Drop-casted Graphene Oxide Love wave sensor for detection of humidity and VOCs

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ABSTRACT

The rising demand for sensitive analytical techniques have led to a great deal of research interest in the recent years, which has also generated much public awareness of health risks caused by environmental humidity and air pollution. This study reports advancements in highly-sensitive detection methods using Love wave devices fabricated from Graphene Oxide (GO). Under this, solutions of GO were prepared and used to achieve improved efficiency of the oxidation process and enhance the sensitivity of Relative Humidity (RH) and Volatile Organic Compounds (VOCs) detections. This work demonstrates that the detection limit of RH could be set very low due to the certain sensitivity levels. Similarly, GO prepared by us exhibited low detection limit for VOCs, proving the multi-functionality of GO rather than alternative sensing materials. The experiments conducted at room temperature and realized fast response and recovery times. This Love wave sensor provides high accuracy under full scale exposure of target analytes. Eventually, these ultrasensitive GO based devices can pave the way for a wide range of high-sensitivity detection applications.

Index Terms: Humidity sensor, Gas sensor, Graphene Oxide (GO), Love wave sensor, VOCs detection.

I. INTRODUCTION

Nowadays, energy and environmental issues brought about by agriculture, transport and industry have become major challenges strongly influencing the public health and social behavior all over the world. For example, high concentrations of humidity are directly responsible for outbreaks of deadly viruses such as Ebola Virus Disease (EVD) that recently caused havoc in Africa¹. This poses a threat to public health, also due to long-time linked to epidemiology of Ebola virus infections.

Humidity also causes serious side effects from respiratory problems to exhibiting symptoms of various molds and harmful bacteria². Furthermore, detection and control of environmental humidity has direct consequences in industrial processes³ and environmental contamination⁴.

Along similar lines, VOCs represent major public concerns due to their widespread use in commercial products (aerosol and adhesives) and in industrial processes⁵. In high concentrations, they are associated with cancer and damage to the central nervous system and are also known to affect developing embryos⁶. For these reasons, there is an ever-tightening demand on highly selective and sensitive analytical techniques in a number of fields, such as analytical and physical chemistry, medical diagnostics in biotechnology and environmental control. It might be convincingly argued that the development of novel sensing materials and high performance, real-time label-free monitoring detection platforms deserve more attention also to provide public awareness of environment and health risks, rapidly and efficiently.

Recently, graphene based materials have opened new horizons in Physics, Chemistry, Material Science and plenty of technological applications⁷⁻¹⁰. The fabrication of GO coatings is of broad interest in studies dealing with the sensing properties of graphene, especially as chemical devices. Graphene is a suitable material for surface functionalization⁸ and further useful for moisture detection¹¹ and gas sensing applications¹²⁻¹⁵. Graphene and sensors are a natural combination, as graphene's large surface-to-volume ratio is able to enhance the surface loading of desired biomolecules¹⁶. Plenty of noteworthy works are associated with sophisticated sensor designs for humidity¹⁷ or trace-gas detection applications¹⁸. Acoustic devices are typical acoustic wave structures, convenient for chemical sensing applications¹⁹. In the present work, we examine the extension of Love wave sensors, which present a well-known technology to the broad family of acoustic wave sensors²⁰. Promising results are obtained owing to the inherent capabilities of our devices, since the shear horizontal guided surface acoustic wave sensors are mainly used for gas-liquid environment applications.

Here, we propose the amalgamation of GO and Love wave platform as a chemical sensor, subsequently dedicated to the detection of humidity and VOCs vapors, which is able to identify and thus prevent critical concentration levels. We have produced hypersensitive devices using simple methods, involving a thin GO film sandwiched in between the Inter Digitated Transducers (IDTs).

The device structure is based on a dual delay line setup by using two different acoustic wave propagation paths, which correspond to the coated (GO) and uncoated (reference) parts of the sensor. The encapsulation of this differential device allows the evaluation of our devices based on alternative sensing materials and provides certainty toward the expected detection of the target analyte. Figure 1 graphically depicts representative GO-Love wave device under vapor exposures based on two different acoustic paths.

II. METHODS AND MATERIALS

A. Micro-fabrication of Love wave devices

Love wave devices are composed of a piezoelectric AT-cut quartz substrate and inter-digitated electrodes (IDTs), with a particular crystallographic orientation (Euler angles: 0° , 121.5° , 90°) in order to generate pure shear horizontal acoustic waves, as illustrated in the uncoated part of the sensor, named as reference in Figure 1. This polarization allows the Love wave device to work with any adjacent gas or liquid medium.



Figure 1. 3D visualization perspective of the GO - Love wave device under vapor exposures.

