Printable sensors for Nitrogen dioxide and Ammonia sensing at room temperature.

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I. Summary And Motivation

Several studies have found a link between poor air quality and incidences of respiratory and cardiovascular diseases [1]–[6]. A World Health Organisation (WHO) report put the number of deaths caused by household air pollution at 4.3 million in 2012 [7]. Attempts at reducing poor air quality-related mortality have seen specification of safe human exposure limits for daily, and yearly average by government agencies such as Environmental Protection Agency (EPA) and World Health Organisation (WHO). Vehicle exhausts are key sources of Nitrogen dioxide, a key pollutant of ambient air. Other sources of NO_2 includes fossil fuels and industrial engines.[8] NO_2 is very toxic and causes acid rain.[9] Hence the need for sensitive, but more importantly selective sensors to monitor the levels of NO2 in breathable air. It is also desired that these sensors be able to provide fast response at room temperature.

Exhaled breath testing has been known to be a quick, safe and non-intrusive approach to early detection of declining health due to the presence of biomarkers corresponding to underlying diseases in them. Volatile Organic Compounds (VOCs) and ammonia are some of these markers.[10] Ammonia is passed out in urine and the concentrations of ammonia in exhaled breath only increases as health declines and reaches 1ppm in the event of kidney failure[11] Chemiresistors are good candidates for these sensitive and selective sensors and research is ongoing to develop new material composites with the desired properties for this purpose.

In this work we present chemiresistors based on two new material composites with potential to for applications in ambient air quality monitoring and breath analysis at room temperature. These composites can be printed or drop-casted on interdigitated electrodes on flexible substrates such as Polyimide (PI) and Polyethylene (PET). The NO_2 sensor, with Graphene-Carboxymethylcellulose (CMC) sodium salt active material composite shows sensitivity and selectivity to NO_2 at room temperature while the NH_3 sensor, based on a Polyaniline – Zinc Oxide composite shows sensitivity at room temperature.

II. Advances over Previous Works

Graphene as a gas sensing material has a high sensitivity but poor selectivity.[14]–[16] Cross talk between sensors and analytes limits its application without some modification. However, sensors with composites of graphene and other materials with affinity for specific gases can be used to tune the response of sensors to such gases and reduce their response to undesired analytes.

Ko et al., [12] demonstrated NO_2 sensing with graphene and showed sensitivity to 100ppm NO_2 at room temperature. Yavari and Koratkar [13] highlighted a number of related works based on graphene and related materials showing sensitivities ranging from 100ppm to 6ppm. Some of the sensors were functionalised to provide selectivity.

In this work we use graphene composite with CMC, a well-known polymeric binder with affinity for NO_2. We show that this sensor is selective to NO_2 compared with NH_3 and CO_2. For NH_3, we use polyaniline (PANI) as a conductive filler in the PANI/ZnO composite. This eliminated the need for annealing of the sensor after drop-casting or printing.

III. Results and Methodology

Liquid exfoliated graphene-based composite was formulated into printable ink as described by Karagiannidis et al.,[17] and drop casted on interdigitated electrodes (shown in Figure 1), fabricated by lithography on Polyimide (PI) flexible substrate, dried at 80˚C for 1 hour and exposed to increasing concentrations of different gases and the responses, measured as variations in the resistance of the sensor according to equation (1), were compared as shown in Figure 2.

$$\frac{R_a - R_g}{R_a} \; x\,100\% \qquad (1)$$

Figure 1 – Fabricated interdigitated electrodes on which graphene-CMC composite is drop-casted.

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Where R_a is the resistance of the sensor in air and R_g is the resistance of the sensor in the gas. The order of the variables in the numerator of equation (1) is reversed in the NH_3 case.

The Figure 2 shows the response of the graphene-CMC sensor to increasing concentrations of NO_2, NH_3 and CO_2. A response of ~10% was observed to 20ppm NO_2, a further ~20% at 40ppm and ~5% at 80ppm. Although the sensor does not recover, as shown in Figure 2, it is clear that the sensor is selective to NO_2, giving <5% response to increasing concentrations of CO_2 and NH_3 in all cases investigated. The sensor seems to saturate at 60ppm and thus gave little/no response as the concentration was increased further to 80ppm. More work is needed to overcome this challenge.

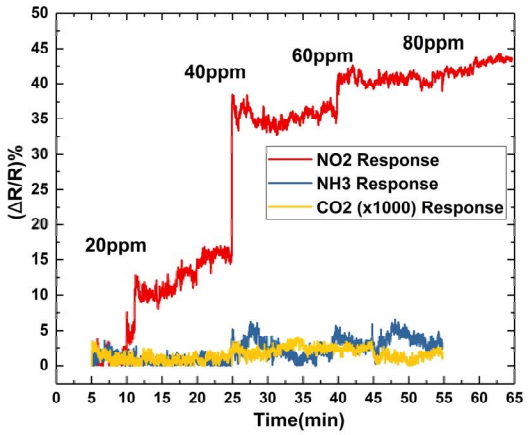

Figure 2 – Graphene-CMC composite sensor response to NO_2, NH_3 and CO_2 of increasing concentration showing the sensor sensitivity and selectivity to NO_2.

The PANI/ZnO nanoparticle ink composite was prepared by adding 50mg of PANI into 2ml ZnO ink and mixed thoroughly in a speed mixer for 5 minutes. The resulting ink was then drop casted on PET substrate and contacts were made to it using silver paste. The sensor was then dried on a hotplate at 100˚C for 15 mins. The sensor was then allowed to cool down to room temperature before exposure to NH3. The response of the sensor to increasing concentrations of NH3 is shown in Figure 3 at room temperature.

