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Graphene oxide as sensitive layer in Love-wave surface acoustic wave sensors for the detection of chemical warfare agent simulants

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ABSTRACT

A Love-wave device with graphene oxide (GO) as sensitive layer has been developed for the detection of chemical warfare agent (CWA) simulants. Sensitive films were fabricated by airbrushing GO dispersions onto Love-wave devices. The resulting Love-wave sensors detected very low CWA simulant concentrations in synthetic air at room temperature (as low as 0.2 ppm for dimethyl-methylphosphonate, DMMP, a simulant of sarin nerve gas, and 0.75 ppm for dipropylene glycol monomethyl ether, DPGME, a simulant of nitrogen mustard). High responses to DMMP and DPGME were obtained with sensitivities of 3087 and 760 Hz/ppm respectively. Very low limit of detection (LOD) values (9 and 40 ppb for DMMP and DPGME, respectively) were calculated from the achieved experimental data. The sensor exhibited outstanding sensitivity, good linearity and repeatability to all simulants tested. The detection mechanism is here explained in terms of hydrogen bonding formation between the tested CWA simulants and GO.

1. Introduction

Chemical warfare agents (CWAs) are powerful weapons and a threat for civil safety. CWAs are extremely toxic synthetic chemicals that can be dispersed as a gas, liquid or aerosol or as agents adsorbed to particles to become a powder. About 70 different chemicals have been used or stockpiled as chemical warfare agents during the 20th and 21st-centuries. These agents are classified according to their mechanism of toxicity in humans into blister agents, nerve agents, blood agents, and pulmonary agents [1].

CWAs are extremely hazardous and potentially lethal and their use is restricted in conventional laboratories. Therefore, the research on CWAs is commonly conducted using simulant compounds [2–6]. Ideal chemical agent simulants would mimic all relevant chemical and physical properties of real CWAs without their intrinsic toxicological properties. Although a number of compounds have been used as CWA simulants, no individual compound is ideal because a single simulant cannot satisfactorily represent all environmental fate properties of a given CWA. Thus, a number of different chemicals have been proposed as CWA simulants [7–8] depending on the physicochemical property to be measured in detection experiments.

Conventional analytical methods used for CWA and CWA simulant detection such as gas chromatography–mass spectrometry (GC–MS) [9–10] are bulky, expensive and require specific sample preparation as well as technically trained personnel. Instead, chemical sensors offer a wide variety of advantages over the conventional analytical instruments such as low cost, short response time, easy manufacturing, and small size. In this context, surface acoustic wave (SAW) devices have gained enormous interest for sensor applications due to their high sensitivity, high resolution, high stability and a frequency output signal which is easy to process [11–13]. In the last decades, SAW sensors have taken advantage of the progress of the telecommunication technologies where SAW devices are used as piezoelectric resonators for radio frequency (RF) and their development has been parallel to it.

In order to achieve high sensitivity in SAW sensors, it is essential to confine the maximum amount of acoustic energy near the surface of the substrate and minimize wave scattering into the bulk of the substrate [14]. To achieve this, Love-mode acoustic wave devices

Abbreviations: CWA, chemical warfare agents; GO, graphene oxide; SAW, surface acoustic wave; IDT, interdigital traducer; DCE, 1,2-dichloroethane; DMA, dimethylacetamide; DMMP, dimethylmethylphosphonate; DPGME, dipropylene glycol monomethyl ether

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have been developed. These devices are based in the excitation of shear horizontal surface acoustic waves (SH-SAW) in a piezoelectric substrate, guided by a layer deposited over it, named waveguide layer [15]. In Love-wave devices the interdigital traducers (IDTs) are covered by the waveguide layer and so are protected allowing them to be used in harsh environment (in both liquid and gas) without IDTs damage. IDTs are on both sides of the substrate each, one is emitter and another one is receptor. The IDTs convert the incoming electrical radio frequency (RF) signals into mechanical waves which propagate along the surface of the device between the IDTs. Love-waves propagate in layered structures consisting of a piezoelectric substrate (usually quartz, lithium niobate, and lithium tantalate) with a guiding overlay (dielectric material such as silicon dioxide, parylene, polymethylmethacrylate, photoresists, or novolac resin). For gas/liquid detection, a third layer called sensitive layer is added. Adsorbed analytes (gases or liquids molecules, virus, toxins…) on the sensitive layers cause a perturbation in the propagation velocity of the Love-waves due to the change in the surface mass density. The velocity changes can be measured indirectly with very good precision using the device for controlling the frequency in a delay line (DL) based oscillator circuit and measuring the frequency shifts due to the adsorbed analytes.

A key issue in the design of SAW sensors is the choice of sensitive layer. Suitable sensitive layers should allow measuring changes in the velocity of the acoustic wave that would be then selectively assigned to the adsorption of the tested analytes. A wide variety of materials have been successfully used as thin film sensitive layer for SAW sensors, including polymers [16–19] and carbon nanotubes [20–22], but they have still not been so extensively explored as those reported for resistive sensors. Nanomaterials such as graphene-based materials offer promise for the development of highly sensitive layers for analytes detection in Love-wave SAW devices due to their ultrathin 2D structure and high surface to volume ratio and high surface area.

