Microdroplet Based Organic Vapour Sensor on a Disposable GO-Chitosan Flexible Substrate

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I. Summary And Motivation

With rising hazardous organic vapours in the environment, the detection of volatile organic vapour compounds (VOCs) is important for human safety. To this end, this paper presents a conductive droplet-based disposable sensor. Unlike conventional sensors, the droplet system is easily replaceable and is capable of detecting multiple vapours based on surface tension gradient. The response time for the presented sensing arrangement was found to be 3-4 seconds which is better than the solid-state counterparts. The chemiresistive sensor used in this work, is fabricated on 2.5 µm thick ultra-flexible graphene oxide-chitosan (GOC) bioresorbable substrate with Pt electrodes which are 60 µm apart. The presence of GO in the GOC substrate provides optimum hydrophobicity to the droplet for efficient operation. The electrostatic interaction and strong hydrogen bonds between GO and polysaccharide groups in chitosan provides tunable hydrophobicity and stability to the droplet. Moreover, biocompatibility, low-toxicity and bioresorbability of GOC substrate are highly desirable in the disposable sensing applications. With a conductive droplet of ~10 µL of aq. NaCl as an active sensing material, dispensed in-between the Pt electrodes, it was observed that the droplet shows 14-21% change in resistance in presence of VOCs.

II. Advances over Previous Works

Over past few decades, a number of organic vapour sensors have been developed utilizing various materials such as metal-oxide, carbon materials, polymer composites etc.[1, 2]. Many of these sensors require high operating temperature and are unsuitable for multiple vapour detection. The deteriorated performance of many of the existing sensors during prolonged exposure of vapour is another issue which renders them useless after sometime. A replaceable and disposable sensor can provide the solution in such a scenario. Recently, solid-state metal-oxide sensors have been explored to overcome such issues, but currently they are not so economic [3-5]. Hence, the metal-oxide based sensors are currently not feasible for disposable applications. Moreover, multiple use of a sensor for different users creates the concern of hygiene. These challenges are driving the research towards development of affordable, flexible, and disposable sensors [6, 7]. As a result, sensors on flexible substrates are being explored for detection of pH [8, 9], temperature [10], and body-fluid [8] etc. Many of these sensors perform better compared to their conventional solid-state counterparts. Further, being flexible, these sensors have the advantage of being suitable for use in wearable applications. However, disposability of these sensors has not attracted much attention. In this regard, our recent work [11] demonstrates GOC based substrate which is biocompatible and biodegradable and thus is a good candidate for disposable application. Further, the droplet based sensing makes it reusable also for a few testing. Droplet being the active material, the sensor can be used a few times just by replacing the previous droplet with a new one. The droplet system also shows better response time, as discussed in previous section. Droplet based sensors [12, 13] also provides has the additional advantage of being reused with minimum physical interventions. Microfluidics based sensors are gaining attention for their ease of implementation. In this line, many droplet-based sensors [13-15] have been reported for a variety of applications but these are not compatible with wearable systems. Hence, droplet on a flexible substrate would attract more attention as the use of flexible substrate could open up a new avenue in bendable electronics for droplet based works.

III. Results and Methodologies

A. Materials: Graphene oxide (GO) (ultra-high concentrated single layer graphene oxide solution, 6.2 g/l) procured from Graphene Supermarket, US. Cellulose acetate butyrate (CAB), chitosan, ethyl-L-lactate, acetic acid, iso-propyl alcohol (IPA), methanol, ethanol have been procured from Sigma Aldrich, UK. All chemicals were used as procured.

B. Fabrication Process: The fabrication process of the flexible chemiresistive sensor was the same as the work reported previously [11, 16, 17] . The major fabrication steps are shown in Fig. 1(a). The Pt electrodes (having dimensions 1 mm^2 with a separation gap of 60µm) were then deposited on the GOC flexible film using hard-mask. The fabricated flexible substrate

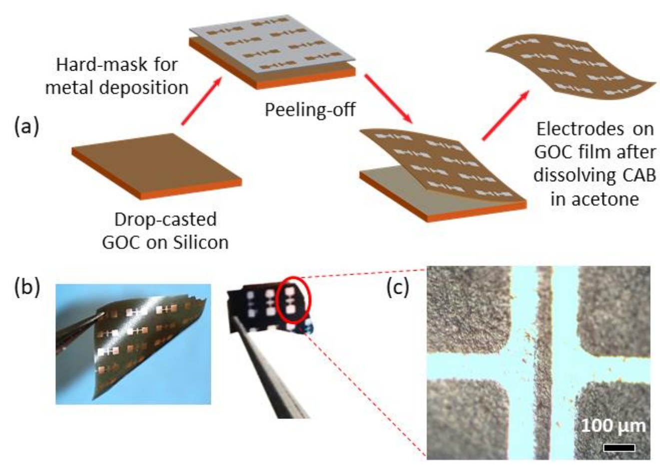

Fig. 1: (a) Fabrication steps; (b) the fabricated electrodes on flexible substrate; (c) optical microscopic image of the fabricated electrode.

and the microscopic image of the electrodes are shown in Fig. 1(b) and 1(c), respectively.

