Synthesis of Amide Functionalized Graphene Oxide for Humidity Sensing Application

(Amide Functionalized Graphene Oxide for Humidity Sensing)

Dinesh Kumar and Sumita Rani
Electronic Science Department, Kurukshetra University
Kurukshetra, Haryana, India
Email dineshelsd2014@gmail.com

Abstract— **Amide functionalized graphene oxide (AGO) was synthesized by chemical method at room temperature. Fourier transform infrared spectroscopy, X-ray diffraction and scanning electron microscopy measurements were carried out to verify the functionalization. Thin films of graphene oxide (GO) and AGO were formed by spin coating on SiO$_2$/p-Si (100) substrate. The variation in the I-V characteristics was recorded at different humidity level. It has been observed that in GO the variation in resistance with humidity is relatively small as compared to AGO. The resistance of the AGO film was approximately 9.87 kΩ at 10% relative humidity (RH), and decreases to 1.5 kΩ at 90% RH.**

Keywords- Amide functionalized graphene oxide; relative humidity; I-V characteristics.

I. INTRODUCTION

Humidity plays an important role in every part of the earth processes. To have a desirable surrounding environment, it is necessary to monitor, detect and control the ambient humidity by precise sensors [1]. In today's modern world, there exist various kinds of humidity sensors that have applications in industrial processing and environmental control. Like for fabrication of integrated circuits in semiconductor industry it is essential to monitor moisture levels constantly. In medical field, humidity sensors are essential for respiratory equipment, sterilizers, incubators and biological processing. In agriculture, humidity sensors are used for green-house air-conditioning, plantation protection, soil moisture monitoring, etc. In general, humidity sensors are used for moisture detection by various paper, textile and food processing industries. In modern humidity sensor there is requirement of high sensitivity and wide detection range for fast response and short recovery time to meet industry applications. Thus nanomaterials, such as silicon nanostructures, ceramic nanomaterials, semiconductor nanoparticles and metal oxide are widely used for moisture sensing application due to high surface to volume ratio [2][3].

Graphene oxide (GO) because of its large surface area and electrical properties can be potentially used for ultrasensitive sensor applications [1][3]. As GO has hydroxyl, epoxy and carboxylic acid functional group bonded in two-dimensional network of sp^2 and sp^3 hybridized carbon atoms arranged in a honeycomb structure [2]. The oxygen containing functional groups of GO enhance hydrophilic properties of it but these groups makes it an insulator by decreasing its conductivity [1][4]. But oxygen functional groups of GO allow fast passage of water within the GO layers [5], which makes fast response of the sensor based on GO. But improving the electrical properties of GO by surface modification via noncovalent or covalent functionalization is a promising way for fabrication of high performance GO-based sensor [6][7]. Already functionalized GO have been successfully used for detection of acetone, hydrogen sulfide, nitrogen dioxide (NO$_2$), etc [8][9]. Covalent functionalization of GO enhance its physicochemical properties, for instance, isocyanate-treated GO has been exfoliated and form a stable dispersion in polar aprotic solvents [10]. Such functionalization improves the mechanical, electrical, thermal properties [7] and dispersion of functionalization GO in to organic solvents [11].

In view of above observations, heteroaryl/phenyl amine was grafted onto GO sheets by the amide formation between amine functionality of heteroaryl/phenyl amine and oxygen-containing groups (e.g., carboxyl and lactone groups) of GO to give amide functionalized GO (AGO). Section 2, explains the synthesis and amide functionalization of GO. In Section 3, there is discussion about the various characterization of prepared GO and AGO. The effect of surface functionalization on humidity sensing application of GO was also discussed in Section 3. The conclusion of the work is given in Section 4.

II. EXPERIMENTAL

A. Materials

Graphite powder (purity 99.99%), sodium nitrate (99.0%), sulphuric acid, potassium permanganate (99%), hydrogen peroxide, hydrochloric acid, sodium hydroxide (NaOH), hydroxybenzotriazole (HOBt), 2-aminothiazole, N,N'-dicyclohexylcarbodiimide (DCC) were used to prepare GO and AGO.