In recent years, carbon nanotube- and graphene-based sensors have been developed for the detection of nerve agents and organophosphorus pesticides [23–28]. Graphene oxide (GO) is a very attractive nanomaterial for sensor applications as it combines 2D structural features of graphene and the presence of oxygen-containing functional groups (mainly, epoxide, hydroxyl and carbonyl groups) [29–32] which can potentially interact with a great variety of analytes. GO is commonly produced by exfoliation in solution of graphite oxide prepared by the Hummers' method (oxidation with $NaNO_3$, H_2SO_4 and $KMnO_4$ of graphite), as reported elsewhere [33]. Recent studies have focused on the applications of the GO in resistive sensors for the detection of pollutant gases (such as CO_2, NH_3, H_2, NO), CWAs and explosives [34–42], but important shortcomings need to be overcome prior to their practical application such as their high operating temperature, low sensitivity, and long response and recovery times. A great advantage of the SAW sensors is that they operate at room temperature and therefore do not require heating. However, to the best of our knowledge, GO has hardly been used in SAW or Love-wave sensors [43–44].

In this work, we present a new Love-wave sensor based on sensitive GO layers. The sensor properties of GO toward the detection of different concentrations of CWA simulants below the median lethal dose (LD_{50}: dose required to kill half the members of a tested population) have been studied here in real time and *in situ*. We have chosen four CWA simulants: 1,2-dichloroethane (DCE) and dimethylacetamide (DMA) as simulants for distilled mustard (HD), dimethylmethylphosphonate (DMMP) as sarin (GB) simulant, and dipropylene glycol monomethyl ether (DPGME) as nitrogen mustard (HN) simulant [7–8,45]. The GO-based sensors presented here provide remarkable response showing high sensitivity and linearity to the CWA simulants tested.

In previous works [46–48], the device has been tested with polymers and nanofibers as sensitive layers detecting very low concentrations of simulants but detection mechanisms have not been considered. The main goal of the present study is to establish the potential applicability of GO as sensitive layer of Love-wave SAW sensor and the interaction of these CWA simulants with GO. We believe that this is the first time they have been employed in Love-wave SAW sensors. Furthermore, GO offers very good properties for its use as substrate to be interfaced with various biomolecules and cells in biological detection and providing new opportunities for the development of biosensors based in Love-wave devices.

2. Experimental details

2.1. Love-wave sensor

The Love sensor is composed of a piezoelectric substrate, a guiding layer and a sensitive layer. In our sensor the three-layer structure consists in ST-cut quartz as substrate where the SH-SAW is propagated perpendicular to the x crystallographic axis, SiO_2 as guiding layer and GO as sensitive layer. To generate and receive the acoustic waves we used a two-port DL. This well-known configuration [49,50], is formed by two identical combs-like metal electrodes whose strips are arranged in a periodic alternating pattern located on the substrate surface (see Fig. 1a). Each period of an IDT consists of multiple strips aligned and connected to the bus-bars periodically. The configuration that we used (shown in Fig. 1a) consists of four strips per period is called of double-electrode-type or split-electrode-type IDT. The period formed by four fingers is $\lambda = 28$ μm, the center-to-center separation between both IDTs (Lcc) is 150λ and the acoustic aperture, W, is 75λ that it is the length of the strips.

The guiding layer was a film of SiO_2 deposited on the piezoelectric substrate by plasma-enhanced chemical vapor deposition (PECVD) with a 3.5 μm thickness and low surface roughness and the synchronous frequency being around 164 MHz. All these parameters were optimized in previous reports [47–48] obtaining a design of delay lines with excellent properties concerning to stability, linearity, reversibility and negligible baseline drift. So, devices exhibiting optimized sensing performances in terms of repeatability, stability and sensitivity were achieved. The dimensions of each device were 9 mm × 4 mm × 0.5 mm.

The sensors were electrically characterised by means of a vector network analyzer (Agilent 5070B) and the oscillator through a spectrum analyzer (Agilent 9320A).

2.2. Materials and reagents

As mentioned above, 1,2-dichloroethane (DCE) and dimethylacetamide (DMA) as distilled mustard (HD), dimethylmethylphosphonate (DMMP) as sarin (GB), and dipropylene glycol monomethyl ether (DPGME) as nitrogen mustard (HN) have been tested as CWA simulants [7–8,45]. All the simulants were purchased from Sigma-Aldrich and used as received without further purification.

2.3. Sensitive layer

In order to promote the mass change due to the adsorption of CWA simulant volatiles and considering that the active area in Love-wave sensors is all the substrate, the sensor was coated with GO. The GO material used (CheapTubes Inc.; purity: 99 wt%) was synthesized by a modified Hummers' method [33]. GO was ultrasonically dispersed in ethanol (0.4 mg/mL), and the resulting GO dispersion was deposited onto the guiding layer by airbrush spraying. The airbrush technique is