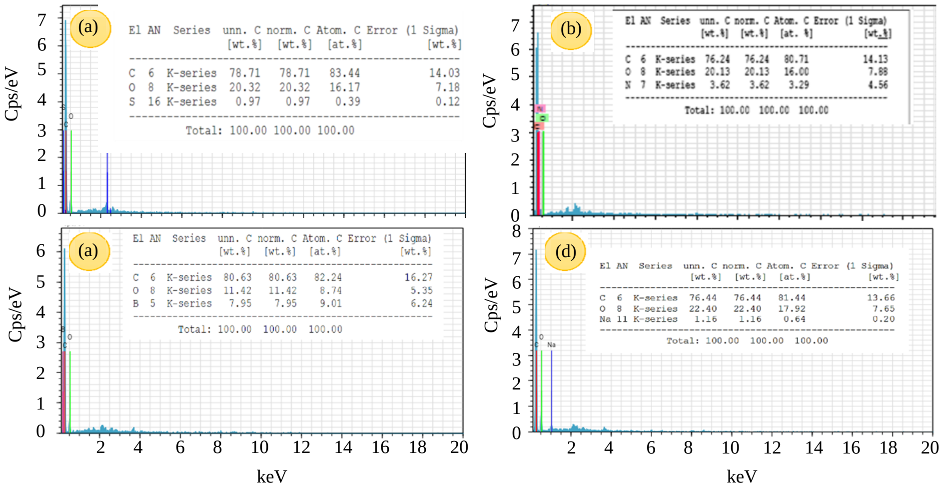


Fig. 7: EDS analysis of RGO synthesized by Hummers method

For the HNO_3 treated RGO the (C-N) and (C = N) stretches at 1187 and 1556 cm^{-1}, respectively approved the successful doping with nitrogen (Zhang *et al*., 2015) and also (C-NO_2) stretch has been seen at 864 cm^{-1} (Fig. 9b).

Doping with boron atoms confirmed by the appearing of the peak at (1018-1020 cm^{-1}), Fig. 9c which belonged to C-B bond (Li *et al*., 2016).While FTIR spectrum in Fig. 9d show (C-OH) and (O-H) bond stretching at 1150, 3464 cm^{-1}, respectively which means that graphene had acquired (-OH) groups from sodium hydroxide (Kong *et al*., 2014).



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El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]          [wt.%]
------------------------------------------------------
C  6  K-series  78.71   78.71   83.44            14.03
O  8  K-series  20.32   20.32   16.17             7.18
S  16 K-series   0.97    0.97    0.39             0.12
------------------------------------------------------
         Total: 100.00 100.00 100.00
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El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at. %]         [wt.%]
------------------------------------------------------
C  6  K-series  76.24   76.24   80.71            14.13
O  8  K-series  20.13   20.13   16.00             7.88
N  7  K-series   3.62    3.62    3.29             4.56
------------------------------------------------------
         Total: 100.00  100.00  100.00
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El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]          [wt.%]
------------------------------------------------------
C  6  K-series  80.63   80.63   82.24            16.27
O  8  K-series  11.42   11.42    8.74             5.35
B  5  K-series   7.95    7.95    9.01             6.24
------------------------------------------------------
         Total: 100.00  100.00  100.00
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```
El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]          [wt.%]
------------------------------------------------------
C  6  K-series  76.44   76.44   81.44            13.66
O  8  K-series  22.40   22.40   17.92             7.65
Na 11 K-series   1.16    1.16    0.64             0.20
------------------------------------------------------
         Total: 100.00  100.00  100.00
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Fig. 8: EDS elemental analysis of: a) H_2SO_4 treated RGO; b) HNO_3 treated RGO; c) H_3BO_3 treated RGO and d) NaOH treated RGO