As shown in Figure 2, the IDTs were fabricated by the evaporation of 70nm of gold (Au) with 40nm titanium (Ti) layers to achieve a good adhesion between the metallization, the quartz and the guiding SiO₂ film. The IDTs are each composed of 45 split finger pairs with a 40 μ m periodicity, corresponding to the wavelength. Then, a 4.1 μ m silicon dioxide film has been deposited by Plasma Enhanced Chemical Vapor Deposition (PECVD) as a guiding layer, which allows to trap the mechanical energy near the surface and therefore, to ensure the sensitivity due to the surface perturbations. Especially, for the gas molecules, the addition of a chemical sensitive film (GO) on the acoustic wave propagation path permits to amplify the immobilization of the targeted molecules and subsequently the mass loading effect of the coated device.

B. Graphene oxide preparation and characterization

The sample of GO used in the present study was obtained from commercial graphite by Hummers²¹ oxidation followed by subsequent exfoliation of the resulting GO by sonication in water. Inks of permanent GO suspensions with concentration of 1.2 mg×ml⁻¹ were prepared. Analytically, a particular method has been utilized to produce high quality oxidized graphene, that is, a mixture of concentrated H_2SO_4/H_3PO_4 (360:40 mL) was added to a mixture of graphite flakes (3g) and KMnO₄ (18g) to produce an exothermic reaction that was controlled in an ice bath. Then, the mixture was heated to 50 °C and stirred for 24 h, then cooled to room temperature (RT) and poured onto ice (400



Figure 2. Technological steps of Love wave devices.

mL) that contained 30% H₂O₂ (3mL). The suspension was filtered, washed with aqueous HCl (1:10, 37%) and water and the resultant solid suspension was centrifuged and dried at 60 °C. The GO suspensions were prepared by exfoliation of the GO solids by sonication in Milli-Q water for 2 h with an ultrasound source (400 W) to give aqueous suspensions of GO sheets with a concentration of 500 mg L⁻¹. Drying of these GO suspensions renders powdered black solids with a specific surface area of 29 $m^2 \times g^{-1}$ which falls in the range of the reported values for these materials. Figure 3a shows Raman spectra for high oxidation of graphene sensitive coatings. Infrared (IR) spectroscopy of these GO powders is presented in the Figure 3b below, wherein the characteristic vibrations of OH, COOH, C=C and C-O groups appearing at 3430, 1726, 1626 and 1055 cm⁻¹, respectively, can be observed.



Figure 3(a). Raman spectra recorded with λ = 514.5 nm Ar ion laser excitation source. D-G bands are indicated.



(b)

Figure 3(b). Infrared Spectroscopy of GO powder. Characteristic vibrations of OH (3430 cm⁻¹ attached heteroatoms), of COOH (1726 cm⁻¹), of C = C (1626 cm⁻¹) and C - O (1055 cm⁻¹), respectively, can be seen.

Exfoliation and single layer configuration of the GO suspended in water was assessed by AFM measurements of the flake thickness. Figures 4a and 4b show a typical AFM image of GO flakes that has a vertical height of 1.4 nm, which is in the range of the reported literature²² values.

C. Graphene oxide deposition on Love wave devices

The sensors were heated at 80°C. The graphene solution was maintained at room temperature and a circular spot was deposited by using drop casting²³ on the area between the transducers. The ink was administered from a distance of 1mm and a drop size was of 0.05ml×min⁻¹. In total 2 drops per site were used and the ink was allowed to dry for 1 hour. Subsequently, particular GO surfaces were selected for record the SEM images of the top and tilted-section GO areas, as shown in Figures 5a and 5b. The thickness of the GO film corresponds to 285-338 nm and the SEM images



Figure 4. (a) Typical AFM image of GO sheets. (b) Single layer thickness of GO sheet at 1.4nm.

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Figure 5. a) SEM images from the top, and (b) tilt-sectional areas of the GO sensing layer.



Figure 6. (a) Attenuation and (b) phase of the uncoated-coated Love wave devices, respectively.

illustrate uniformly deposited GO film based on the initial conditions of the droplet formation, especially in the outer walls of the droplet area, due to the optimization of the drop-casting technique.