B. Preparation of GO

Graphite (2 g) and NaNO$_3$ (1 g) were mixed in cooled concentrated sulphuric acid (46 ml) under stirring in ice bath. KMnO$_4$ (6 g) was gradually added to the above placed mixture with stirring and cooling so that the temperature of mixture was maintained between 10–15°C [12]. The reaction mixture was then stirred at 40°C for 30 minutes. Subsequently, 80 ml of high purity water was added to the

formed paste, followed by another 90 minutes stirring at 90°C. Successively, to stop the oxidation reaction additional 200 ml water was added. 6 ml of 30% H_2O_2 was added in above mixture sequentially to destroy the excess $KMnO_4$. The complete removal of $KMnO_4$ was indicated by color changed to yellow. Sometimes the solution's color was yellow before addition of H_2O_2 which indicated complete reduction of $KMnO_4$. The solution was then washed with HCl (10%) to remove sulphate. Subsequently, it was filtered and washed several times with DI water. The filtered paste was dissolved in 100 ml DI water. The solution was ultrasonicated for 1 hour and centrifuged for 20 minutes at 4000rpm. GO powder thus obtained was collected and dried at room temperature.

C. Preparation of AGO

The AGO was obtained by condensation of amine group of heteroaryl/phenyl amine with lactone group of GO. AGO was synthesized by dispersing GO (0.3 g) in 30 ml DMF by ultrasonication for 60 minutes at room temperature. Then, NaOH (0.3 g; 7.5 mmol) was added and resulting solution was stirred for 60 minutes at room temperature. Subsequently, 2-aminothiazole (3.1 mmol), HOBt (3.1 mmol) followed by DCC (3.1 mmol) addition to the above reaction mixture and stirred for 24 hours at room temperature. AGO powder collected by centrifugation was added to pure DMF and the resulting suspension was again centrifuged to remove side products. This process was repeated twice with DMF and then with water to remove DMF to give pure AGO. The prepared AGO was dried at 60°C overnight.

D. Characterization

The crystal phase was characterized by X-ray diffraction (XRD) XPERT-PRO diffractometer (45 kV, 40 mA) equipped with a Giono-meter PW3050/60 working with Cu K_α radiation of wavelength 1.5406Å in the 2θ range from 5 to 80°). The functional surface group was studied by Perkin Elmer Fourier transform infrared (FTIR) model SPETRUM 65 system. Dried solid samples were mixed with KBr powder and were pelletized before performing the scan from wave number 4000 to 400 cm^{-1}. SEM characterization was carried out by using JSM-6510LV Series Scanning Electron Microscope (SEM) having pre centered W hairpin filament (with continuous auto bias) and equipped with accelerating voltage of 500 V to 30 kV with high magnification of 300,000.

III. RESULTS AND DISCUSSION

The oxygenated GO sheet prepared by the chemical method was treated with NaOH to open the lactone groups (–CO-O–) on the basal plane and convert them into hydroxyl and carboxyl groups. Treatment of resulting reaction mixture with organic amines in the presence of DCC and HOBt leads to the amidation of the carboxyl groups to give AGO. The chemical changes occurring in the GO after treatment with amine can be verified easily by FTIR, XRD, and SEM techniques.

Structural changes of AGO were investigated by comparing the FTIR spectra of GO and AGO (Figure 1). The most characteristic features in the FTIR spectrum of GO was the adsorption bands corresponding to the C=O carbonyl stretching at 1721 cm^{-1}, the stretching bands for C=C bonds at 1591 cm^{-1}, the O–H deformation vibration at 1392 cm^{-1} and the C–O stretching at 1051 cm^{-1}[13][14]. The FTIR spectra of AGO reveals a new peak at about 1634 cm^{-1} corresponding to the amide carbonyl (C=O) stretch (amide I) and the peak at about 1585 cm^{-1} for amide II (C–N in-plane stretching and CHN deformation) [15], which demonstrate that amines has been grafted onto GO as amide bond.
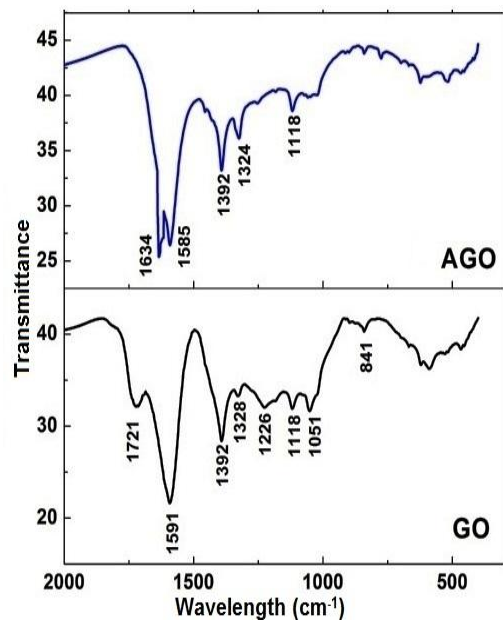