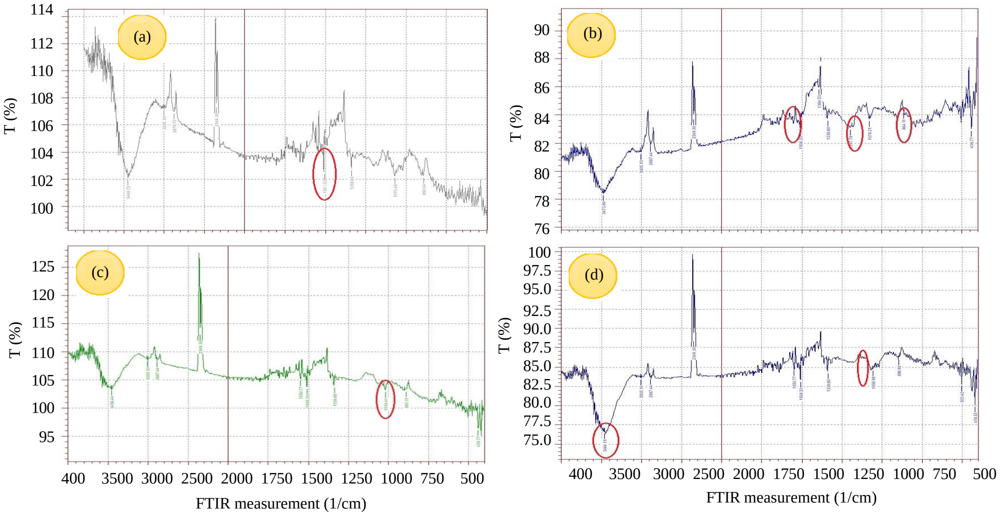

Fig. 9: EFTIR spectrums of: a) H_2SO_4 treated RGO; b) HNO_3 treated RGO; c) H_3BO_3 treated RGO and d) NaOH treated RGO

Evaluation of graphene and doped graphenes as NO_2 gas sensor: Using the gas sensing system in Fig. 3 the electrical resistivity of the RGO films were followed on exposure to 50 ppm of NO_2 gas (40l/h for 10 min), then Graphite films showed sensing sensitivityof 1.31% at room temperature and the response time and recovery time was 23.4 and 69.9 sec, respectively, on rising graphite film temperature up to 50°C the sensitivity increased and became 2.31% at response time of 30 sec while the recovery time was being less 54 sec at higher temperature the graphite films losted their sensitivity capabilties (Fig. 10).

Untreated RGO film showed much higher sensitivity and better response and recovery times in comparison with the above graphite films as shown in Fig. 11. The results of rising RGO films temperature always led to worsen the sensing parameters.

Figure 12 shows the sensitivity of H_2SO_4 treated RGO as a function of temperature a sensitivity of 27% was achieved at RT which seems somehow better than untreated RGO (24%), even at 50°C the sensitiviy of S-RGO is higher than untreated RGO The response time is nearly same as for RGO but the recovery time is better.

Doping with nitrogen improve the sensitivity towards NO_2 gas up to 100°C and sensing failed at 200°C as shown in Fig. 13.

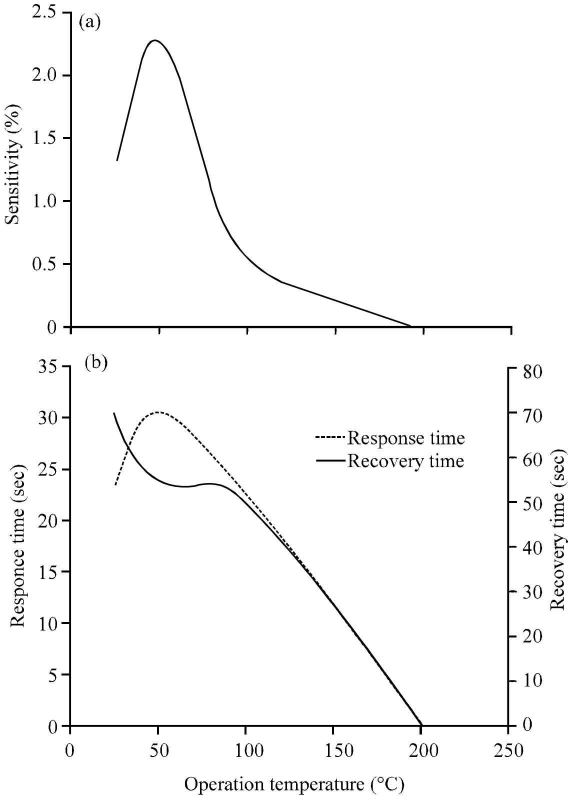

Fig. 10: a) Sensitivity against temperature and b) Recovery and response time plots for NO_2/graphite system