III. ELECTRICAL CHARACTERIZATION OF GRAPHENE OXIDE BASED LOVE WAVE DEVICES

Electrical characterization (S - parameters) of the platform was performed using a network analyzer (ANRITSU-MS2026B). A wide high-accuracy spectrum has been selected in the radio-frequency network analyzer to determine the minimum of insertion loss, of the uncoated and coated delay lines, and to obtain performance characteristics of the coated sensor. Figures 6a and 6b illustrate the transmission line characteristics (S_{21}) in terms of the attenuation and the phase, respectively. The minimum of insertion loss for the uncoated devices is about -30 dB, corresponding to a synchronous frequency equal to 114.595 MHz and the phase shows a linear evolution in the useful frequency range. Compared to the coated delay line with the

GO sensing layer, S_{21} parameters are strongly modified after the deposition. From the insertion loss curve as a function of frequency, the supplementary insertion loss due to the GO deposition is about 34 dB, near the synchronous frequency. Also, the frequency shift in phase corresponds to 55.625 kHz. Electrical characterization shows that even high GO thicknesses can be deposited on the top of the Love wave sensor. Analytically, in order to maintain the Love wave excitation, that is, a thick over-layer such as GO in this case, will have eventually a lower shear wave velocity, since the GO thickness is increased. Then, most of the acoustic wave energy will propagate in the GO sensing layer, and thus the sensitivity will be significantly increased due to surface perturbations.

IV. RESULTS AND DISCUSSION

A. Graphene Oxide based Love wave devices under vapor exposures

The data gathered in this pilot study of GO based devices suggest that the valorization of GO as a sensitive layer is essential, since GO has attained a great deal of research interest in the literature. Analytically, low concentration sequencing vapors were flown over the GO-Love wave devices. The vaporizer equipment is composed of a part based on saturator providing the generation of a vapor in a given concentration and a given flow rate. A dilution stage is taking place in order to adjust the concentration of the vapor in a carrier gas (Nitrogen) and also the control of the "speed" (pressure) of the dilution. Following the principles according to the Figure 7a, the influence of the critical temperature on the vaporizer through the equilibrium thermodynamics law is that the system requires enough energy to be able to activate the liquid to gas phase transition. The saturator is providing the generation of a steam heated cylinder filled with the desired initial solution (RH or VOCs) in the liquid phase, which is circulated through nitrogen at a fixed flow rate. Thus, the fixed gas flow rate is related to the concentration that is generated from the saturator and it depends on the critical temperature. The generated concentration is certified by the manufacturer at a temperature and calibration data, and therefore corresponds to the desirable concentration that is planned. In order to have a variable concentration, a portion of N₂ is driven from an alternative side of the vaporizer and it has been used for the dilution of the original solution, after the phase transition. Finally, by adjusting the amount of the nitrogen with a Mass Flow Controller (MFC), the resulting concentration is controlled. The assembly is controlled by a Programmable Logic Controller (PLC), which allows different concentration levels to be translated on certain sequences by programming a user interface control panel (OP3 Operator Panel). The desired concentration values are extracted from the equation (1) below:

$$C = \frac{P(T)}{F} \tag{1}$$

where C is the initial concentration (mg/Nm^3) with N from table I, P(T) is the permeation rate of the desired substance $(ng \times min^{-1})$, that is known at the critical temperature and F is the dilution flow rate of nitrogen $(ml \times min^{-1})$. Generally, certain abbreviations have been used, as is shown in Table I:

To convert the concentration from mg/Nm3 (N corresponds to the Normal conditions; Table 1) in PPM/V, the initial concentration is multiplied by the following factor K:

Table I. Provided definitions upon certain conditions

Abbreviations	Conditions
N: Normal conditions	Temperature of 0 °C and Pressure of 1.013 bar
STP: Standard Temperature and Pressure conditions	Temperature of 20 °C and Pressure of 1.013 bar
Calibration conditions	Critical Temperature of the substance and Pressure of 1.013 bar

$$K = \frac{V}{Mw} = \frac{V_0 T}{273.15 Mw}$$
(2)

where V is the molar volume at a certain Temperature in $^{\circ}$ K, Mw is the molecular weight of the substance and V₀ is the volume of one mole of an ideal gas at STP conditions, which occupies 22.41 liters.

That means:

$$C(ppm) = \frac{KP(T)}{F} \xrightarrow{(2)} C(ppm) = \frac{24.45P(T)}{MwF} \quad (3)$$

where C is the initial concentration (ppm), P(T) is the permeation rate ($ng \times min^{-1}$) of the desired substance (RH or VOCs), that is known at the critical temperature (calibration conditions) and F is the diluted flow rate of nitrogen ($ml \times min^{-1}$). Furthermore, the coated GO-Love wave devices are linked through the physical parameters of sensitivity and the frequency shift, which can be described as²⁴:

$$Smf = \frac{1}{\Delta \rho_b b} \frac{\Delta f}{f_0} \tag{4}$$

where Δpb corresponds to the density of the sensitive layer following the deviation of $pb+\Delta pb$, (higher density levels due to the adsorption of the analytes in the vapor state) and b is the thickness of the sensing layer. Notably, Δf is the frequency shift based on the mass loading effect and f_0 is the resonant frequency without mass loading effect. Our first approximation is based on the interpretation that the mass loading effect is considered by the sorption of chemical compounds and modifies only the density of the sensing layer (Equation 4). Based on the real-time detections of the GO-Love wave sensor, the sensitivities are extrapolated experimentally by:

$$S = \frac{\Delta f}{\Delta C} \tag{5}$$

where Δf is frequency shift and ΔC represents the difference between the initial and the targeted concentration of the analytes. Analytically, as represented in the Figures 7 (b) and 7 (c), the real time detection of RH