Figure 1. FTIR spectra of GO and AGO

XRD patterns for graphite, GO and AGO are shown in Figure 2. GO shows a diffraction peak at 2θ = 11.42˚, which is the characteristic peak of the GO, with increase in interspacing from 0.34 nm (graphite) to 0.77 nm.
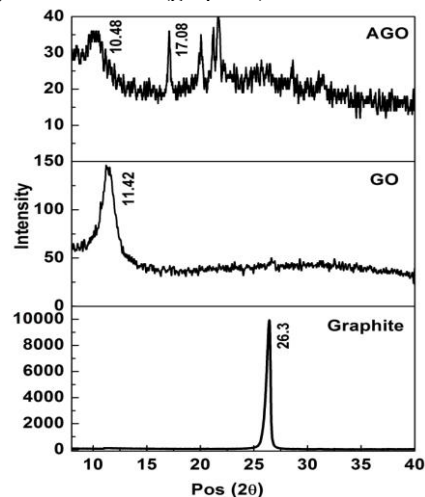

Figure 2. XRD of graphite, GO and AGO

Due to the functionalization of GO the peaks shift to the lower value of angle (2θ) and increase in the interlayer spacing from 0.77 nm (GO) to 0.84 nm for AGO, was observed. The larger value of interlayer spacing suggests the incorporation of additional functionality on the surface of the basal plane of GO. AGO shows peaks at 17.08˚, 20.1˚ and 21.69˚ correspond to 2-aminothiazole group.

The SEM images represent the surface morphology of the GO and AGO (Figure 3). These images show that the resulting sample of AGO was obviously different from GO. Morphology of GO was observed to have flaky texture indicating its layered microstructure. Different surface morphology of AGO clearly indicates the surface modification of GO after functionalization.
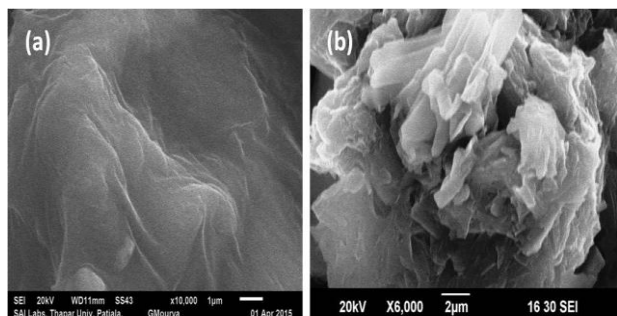

Figure 3. SEM image of GO and AGO

The DC electrical properties, i.e., current–voltage (I-V) characteristics of the GO and AGO films were measured with a voltage sweeping mode at various humidity points. To measure the I-V characteristics one electrode was loaded with the sweeping voltage bias, and the other electrode is grounded. I-V characteristics of GO and AGO films was investigated for 2 to 5 V sweeping voltages at various humidity levels, respectively. The different percentage of humidity level was achieved in sensing chamber by introducing the water vapors.

Figure 4a shows the measured I-V characteristics of GO film in the relative humidity (RH) range of 10% to 90%. From Figure 4a it is clear that the channel current of the GO film increases with increasing RH, indicating that the water adsorption results in a decrease in the resistance of GO films [16]. Water adsorption easily takes place in GO because of presence of large number of oxygen containing functional groups in it. The result revealed that GO is a weak conductor with a continuous water adsorption onto GO films. It is also clear that the current increases with increase in humidity level. At higher humidity (>60%) GO films gives good response.

The sensor resistance (R$_s$), as a function of humidity is calculated by :

$$R_s = \delta V/\delta I$$

where, δV is incremental voltage and δI is incremental current.

