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Sensitivity of Layer-by-Layer Deposited GO/PDAC to Volatile Organic Compounds

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Abstract

Films prepared by layer-by-layer deposition of graphene oxide/Poly(diallyldimethylammonium chloride) (GO/PDAC) have been investigated for detection of volatile organic components (VOC), such as acetone, ethanol, isopropanol and methanol. The films were deposited on top of silver interdigitated electrodes fabricated by inkjet-printing on a polyethylene naphthalate (PEN) substrate. The sensitive films were prepared with different bi-layers of GO/PDAC having different conductivities after thermal annealing converting GO to reduced GO. All fabricated sensor elements show a high selectivity towards Methanol compared to other detected VOCs. The resistance changes measured in existence of 2000 ppm concentration of VOCs relative to the resistance measured in ambient air at room conditions is 50% for methanol, 10% for acetone, 9% for ethanol, and 1% for isopropanol. This confirms the sensitivity of GO/PDAC to VOCs, which enables it to be considered as sensitive material to methanol. By further functionalization, the sensitivity to different VOCs can be adjusted, so that selective multi-sensor systems can be realized.

Keywords-component; Chemical sensors, Volatile Organic Compound (VOC), Graphene Oxide (GO), Reduced Graphene Oxide (rGO), Layer-by-Layer deposition, Methanol, Acetone, Ethanol, Isopropanol

1 Introduction

Detection of organic volatile compounds (VOCs) has become a very hot topic as they are a major contributor to bad indoor air quality. They are considered as dangerous environmental pollutants because they can cause health problems. For example, methanol is used as a reagent for chemicals such as cholesterol, in spray paints, in glass cleaners and as a fuel for picnic stoves and soldering torches [1]. Due to its toxicity, it was banned by the European Union from use in windscreen washing and defrosting liquids [2]. For the diagnosis of human diseases, the analysis of VOCs produced by the body, e.g. by breathe monitoring, is an invasive and economic method for early detection of diseases. And it is also an alternative approach for blood analysis [3-4].

VOCs are detected usually by gas chromatography/mass spectrometry techniques (GC-MS). However, due to its time, cost and complexity, rapid, easy and portable approaches are preferred [5]. Several sensor materials were developed to detect VOCs, *e.g.*, Si-doped epsilon-WO_3 nanostructures [6], SnO2-reduced graphene oxide [7] and nanostructured Pt-doped SnO_2 sensors [8] were used to detect acetone for diabetes patients.

Graphene oxide (GO) is used for different sensors, e.g. force, humidity, chemical sensing [9]. The inclusion in both conductive or insulating polymer and hybridization with nanoparticles can be performed in a manifold manner to increase its sensitivity and selectivity [10-13]. Graphene oxide multilayers reduced by hydrazine were already used to detect different VOCs where number of layers was controlled to tune the sensitivity [10]. Hybrid GO: ZrO2 and GO:CeO2 and GO:PEDOT were utilized as an electronic nose to distinguish different VOCs [5].

In this paper, we propose an easy processable and low cost GO based sensors for the detection of VOCs. GO is layered chemically derived graphene containing oxygen functional groups (epoxy, hydroxyl, carboxyl and carbonyl). These functional groups make it an insulator and having a resistance of hundreds of Mega Ohms [9]. The hydrophilic nature and surface properties of GO are altered by the change of its oxygen quantity. Thus the functional groups contained in GO give the sensitivity properties of GO and its derivative, the so-called reduced graphene oxide (rGO). The fabricated sensor is based layer-by-layer deposition and optimal thermal annealing. This process is followed by the characterization of optical and electrical properties. The sensor sensitivity to different VOCs i.e. methanol, acetone, isopropanol and ethanol is investigated and show a basis for detection of VOC especially to methanol based on piezoresistive change of the sensor resistance.

2 Experimental Investigations

2.1 Materials

GO utilized in this work was purchased from Graphenea Inc. with the initial concentration of 4 mg/mL. The GO was diluted in deionized water to 1 mg/mL. Slight sonication is required to prevent agglomeration after dilution. PDAC (20 wt.%) was purchased from Sigma Aldrich (CAS-No. 6062-79-32). All solvents for producing the vapor concentration are acetone, isopropanol, ethanol and methanol and are analytical grad from Sigma Aldrich.

2.2 Sensor Preparation

Silver interdigitated electrodes were initially inkjet printed on polyethylene naphthalate (PEN) substrate and annealed at 150 °C. The line width and finger spacing of the interdigitated electrodes are 250 µm. The total area of the sensor is 16 mm2. Next, prior to layer-by-layer deposition, PEN substrates are plasma cleaned and immediately dipped in a beaker of diluted PDAC in distilled water to 1%. The bi-layer of PDAC/GO is deposited by alternating dip coating the silver electrode/PEN for 5 m in GO (diluted to 1% in distilled water.) and PDAC. Cleaning with HCl diluted solution and drying with nitrogen, between alternating depositions was maintained. Finally, the film was dried with nitrogen. In this work we have opted to form 1, 2, 4, 6, 8 and 10 bilayers of PDAC/GO. After the film deposition the electrode with PDAC/GO bilayers is left overnight. The GO in a bi-layer deposited onto the electrodes was later reduced by thermal treatment. This was done by placing the electrodes on a hotplate in air atmosphere.