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Figure 7. (a) Experimental setup of the gas line measurements. (b) Dynamic responses of GO - coated and uncoated delay lines towards RH with the extended magnification and (c) towards C_2H_6O vapors (adsorption - desorption).

and C₂H₂O vapors shows clearly the evolution of the frequency shift as a function of the concentration levels of the target analytes. The influence of two different and subsequent exposures (ΔC) is directly correlated with the frequency shift Δf , which is mainly based on the deviation from the baseline. Baseline corresponds to the initial concentration of 2% and 30 ppm for RH and ethanol, respectively. Standard deviation from the baseline provides useful information about the certainty of the compounds' detection and the estimated detection limit. Furthermore, the experimental sensitivity values correspond to 32 kHz/5% and 112 Hz/ppm, for RH and ethanol, respectively. Therefore, the appearance of RH and VOCs detections in depth, as perceived and recorded by analogous measurement setups shows that this study primarily unifies the plurality of applications related with GO films as a sensitive medium.

B. Discussion

This work focuses on the application related to the detection of low humidity and demonstrates that the detection limit of RH could be set significantly low. Figure 8a represents the sensitivity of the GO-Love wave structure within a useful range of 5% to 40% of RH which is higher than alternative devices that have been reported previously¹⁷. Notably, higher amounts of RH detections can be observed in the Figure 5b (extended magnification - 70% of RH). Interestingly, the frequency shift of Love Wave device B7 shown in Figure 8a demonstrates a saturation behavior which might be caused by the hysteresis of the sensor device, since RH approaches higher values in every subsequent cycle of the humidity vapor exposures (Figure 5b - extended magnification). Furthermore, since the present GO layer is delimited between the IDTs, there is overwhelming evidence that the sensitivity could be further increased by prolonging the GO deposition area, which is allowed on Love wave devices. This is a great potential, especially in this platform, since the surface area of the sensitive layer gravimetrically affects the sensitivity of our devices.

Similarly, Figure 8b represents the comparison of Love wave devices coated with alternative sensing materials under ethanol (C_2H_6O) vapor exposures. Analytically, standard conventional sequence of different ethanol concentrations has been introduced on GO devices, showing that GO exhibits sensitivities even two orders of magnitude higher than materials, such as TiO₂, SiO₂ and Molecular Imprinted Polymer (MIP)²⁵⁻²⁶.

It has been recently reported that there is a correlation between the possible number of adsorbed layers (water molecules) and the fraction coverage of GO^{27} . In particular, the ability to adsorb moisture on



Figure 8. (a) Humidity comparison responses of different acoustic wave devices (Lamb and Love wave sensors) based on GO; Lamb wave sensors are adapted from literature (Ref. 17) and Love wave sensor from this study. (b) Comparison of Ethanol (C_2H_6O) responses between different sensitive layers coated on Love wave devices. Silica mesoporous, MIP and TiO₂ are adapted from literature (Ref. 25-26) and GO from this study.

the sensing layer is associated with the oxidation method of GO^{11,17,27}, the length¹⁷and the height^{11,27}of the coated layer, since the ability to achieve lower detection limits corresponds necessarily to the amalgamation of Love wave devices and GO, especially for high GO thicknesses. Moreover, compromising between the cost of the fabrication techniques and the sensitivity levels of an alternative deposition method, low cost devices can be fabricated by utilizing inkjet-printing GO, which it can be a potential application in industrial processes and commercialization. But the Inkjet-Printed GO devices reported a lower sensitivity than that of the drop-casted²⁸, and subsequently, future work will focus on improving the performance of the GO solution to achieve higher sensitivity levels with low cost fabrication techniques.

V. CONCLUSION

This GO based acoustic wave sensor provides high sensitivity, especially in low concentrations of RH and C_2H_6O , respectively. The real time detection of the GO coated sensor provided promising results, since it was reported high performance of 32 kHz/5% and 112 Hz/ppm, for RH and ethanol, respectively. Moreover, the measurements are highly reproducible and future work will focus on realizing functionalized graphene based acoustic wave devices and enhancing the performance of sensitivity and selectivity to a specific target gas, thus paving the way towards hypersensitive and selective gas - moisture applications.

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