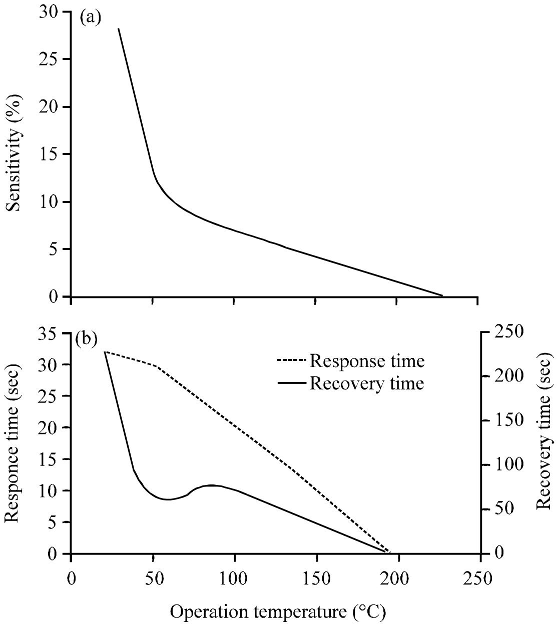

Fig. 11: a) Sensitivity against temperature and b) Recovery and response time plots for NO_2/untreated RGO sample

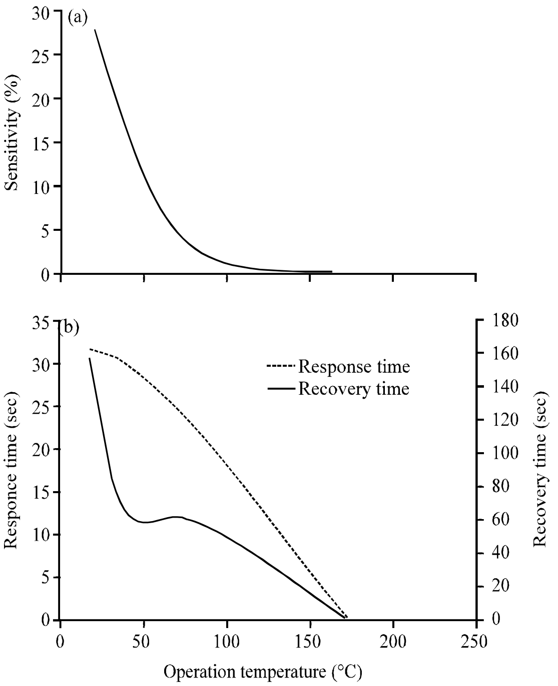

Fig. 12: a) Sensitivity against temperature and b) Recovery and response time plots for NO_2/H_2SO_4 treated RGO system

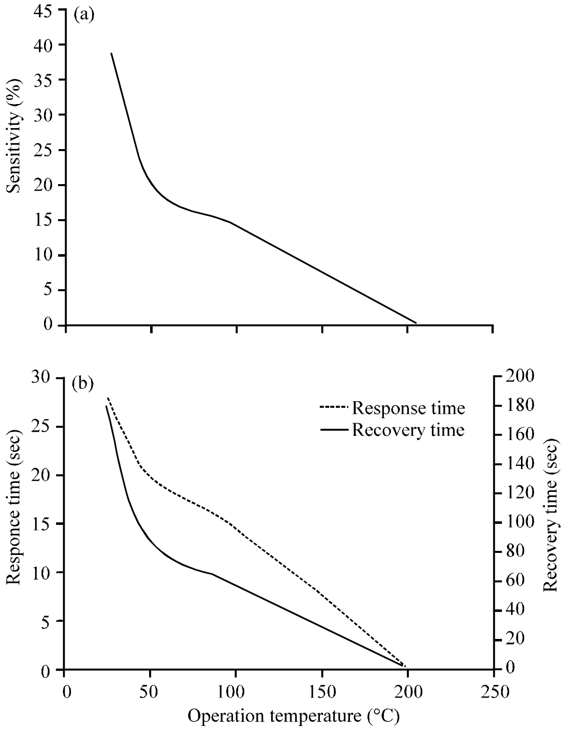

Fig. 13: a) Sensitivity against temperature and b) Recovery and response time plots for NO_2/HNO_3 treated RGO system