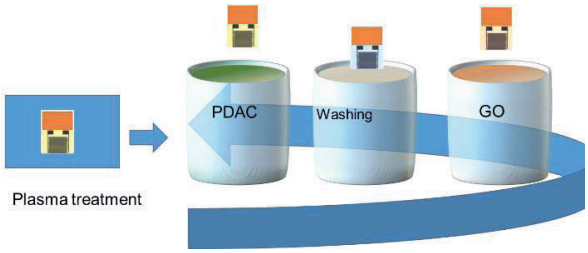

Fig 1 Layer-by-layer deposition of GO-PDAC

2.3 Characterization and Measurement Setup

Raman spectra, excited with diode-pumped solid state high brightness laser (excitation wavelength 532 nm), were collected on a DXR Raman microscope (Thermo Scientific, USA) equipped with an Olympus optical microscope and a CCD detector. The laser beam was focused on the sample using an objective (magnification 10×). The scattered light was analyzed by the spectrograph with a 900 lines mm^{-1} grating. Laser power on the sample was kept at 1 mW to prevent thermal degradation of the samples.

For the measurement of VOCs, experiments were performed at room temperature, and resistance measurement was taken by Keithly 2602 sourcemeter. The sensors were exposed to different gas concentrations. To generate certain concentration of VOCs, amount was injected in a sealed chamber i.e. glass bottle of 2.5 L using Hamilton syringe. The concentration of VOC was calculated according to the flowing equation (1) [12]:

$$V_{inj} = \frac{MPV_S}{R\rho} \cdot \frac{C}{T} \quad (1)$$

Where, M (g/mol) is the molecular weight of the liquid and it is 46, 48, 32.04 and 60.1 g/mol for ethanol, acetone, methanol and isopropanol, respectively. ρ (g/ml) is the density and it is 0.816, 0.788, 0.79 and 0.786 g/mL for ethanol, acetone, methanol and isopropanol, respectively. T (K) is the temperature of the chamber, V_s is the test chamber volume (i.e. 2.5 L), P is atmospheric pressure (101325 Pa), R is ideal gas constant (8.31441 J/(mol·K)) and C is resulted concentration of desired gas by injection of V_{inj} of liquid VOC. The relative response of the resistance was calculated by equation (2):

$$\frac{\Delta R}{R}\% = \frac{R_{gas} - R_{air,initial}}{R_{air,initial}} \quad (2)$$

Where $R_{air,\ initial}$ is the resistance of the sensor measured in air initially before injection of any concentration of VOC and R_{gas} is the resistance measured upon injection of certain gas concentration.

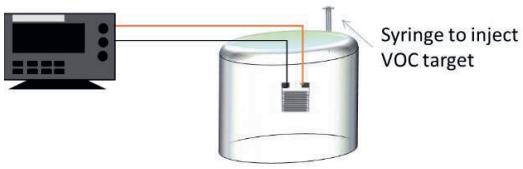

Fig 2 Schematic of gas sensing setup

3 Results and Discussion

The Raman spectra of PDAC/GO layers reduced at different temperatures show typical features of a highly disordered material [14-17] with D (disorder) and G (graphitic) bands, located around 1350 and 1580 cm−1, respectively, being the most pronounced features of the spectra (Figure 2). Also, the overtone bands, i.e. 2D region, are clearly visible. These bands are found at around 2670 cm−1 and 2930 cm−1. Following Ref. [18] the first band is denoted as 2D (G') while the second one is denoted either as D+D' or D+G. These bands are considered to be defect-activated and dependent on the number of layers in graphite/graphene. Moreover, their appearance is also associated with wrinkled graphene layers, which contain significant amount of defects [18]. There are variations of relative intensities of observed bands (certain increase of G-to-D band intensity and decrease of 2D region with increasing temperature), but the overall conclusion is that thermal treatment did not change the disorder in rGO significantly. However, we expect that conductivity of rGO is changed with respect to that of parental GO (which is very poor conductor). This conclusion is in line with previous results

considering conductivity changes of electrochemically reduced GO, showing that significant increase of conductivity is expected upon very mild reduction [19] and color change upon thermal treatment. We note that Raman spectroscopy showed homogeneous distribution of PDAC/rGO over silver electrodes and substrate.

