Hydrocarbon Sensing in Aqueous Solutions Using a Functionalized Graphene Chemiresistor

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Chemiresistor sensors based on carbon black/polymer composites, carbon nanotube/polymer composites and conductive polymers (e.g., polyaniline nanofibres and PEDOT-PSS) have been used extensively to detect a wide variety of analytes (e.g., benzene, aniline, chloroform) in the vapor phase [1, 2]. However, there is a need for direct detection of aromatic hydrocarbons (e.g., benzene and toluene) dissolved in water for environmental monitoring and oil exploration applications. Chemiresistors are particularly attractive due to their potentially very low per unit cost and are simple to operate. Most chemiresistor designs are not suitable for direct sensing in aqueous environments due to interfering conductive pathways through water. However, if micron sized electrodes are used, a very small double layer capacitance between the sensing film and the bulk water is formed [3]. This results in a large effective impedance through the conducting aqueous medium (e.g., deionized water or seawater) allowing for the conductivity of sensing film to be measured independently. This principal has been demonstrated using conducting films of hexanethiol functionalized gold nanoparticles to sense toluene dissolved in water with a 100 ppb detection limit [3]. The proposed response mechanism is based on the swelling of the nanoparticle film resulting in an increase in the effective distance between the individual nanoparticles leading to a decrease in the inter-particle tunneling current.

Recently, hydrazine reduced dispersions of graphene oxide have been used in to detect NO_2, NH_3 and 2,4-dinitrotoluene in a chemiresistor type platform [4]. The sensor response is based on a charge transfer mechanism in which the analyte affects the electronic states of the graphene causing a change in conductance [5]. In this study, we demonstrate that dispersions of octadecylamine functionalized graphene nanosheets [6], which have been drop cast onto interdigitated microelectrodes (5 µm wide and 5 µm separation) can be used for directly sensing aromatic hydrocarbons dissolved in water. The graphene nanosheets range from 0.5 to 3 µm in size which implies that there are only a few interconnects between the separate graphene nanosheets spanning the electrodes. The equilibrium response to varying concentrations of toluene in water is given in Figure 1. The detection limit for benzene, toluene, ethylbenzene, xylenes and cyclohexane ranges from 3 ppm to 10 ppm. The response time to analyte solutions is generally less than 60 seconds and restores to the baseline in less than 120 seconds when exposed to pure water (see Figure 2 for toluene responses). Based on the comparable responses to cyclohexane (response slope $\Delta R/R_0 \sim 19.1 \times 10^{-5}$ / ppm) vs. benzene (response slope $\Delta R/R_0 \sim 9.09 \times 10^{-5}$ / ppm), we deduce that the mechanism is most likely attributed to swelling and not chemical doping. If chemical doping contributed significantly to the sensing mechanism, the response to cyclohexane which cannot participate in pi-pi interaction would be diminished.

We are currently working on incorporating other functionalized graphene nanosheets and/or other chemiresistor materials (e.g., conducting polymers and carbon nanotubes) into sensor arrays for improved analyte differentiation.

References

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Figures

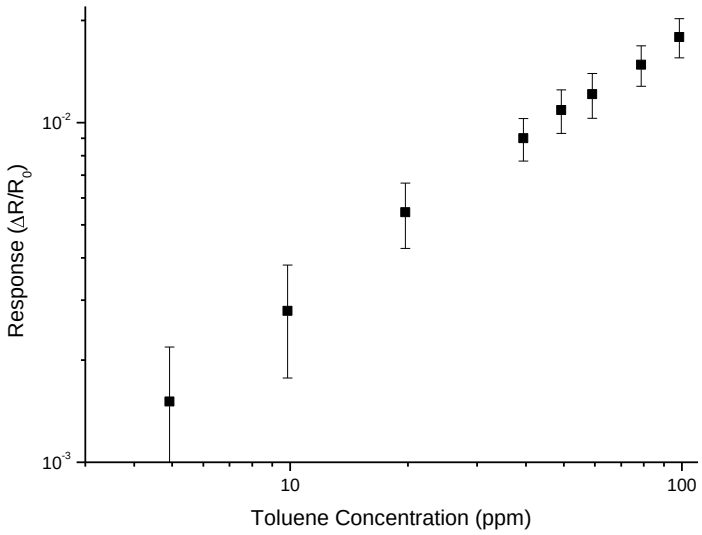

Figure 1. Equilibrium responses of ODA functionalized graphene chemiresistors to toluene (5 to 100 ppm)

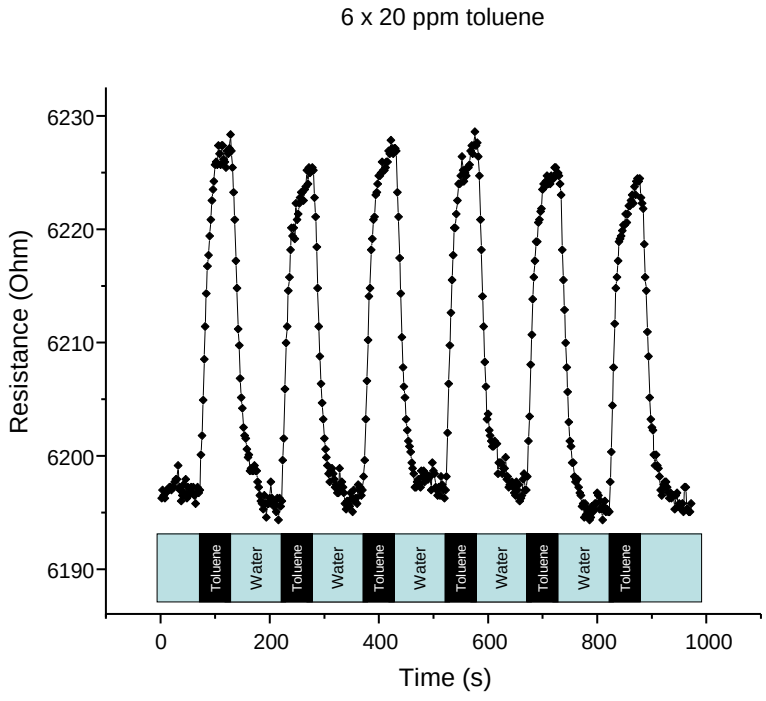

Figure 2. Response to cycling of 20 ppm toluene in water (45 seconds) and de-ionized water (90 seconds)