

# Fundamental Study on Thermally and Chemically Robust Molecular Sensors

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## 論 文 内 容 の 要 旨

**Thesis Summary**

Although a large number of polymer sensors and metal oxide sensors have been commercialized and are extensively utilized in various fields nowadays, the upcoming era of IoT put forward higher technical demands on them. Long-term stability and suitable design of sensor device are key issues that determine the performance of the final sensor in practical application. In this thesis, we demonstrate that based on the understanding of chemical reaction on sensing material's surface, the long-term stability and selectivity of target molecule can be achieved.

The chemical reaction on PEG-carbon black nanocomposite sensor for degradation mechanism was well investigated by using a dual-use device with capable check for FT-IR and sensing performance. The results were shown in chapter III. By comparing the sensing properties and the IR spectroscopy on a same device, it revealed that the oxidation induced consumption of PEG was a key factor for the degradation of sensing performance. Depending on the mechanism, an anti-oxidizing agent (*i.e.* ascorbic acid) was incorporated into the PEG-CB nanocomposite sensor to inhibit the PEG oxidation and successfully proved its long-term sensing stability in ambient air for 30 days. Because the oxidation is a typical problem for polymer materials, the proposed method was feasible to various polymer-carbon nanocomposite sensors to promote their long-term stability. After that, in chapter IV, we investigated the material dependence of metal oxides (*i.e.* ZnO, ZrO<sub>2</sub>, TiO<sub>2</sub>) on the molecular adsorption behaviors of volatile molecules. Spectroscopic and spectrometric analyses revealed that the Lewis acidity of metal cations give a strong impact on the bonding strength of molecules but not on the adsorption amount. Since the performance of catalyst/molecular sensor/molecular filter is essentially determined via the adsorption/desorption behaviors of molecules on material surface, the proposed nanowire array structure based analytical platform and the obtained implications in this study offer a foundation to design the performance of these nanoscale metal oxides based applications. In chapter V, we found in-situ fabrication of hydrothermally grown ZnO bridging nanosensors can substantially suppress the unintentional variations of electrical resistances between electrodes and significantly enhance the sensing responses for NO<sub>2</sub> with the smaller standard deviation and the lower limitation of detection compare with conventional shape edge seed layers. In chapter VI, we fabricated a highly active metal oxide surface with sol-gel processed ZrO<sub>2</sub> coated on ZnO nanowire array. This surface can achieve selective ketone sensing in mixture, because aldehyde *i.e.* nonanal is easily oxidated by activated oxygen on sol-gel ZrO<sub>2</sub> surface while ketone *i.e.* 2-nonanone with higher resistivity for oxidation remains on the surface. By combine this ZrO<sub>2</sub> coated ZnO nanowire array as molecular selector with PEG-carbon black sensor, selective ketone sensing can be obtained. At the same time, this ZrO<sub>2</sub> surface exhibited excellent thermally robust for keep its selectivity at 400 °C for near  $3 \times 10^7$  years.

However, there are still many obstacles in the practical application of metal oxide gas sensors. The effect of ambient environmental factors like temperature, humidity and ambient light cannot be ignored. In particular, the application of biomarker detection in human respiration is not accurate enough, because the large amount of moisture contained in the respiratory gas can disturb the sensing results. Integrating multiple detection devices based on different principles should be a possible way to improve recognition capabilities. In order to realize the next generation of innovation in the area of chemical sensors, the exploration of high-quality materials and new integration methods should be further explored.