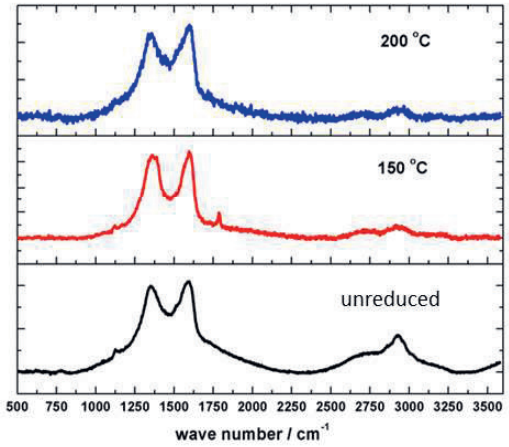

Fig. 3. Raman spectra of PDAC/rGO for unreduced and reduced at 150 and 200 °C

Due to the poor conductivity of PDAC/GO and partially reduced PDAC/rGO treated at low temperature, temperature of 200 °C was used to thermally reduce GO in PDAC/GO films. Therefore the resistance can be measured. In Fig. 4, the relation between electrical resistance and no. of layer is shown which concludes that a successful homogenous layer-by-layer deposition. The resistance was changed by two orders of magnitude to decrease from about 500 kΩ to several kΩ. After 8 layers, it seems that there is no significant change in the resistance in relation with number of layers.

Fig. 5 shows the relative response of resistance of the PDAC/rGO films exposed to various vapors i.e. ethanol, acetone, isopropanol and methanol in a concentration of 2000 ppm. These VOCs can be classified as aprotic polar vapors (acetone) and protic polar vapors (isopropanol, ethanol and methanol). In both cases both has a hydrogen atom bounded to an oxygen atom. Among them only isopropanol shows a negative response which has the lowest polar bond. The sensors show the highest sensitivity to methanol which could be explained that methanol has the highest polar bond. In addition, its smallest molecular size can easily diffuse and interact with the conductive layer of PDAC/GO [20].

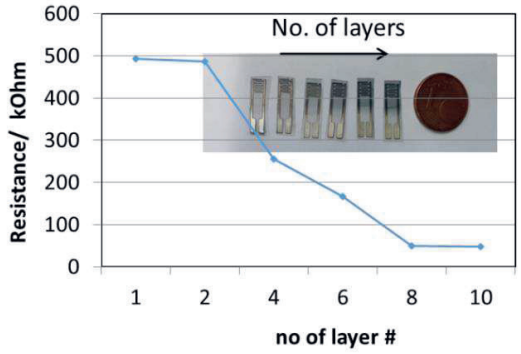

Fig. 4 Resistance change by no. of bi-layers reduced at 200 °C, Inset: photograph of the sensors

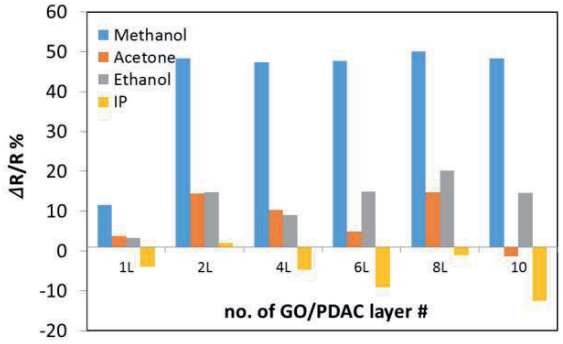

Fig. 5 Measured sensitivity of methanol, acetone, ethanol and isopropanol at 2000 ppm

For the measurements of response to methanol, Fig. 6 shows the relative change of resistance to different concentrations. It is noticed that resistance increases when more concentrations of methanol is added to the chamber. The sensitivity decreases by increasing the multilayer PDAC/rGO. However, for thicker films, the linearity is improved.

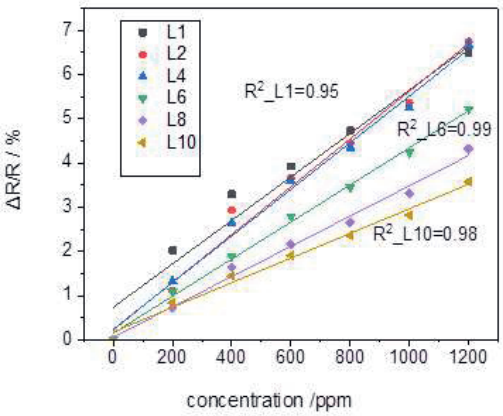

Fig. 6 Relative responses of resistance of the PDAC/rGO at various methanol concentrations

4 Conclusion

A sensor based on PDAC polymer and reduced graphene oxide was fabricated by layer-by-layer technique accompanied by relatively low temperature reduction. Different VOC vapors were used to test the sensing properties of these fabricated sensors. The relative resistance changes were 50% for methanol, 10% for acetone, 9% for ethanol, and 1% for isopropanol. This confirms the sufficient sensitivity of GO/PDAC to VOCs and that functionalization using layer by layer deposition is suitable as it improves response and presents a basis for detection of different VOCs specially methanol by measuring the change in electrical resistance. By further functionalization, the sensitivity to different VOCs can be adjusted, so that selective multi-sensor systems can be realized.

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