C. Characterisation: The experiment was carried out with a sessile conductive droplet of 1.7M aq. NaCl salt solution. The salt solution of different concentration was prepared at room temperature. Initially, a droplet of ~10 µl was dispensed in between a pair of Pt electrodes deposited on the GOC substrate. Fig. 2(a) and 2(b) describe the set-up employed to perform the experiments. The electrodes were connected to the digital multimeter (Agilent 34461A) for recording the electrical resistance across the droplet as shown in Fig. 2(a). In order to characterize the effect of VOCs, another droplet of an organic vapour kept at a distance of ~1 cm and the electrical response was recorded. Fig. 2(c) shows the schematic of induced Marangoni motion inside the droplet due to introduction of vapour which creates a surface tension gradient on droplet surface.

D. Results: The droplet on the flexible substrate was electrically characterized in ambient condition inside laboratory in a calm environment. It was observed that after dispensing the droplet, it took 1-2 seconds for the droplet to stabilize electrically as illustrated in Fig. 3(a). This happens due to the time required for the mechanical stability to take place. Further, the normalized resistance, $R_N (= R/R_0$, where R_0 is the base resistance of the droplet) across the droplet decreased by 14-21%, as shown in Fig. 3(b) due to the presence of different organic vapour of iso-propyl alcohol (IPA), methanol, and ethanol. The percentage change in resistance (ΔR) for each vapour is shown in Fig. 3(c). The ΔR can be correlated with the surface tension gradient ($\Delta\gamma$) between the water-air and water-organic vapour interface as shown in Fig. 3(d). The response of the sensor was found to be higher for higher surface tension gradient between the vapour-water and air-water interface. The sensor in this case is disposable and it was chemically stable on the GOC substrate up to 2-3 times of use.

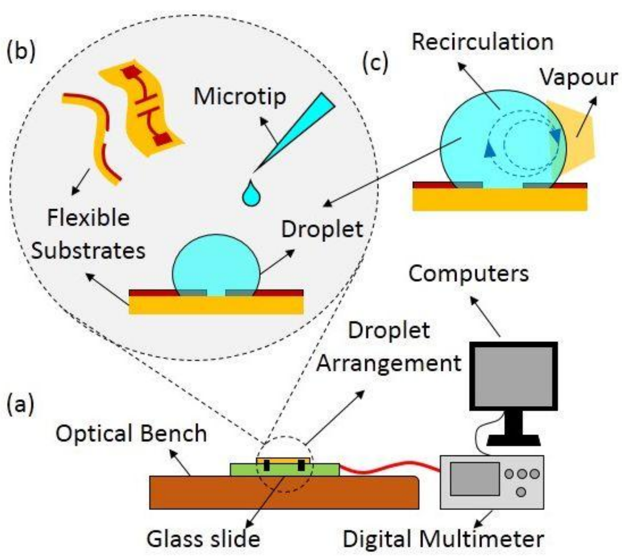

Fig. 2: (a) The scheme of the experimental set-up; (b) the schematic illustration of droplet set-up on flexible substrate; (c) the scheme of Marangoni circulation due to exposure of vapour near the droplet surface.

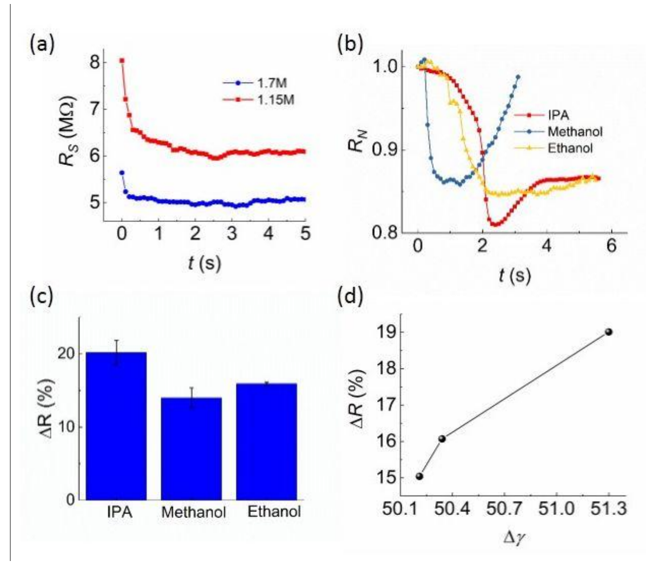

Fig. 3: (a) The electrical stability response of the aq. NaCl (conc. 1.7M and 1.15M) droplet in an ambient condition; (b) and (c) sensor response in presence of 3 organic vapours and the percentage change in resistance, respectively; (d) the response with the gradient of interfacial tension.

IV. Conclusions

A study was performed to check the capability of vapour sensing of a mocrodroplet based sensor. It was observed that the microdroplet require 1-2 seconds in order to stabilize on the flexible GOC substrate. The sensor showed responses for different organic vapours such as, IPA, methanol, and ethanol due to the on-set of solutal Marangoni motion inside the droplet. The motion inside the droplet was related to the surface tension gradient between the air-water and vapour-water interface. The sensor showed a 14-21% change in resistance for the vapour exposures. The response time of the microdroplet-system was found to be 2-3 seconds. The GOC substrate was chosen due to biocompatibility, low-toxicity and bioresorbability which makes it suitable for disposable application. Additionally, the hydrogen bonds and electrostatic nature of GOC provides optimum hydrophobicity to the droplet system. Studies with different other flexible substrates is kept as a future scope of this research. The primary goal of this research is to explore the possibility of flexible droplet-based microfluidic devices for sensing applications.

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