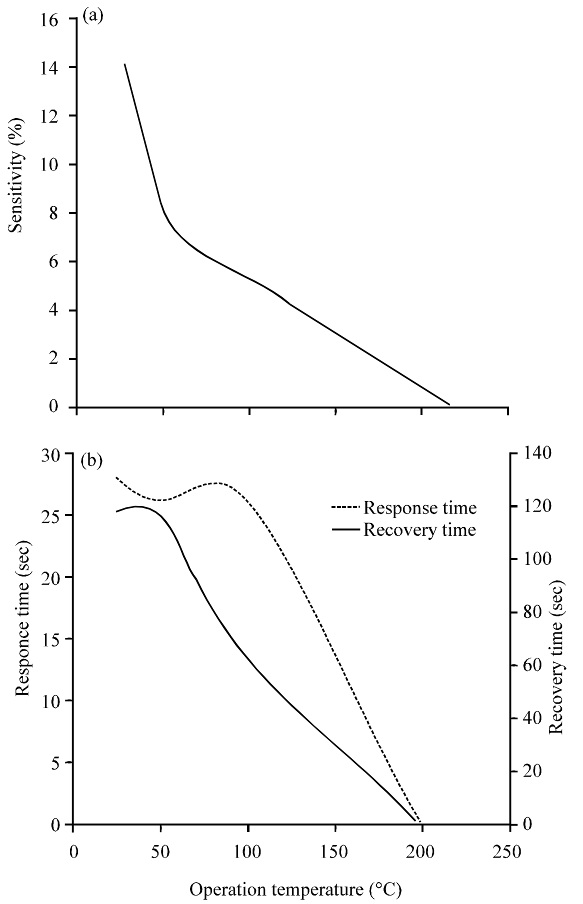

Fig. 14: a) Sensitivity against temperature and b) Recovery and response time plots for H_3BO_3 treated RGO system

The doping of RGO with boron have negative effect for the sensing of NO_2 gas as the sensitivity did not exceeded 14%, Fig. 14 which is higher than bulk graphite but less than untreated RGO this manner may attributed to the defficiency of pair of electrons which reduced the power of force of adsorption of NO_2 gas. Similar to boron, sodium doping also led to decreases the sensitivity of the RGO as shown in Fig. 15.

From the data and charts for all NO_2 gas sensor systems, one can conclude that the graphene doped with nitric acid sample had the best sensitivity towards NO_2 gas at 25°C (Room temperature) and graphite sample had the worst sensitivity towards NO_2 gas.

Decrease sensitivity: Figure 16 shows the decrease sensitivity.

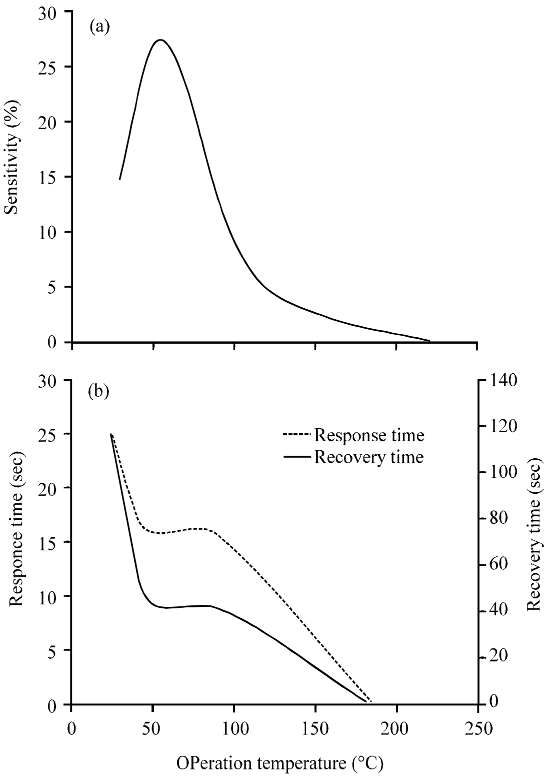

Fig. 15: A-sensitivity against temperature, B-recovery and response time plots for NaOH treated RGO system

Fig. 16: Decrease sensitivity

CONCLUSION

The main goals of the present research are that by the use of simple chemical methods to enhance the sensing properties of graphene toward NO_2 gas.

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