The variation of R$_s$ with humidity is shown in Figure 5. The R$_s$ of the GO film was 0.76 MΩ at 10% RH, which decreases to 0.48 MΩ at 90% RH It can be observed from Figure 4b that for AGO, the variation in current is more as

compared to GO. So, AGO is preferred for moisture sensing as compared to GO. The resistance of the AGO film was 9.87 kΩ at 10% RH, which decreases to 3.52 kΩ at 30% RH. The resistance decrease further with increase in humidity and it become 1.5 kΩ at 90% RH. The resistance of film at 90% RH was approximately seven times smaller than that at 10% RH.
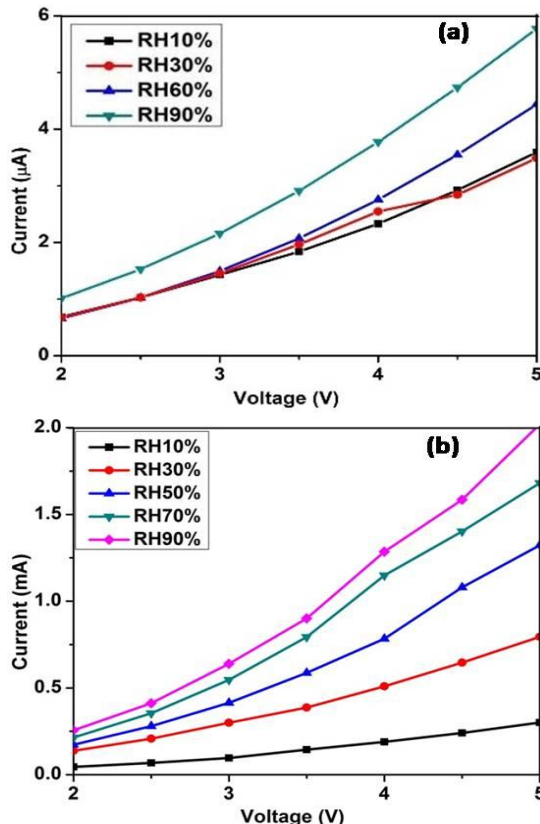

Figure 4. I-V variation in (a) GO and (b) AGO with different humidity from 2V to 5V sweeping voltage
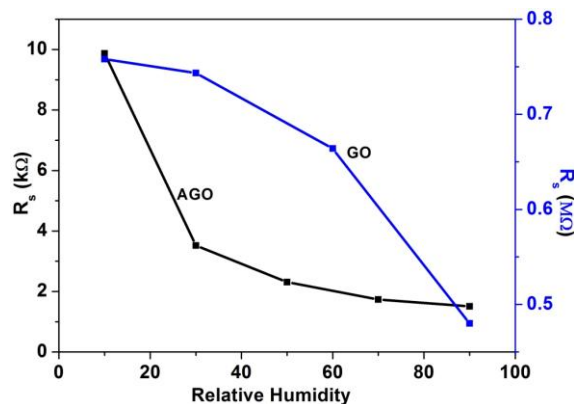

Figure 5. Variation in sensor resistance with humidity

The decrease in the resistance of GO and AGO film can be explained on the basis interaction of water molecules with the film material. At high sweeping voltage, water molecules on the films are ionized and leads to formation of hydrogen ions and hydroxyl ions due to the strong electric

field. The generated hydrogen ions and hydroxyl ions deceases the oxygen containing functional groups of GO and AGO and hence the current increases with humidity. However, in AGO there are less number of oxygen containing groups as compared to GO, so AGO gives better sensitivity. When ambient RH is high, the numbers of adsorbed water molecules are large. As a result, the ionization process generates more hydrogen ions, result in reduction of GO and AGO film. Thereby, AGO exhibits high conductivity at higher applied voltage and at high humidity level.

IV. CONCLUSION

An efficient and easy approach has been used to synthesize the covalent functionalized GO by a simple amidation reaction using 2-aminothiazole. DC measurement method was used to investigate the effect of humidity on the electrical properties of AGO films. Through electrical characterizations, the strong interaction of water molecules with AGO films was observed. The electrical properties of GO and AGO films were affected by humidity and the amplitude of applied voltage. At low RH (<60%), GO films exhibited small variation in current due to the presence of sp^3-bonded hybridized carbon atoms and presence of oxygen containing functional groups. AGO shows much better response at lower and higher RH (10% to 90%) indicates its effectiveness as compared to GO. The results are useful for the development of graphene-based sensors.

ACKNOWLEDGMENTS

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