Selectivity through Optimization of Metal Oxide Morphology: Towards Selective Chemiresistive MWCNT/TiO_2 VOC Sensors

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Hydrocarbon gasses, such as methane and volatile organic compounds (VOCs) not only play a significant role in climate change, but also exhibit many detrimental health effects. In order to monitor, control, and reduce the negative effects of hydrocarbon gasses released in atmosphere through various human activities, inexpensive yet highly sensitive and selective sensors are needed. Over the last years, many groups focused their attention on developing chemiresistive gas sensors using various materials including metal oxide thin films, metal oxide nanoparticles, nanowires, nanoplates, carbon nanotubes (CNTs), graphene, and mixtures of the above. Despite all these efforts, issues regarding sensitivity, reliability, and selectivity still require further effort.

In this work, we explore functionalization of multi-walled carbon nanotubes (MWCNTs) with TiO_2, by atomic layer deposition (ALD), resulting in a MWCNT/TiO_2 system. The deposition conditions during ALD as well as the O_2 plasma pretreatment of CNTs play an important role on the morphology and crystallinity of the oxide coating of CNTs. In contrast with results obtained in our previous work, the TiO_2 metal oxide nanocrystal (MOX NC) growth is possible both on O_2-pretreated and pristine CNTs. In both cases the crystallinity of the films improves with the growth temperature, shown in HR TEM images shown in **Fig. 1**. The response of sensors at room temperature to methane, toluene, and benzene is shown in **Fig. 2**. In particular, we see a decrease of sensitivity with crystallinity, a result that is contrasting our previously observed results using ZnO MOX NCs. Furthermore, we observe a reduced, albeit significant, response to low levels of methane in O_2-treated TiO2 sensors, while no response was observed to benzene or toluene. This contrasts with the untreated TiO2 sensors, which show good sensitivity to methane, benzene, and toluene. This morphology-dependent sensitivity can be used to remove cross-sensitivity to methane, and optimized to help to enhance the selectivity to the specific VOCs, such as toluene and benzene.

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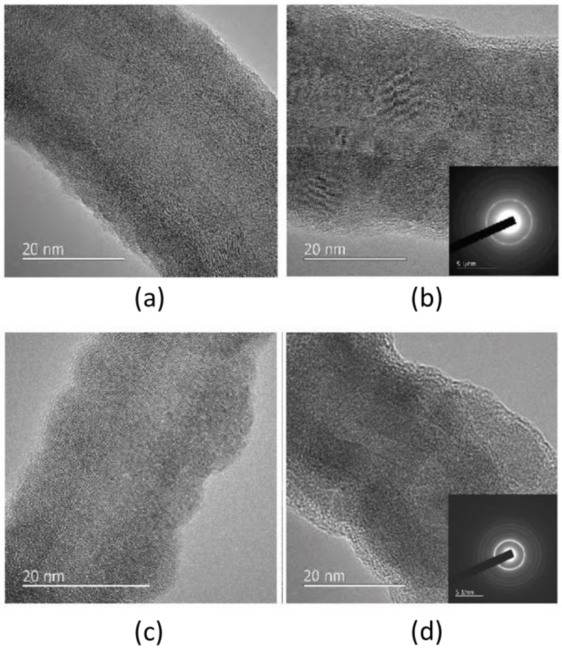

Figure 1: HRES TEM images of MWCNT/TiO2 sensors that were pretreated with O_2-plasma (a,b) and untreated (c,d). The images show the morphology of the functionalized WMCNTs fabricated at low (175 °C – a,c) and high (225 °C – b,d) ALD processing temperatures. In both cases the crystallinity increases with ALD temperature.

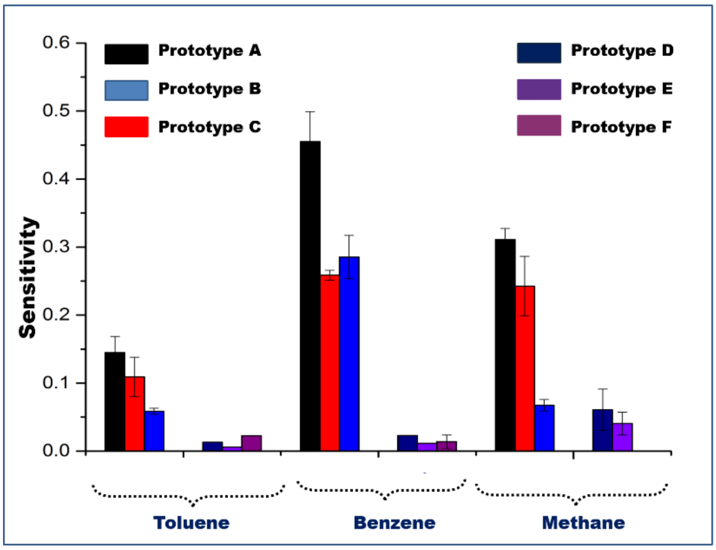

Figure 2: Response of untreated (prototype A B C) and 02-plasma pretreated (prototype D E F) TiO_2/MWCNT sensors to toluene (10 ppm), benzene, (50 ppm), and methane (10 ppm). Each data point consists of an average ΔR Rgas – R0/ R0 * 100) response of five cycles of two separately fabricated sensors. The sensors were exposed for the target gas for 20 min., followed by adsorption phase for 20 min. TiO_2 has been deposited on MWCNT (treated and untreated) at different ALD temperature (prototype A D) 175°C, (prototype B E) 200°C (prototypes C F) 225°C).