UV-Accelerated Detection and Recovery of CH_4 in ZnO Functionalized Multi-walled Carbon Nanotube Sensors

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Functionalized multi-walled carbon nanotube (MWCNT) based chemoresistor sensors have potential to detect sub-ppm levels of CH_4 at room temperature[1,2]. However, recovery of chemoresistor CH_4 sensors is sometimes challenging[1,2], i.e., once exposed to CH_4 it takes a long time for the sensor to return to the baseline resistance. In past work, we presented ZnO-MWCNT chemoresistor sensors that were able to detect single ppm levels of CH_4 at room temperature[2]. In this paper we present a UV-based recovery technique for the ZnO-MWCNT chemoresistor CH_4 sensor resulting in *10 times* improved recovery time compared to existing literature[1] as well as our previous work[2]. ZnO is a wide-bandgap semiconductor (3.37 eV) with a large exciton binding energy (60 meV), which facilitates photo-induced enhancement of sensor recovery[3].

ZnO was deposited on pre-treated MWCNTs using diethylzinc as the precursor (Arradiance Gemstar ALD tool at 175 ^{0}C) (Fig. 1).
The room temperature photoluminescence (PL) peaks illustrated in Fig. 2 suggest good crystalline quality and photonic property of the functionalizing ZnO with a direct bandgap of about 3.36 eV (PL peak at ~370 nm). Hence a UV irradiation (~370 nm) excites electrons from valence band to the conduction band of the functionalizing ZnO, facilitating desorption of CH_4 molecules.

To study the UV-based recovery, the sensor was first exposed to 10 ppm of CH_4 in air for 30 mins; and then *without interrupting the CH_4 flow* the sensor was irradiated by a UV light (390 nm) until the sensor returned to its baseline resistance (Fig. 3). A recovery time of about 3 minutes was observed, which is a 10 times improvement compared to past results[1,2], even when the CH_4 flow was interrupted. This important result, coupled with reproducibility of the resistance increase while UV is off, allows us to dramatically reduce the CH_4 detection time of the sensor. In summary, we were able to reduce the recovery and consequently detection time of functionalized CNT-based CH_4 sensors by utilizing strong UV response of ZnO.

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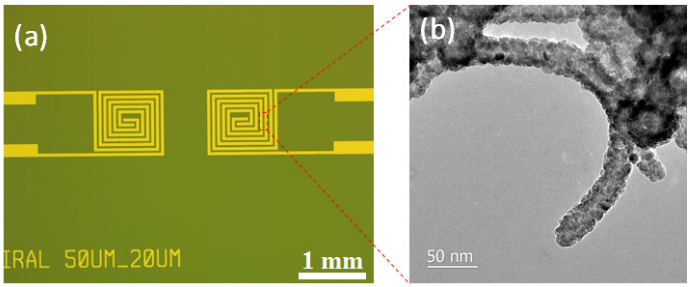

Figure 1: (a) Optical micrograph of a microfabricated ZnO-MWCNT chemoresistor CH_4 sensor. ZnO-MWCNT is deposited on top of interdigitated Au electrodes. (b) Transmission electron microscope image of ZnO functionalized MWCNT.

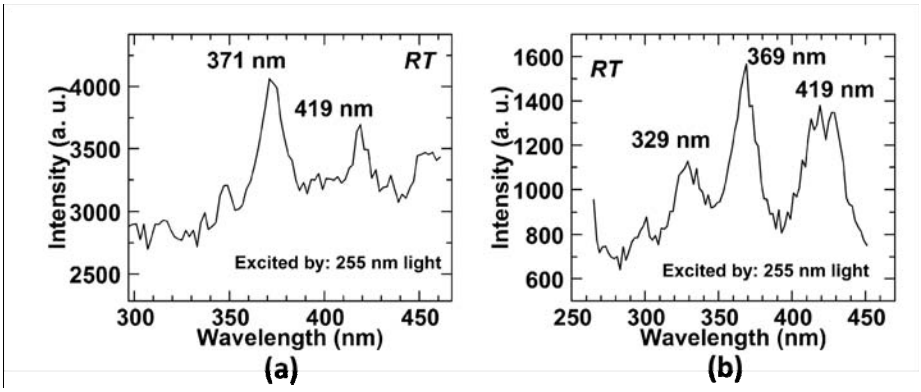

Figure 2: Photolumiescence (PL) spectra of (a) a 20 min UVO pre-treated and (b) 5 min O_2 plasma pre-treated ZnO functionalized MWCNTs. Peak at 369 nm represents near-band edge emission of the wide band-gap ZnO in the ZnO-MWCNT sensor[3]. The peak at 419 nm might be the result of oxygen vacancies in ZnO[3]. Horiba Jobin-Yvon Nanolog Spectrofluorimeter was implemented to conduct the room temperature PL experiments with a 255 nm incident light.

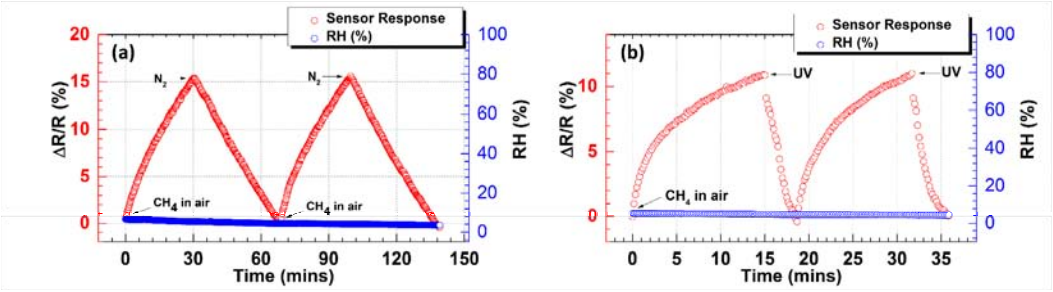

Figure 3: (a) Relative resistance ($\Delta R/R = (R_{gas} - R_{air})/R_{air}$) of the ZnO-MWCNT sensor while exposed to 10 ppm CH_4 in air and recovered by switching from CH_4 to N_2. Average recovery time was almost **35 mins**. (b) The sensors were irradiated with a 390 nm wavelength UV light for recovery (*without stopping* the CH_4 flow). Average recovery time was about **3 mins**. After each UV exposure, the sensor peaked in about 15 min. Relative humidity during both tests was constant at 1~2%.

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