

Metal-oxide Nanocrystals/Carbon Nanotubes Heterostructure Sensors for Selective Sensing of Hydrocarbons (VOCs + CH₄)

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Hydrocarbons are considered the principal cause for climate change. In comparison with other gases, hydrocarbons exhibit health effects and they are responsible for nearly one-fifth of anthropogenic global warming. These include volatile organic compounds (VOCs) and methane (CH₄).¹ Over the last years, nanomaterial-based gas sensors with high sensitivity at room temperature (RT) and low fabrication cost, have been demonstrated.² Recently, various metal oxide (MOX) nanocrystals (NCs)/carbon nanotube (CNT) chemo-resistors have been investigated in order to design sensitive exhaled breath gas sensors³. However, MOX NCs/CNT-based sensors lack rapid recovery time and long-time stability, limiting their utility.

In this paper, we present highly sensitive ZnO NCs/multiwalled CNT (MWCNT) heterostructure chemo-resistive sensors arrays for the selective detection of low concentrations of different hydrocarbons at RT. The atomic layer deposition (ALD) is used to spatially control the growth of MOX on the CNT surface, in terms of morphology and crystallinity, contributing to high sensitivity of the final heterostructure. (Fig. 1) The resulting sensors operate at RT and show fast and reliable response to toluene (C₆H₅-CH₃) and methane CH₄, being not responsive to benzene (C₆H₆) (Fig. 2). The response to C₆H₅-CH₃ and CH₄, although similar in magnitude, has different transient characteristics, allowing for differentiation. The observation of the transient characteristics is enabled by photo-activated sensing and UV promoted de-gassing. For example, the use of periodically UV illumination allows the investigation of the transient response to CH₄, resulting in PPM-level sensitivity at RT with shorter (few seconds) recovery time. (Fig. 3)

¹ (a)<https://www.epa.gov/ghgemissions/overview-greenhouse-gases#methane>; (b) A. Szczurek, B. Krawczyk, M. Maciejewska, *Chemometr. Intell. Lab.*, 125, pp. 1–10. (2013),

² M. Humayun, R. Divan, L. Stan, A. Gupta, D. Rosenmann, L. Gundel, P.A. Solomon, and I. Paprotny, *JVST B* 33(6), pp.06FF01, (2015).

³ (a) Shin, J., Choi, S. J., Lee, I., Youn, D. Y., Park, C. O., Lee, J. H., ... & Kim, I. D. *Adv. Func. Mat.*, 23, 2357-2367, (2013). (b) Valenti, G., Boni, A., Melchionna, M., Cargnello, M., Nasi, L., Bertoni, G., ... & Fornasiero, P. (2016). *Nature Communications*, 7.

⁴ Humayun, T. et al., *JVST A*, in Review

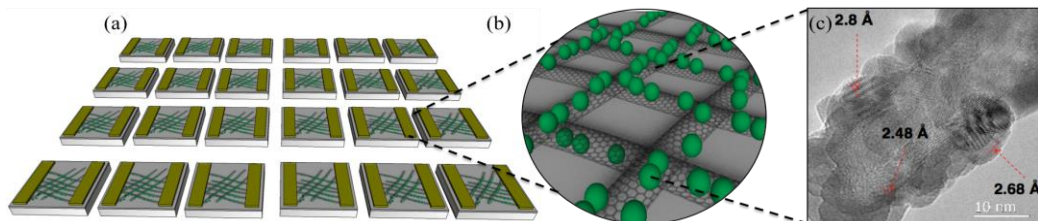


Figure 1. (a) Schematic array of hydrocarbons chemi-resistive sensors. (b) MOX/CNT heterostructure active material (c) Transmission electron microscopy (TEM) image showing uniform distribution of ALD ZnO NCs on MWCNT surface. Mean diameter of the ZnO nanoparticles is 7.74 nm. (Reproduced with permission from [4].)

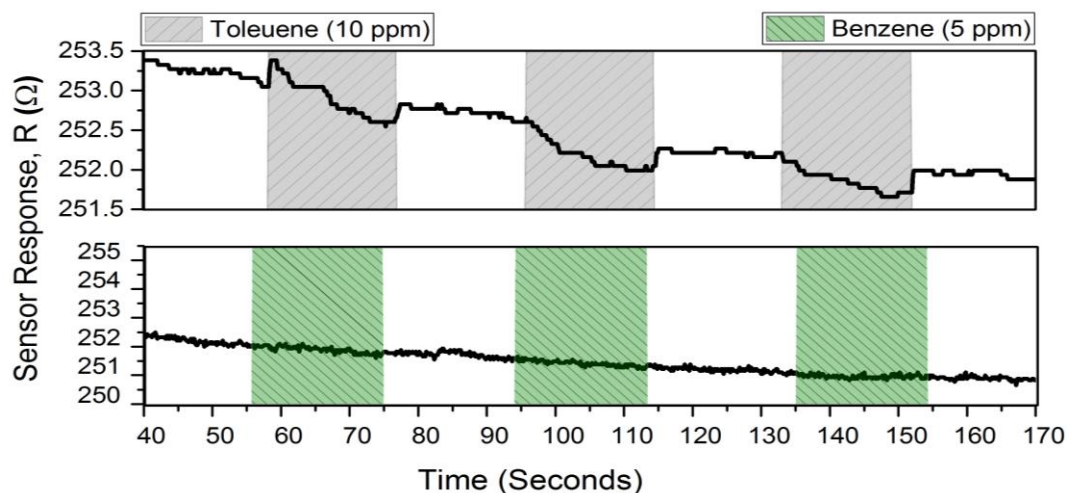


Figure 2. Typical time-resolved curve of the resistance of MWCNT/ZnO chemi-resistor upon exposure to toluene ($C_6H_5-CH_3$) 10 ppm and benzene (C_6H_6) 5 ppm.

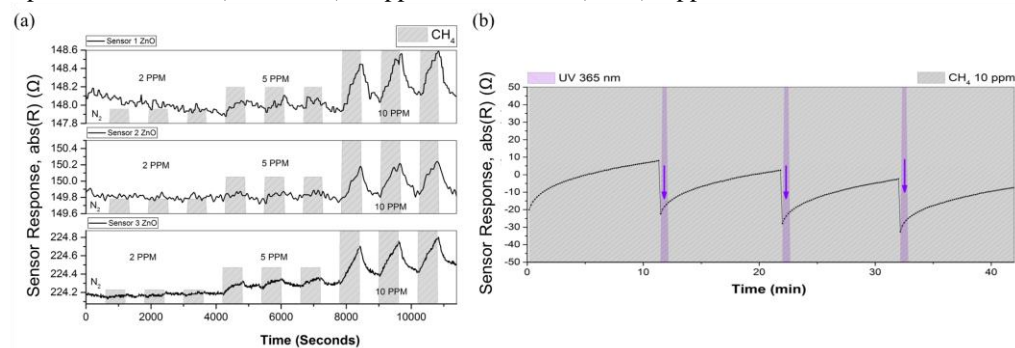


Figure 3. (a) Typical time-resolved curve of the resistance of MWCNT/ZnO chemi-resistor upon exposure to CH_4 10, 5, 2 ppm. (b) Typical time-resolved curve of the resistance of the ZnO-MWCNT sensor while continuously exposed to 10 ppm of CH_4 and recovered to baseline resistance by UV radiation.

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