At 20ppm, the sensor response was ~5%, a further ~7% at 40ppm, and >10% response at 60ppm. This continued to rise to >20% at 100ppm as shown in Figure 3, all at room temperature. The sensor did not give any detectable response at 5ppm. However, the response of the sensor to 20ppm NH_3 at room temperature using ZnO without annealing or UV activation demonstrates the potential of ZnO/PANI composite to be further improved for higher sensitivity.

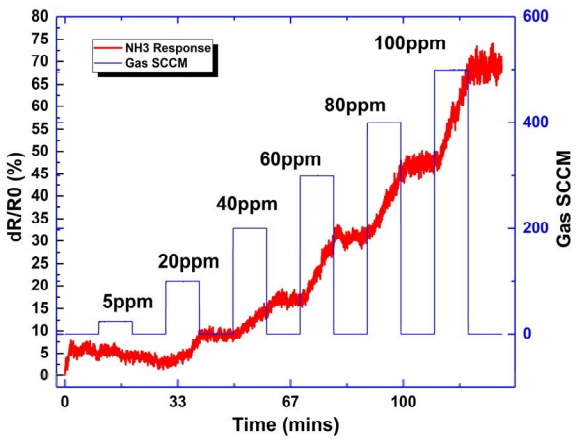

Figure 3 – PANI/ZnO composite NH_3 sensor response to increasing concentrations of NH_3 showing the sensor sensitivity.

Both sensors show potential of higher sensitivity upon further development to allow for application in their targeted areas.

IV. CONCLUSION

In this work we have presented sensors for NO_2 and NH_3 with room temperature functionality. The sensors are formulated into inks which can be printed or drop-casted onto interdigitated electrodes. We have also shown that the sensors are both sensitive to 20 ppm NO_2 and NH_3. The NO_2 sensor saturates at 60ppm. More work is needed to improve the sensitivity of the sensors to enhance their suitability for application in air quality monitoring and breath analysis respectively.

REFERENCES

[1] N. Li, M. Hao, R. F. Phalen, W. C. Hinds, and A. E. Nel, "Particulate air pollutants and asthma: A paradigm for the role of oxidative stress in PM-induced adverse health effects," *Clin. Immunol.*, 2003.

[2] A. C. Pope *et al.*, "Cardiovascular mortality and exposure to airborne fine particulate matter and cigarette smoke shape of the exposure-response relationship," *Circulation*, 2009.

[3] X. Wu *et al.*, "Association between gaseous air pollutants and inflammatory, hemostatic and lipid markers in a cohort of midlife women," *Environ. Int.*, vol. 107, pp. 131–139, 2017.

[4] A. D. Kappos *et al.*, "Health effects of particles in ambient air," *Int. J. Hyg. Environ. Heal.*, vol. 207, pp. 399–407, 2004.

[5] L. Samek, Z. Stegowski, L. Furman, K. Styszko, K. Szramowiat, and J. Fiedor, "Quantitative Assessment of PM 2.5 Sources and Their Seasonal Variation in Krakow," *Water Air Soil Pollut.*, vol. 228, 2017.

[6] Y.-H. Lim, H.-J. Bae, S.-M. Yi, E. Park, B.-E. Lee, and Y.-C. Hong, "Vascular and cardiac autonomic function and PM 2.5 constituents among the elderly: A longitudinal study," *Sci. Total Environ.*, vol. 607–608, pp. 847–854, 2017.

[7] World Health Organization, "Burden of disease from Household Air Pollution for 2012," 2012.

[8] T. Xie *et al.*, "UV-assisted room-temperature chemiresistive NO2 sensor based on TiO2 thin film," *J. Alloys Compd.*, vol. 653, no. 2, pp. 255–259, 2015.

[9] E. Comini, G. Faglia, and G. Sberveglieri, "UV light activation of tin oxide thin films for NO2 sensing at low temperatures," *Sensors Actuators B Chem.*, vol. 78, no. 2, pp. 73–77, 2001.

[10] K. Kim, S. A. Jahan, and E. Kabir, "A review of breath analysis for diagnosis of human health," *Trends Anal. Chem.*, vol. 33, pp. 1–8, 2012.

[11] C. Di, R. Paolesse, E. Martinelli, and R. Capuano, "Analytica Chimica Acta Solid-state gas sensors for breath analysis : A review," *Anal. Chim. Acta*, vol. 824, pp. 1–17, 2014.

[12] G. Ko, H. Y. Kim, J. Ahn, Y. M. Park, K. Y. Lee, and J. Kim, "Graphene-based nitrogen dioxide gas sensors," *Curr. Appl. Phys.*, vol. 10, no. 4, pp. 1002–1004, 2010.

[13] F. Yavari and N. Koratkar, "Graphene-Based Chemical Sensors," *J. Phys. Chem. Lett.*, vol. 2, pp. 1746–1753, 2012.

[14] W. Yuan, A. Liu, L. Huang, C. Li, and G. Shi, "High-Performance NO2 Sensors Based on Chemically Modified Graphene," *Adv. Mater.*, vol. 25, no. 2, pp. 766–771, 2013.

[15] W. Yuan and G. Shi, "Graphene-based gas sensors," *J. Mater. Chem. A*, vol. 1, no. 35, p. 10078, 2013.

[16] R. Pearce, T. Iakimov, M. Andersson, L. Hultman, A. L. Spetz, and R. Yakimova, "Chemical Epitaxially grown graphene based gas sensors for ultra sensitive NO2 detection," *Sensors Actuators B. Chem.*, vol. 155, no. 2, pp. 451–455, 2011.

[17] P. G. Karagiannidis *et al.*, "Microfluidization of Graphite and Formulation of Graphene-Based Conductive Inks," *ACS Nano*, vol. 11, no. 3, pp. 2742–2755, 2017.