An empirical investigation of effective factors of graphene oxide/TiO2 composite utilized for quartz crystal microbalance gas sensor

（課程博士・様式７）（Doctoral qualification by course work, Form 7）

学 位 論 文 要 旨

Abstract of Doctoral Thesis

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論文題目：水晶振動子マイクロバランスガスセンサーのための酸化グラフェン/TiO_2 複合材料に関する効果的因子の実験調査

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論文要旨：

Abstract : Among gas sensing researchers, there is a growing interest in improving the functionality and handiness of sensor devices while applying innovative methods and simple materials. So far, metal oxides have provided a platform for gas detection at small concentrations. Amongst them, TiO_2 has been explored for advanced gas sensors based upon different parameters to detect different gas species. Moreover, graphene and its chemically modified forms attract keen interest in science and technology due to its sheet surface, which functions as a suitable candidate for particle attachment. This study is build up with three main goals considering the mentioned factors: [1] to construct a room temperature gas sensor based on quartz crystal microbalance (QCM) containing graphene oxide (GO)/TiO_2 composite sensor layers, [2] to conduct an empirical analysis of the composite precursors affecting the adsorption of different vapors and [3] to observe the effect of photoinduction on a piezoelectric type gas sensor fabricated with photocatalytic GO/TiO_2 composite.

Two types of domestic gas analyzing devices were designed and developed to carry the sensing experiments. Initial experiments were carried out using ethanol vapor under the static gas flow method, where N_2 gas was used as the carrier gas throughout the research. All the experiments were carried out at room temperature. The oxidized graphite was obtained according to the modified Hummers method. Initial experiments were carried out with ammonium hexaflourotitanate (AHFT) as the TiO_2 precursor. The liquid phase deposition (LPD) technique was used to deposit TiO_2 particles in aqueous GO solution. The composite was coated on the gold-plated QCM resonator by the spin coating method. Since the composite preparation does not undergo any annealing process to remove unnecessary elements from TiO_2, characteristic data indicated that the composite has fluorine and nitrogen additionally. Hence, to study the effect of these elements broadly, three other Ti precursors ($TiCl_4$, titanium(IV) isopropoxide, titanium(IV) butoxide) have been used to prepare the GO/TiO_2 composite via sol-gel method.

Further, all the TiO_2 types and composites are characterized in detail to find the elements available in the materials and how they can affect the gas sensing application. Moreover, effect of UV illumination on the GO/TiO_2 composite coated QCM is investigated, and the QCM frequency shift patterns variation for gas adsorption-desorption under different light conditions are discussed as well. The gas adsorption by different gas types under UV irradiation conditions has also experimented.

The preliminary results denoted that GO/TiO_2 composite has a significant response to EtOH over GO and TiO_2 individually. When 4100 ppm EtOH gas was exposed to the functionalized QCM sensor with GO, TiO_2, and GO/TiO_2 composite of different GO ratios, the most favorable sensitivity was obtained for 30% GO (w/w) in the precursor solution. Further, the sensitivity range of functionalized QCM resonator (GO w/w=30%) for EtOH vapor was ranged from 20,000 ppm to 12 ppm. SEM, TEM, and XRD characteristic data of the composite revealed the formation of anatase TiO_2 on GO sheets through bridging and wrapping of the particles. The BET isotherm results strongly supported to evident the increase in the specific surface area of the composite over GO and TiO_2 individually.

The TiO_2 precursor variation experiments were entirely carried out using the dynamic gas sensor device with a controlled gas flow. The characteristic results illustrated that AHFT utilized non-annealed TiO_2, and the composite has comparably smaller TiO_2 crystallite size and has formed proper crystalline particles. The crystallite size reduction in composite also signifies that GO affects the crystal growth of TiO_2. It has shown that the surface fluorination of the TiO_2 can enhance the crystallization of the anatase phase. Further, it was found that the bulk TiO_2 structure does not get affected by F, N, or Cl on TiO_2 or in the composite. When the GO surface is modified with TiO_2, even though TiO_2 alone has no better gas adsorption ability, the fluorine's attachment on the TiO_2 surface at the same time helps for more gas adsorption. These results conclude that among different TiO_2 precursor materials used for the GO/TiO_2 composite preparation, the most suitable for sensing is composite prepared with AHFT utilized GO/TiO_2 composite. Further, the highest response from the dynamic gas device was obtained by ethanol, while the lowest was shown by acetonitrile gas.

The UV irradiation results would lead to a broad understanding of the reactions behind the gas adsorption on the GO-TiO_2 based composite surfaces for piezoelectric type sensors. Upon UV irradiation, the physisorbed surface OH groups have been reduced. Thus, the effect of surface hydrophilicity variation of TiO_2 and photocatalytic properties may be highly attributed to the changes observed in gas adsorption reactions. Further, we observed that Ti^{3+} ions are formed in TiO_2, and GO is partially reduced upon UV irradiation. Thus, the new curving patterns and the overall decrease in gas sensing upon UV irradiation can be explained with the surface changes observed in the composite.