論　文　の　要　旨

題　目 Difference in adsorption mechanisms for polar and non-polar organic molecules in multi-walled carbon nanotubes-based gas sensors

（多層カーボンナノチューブを基にしたガスセンサーにおける極性有機分子と非極性有機分子の吸着機構の違い）

氏　名　　張　孟莉

In 1991, Japanese scientist Iijima observed multi-walled carbon nanotubes (MWCNTs) using a tunneling electron microscope, and since then, carbon nanotubes (CNTs) have attracted significant attention as a potential material for gas sensors due to their unique chemical and physical properties. Compared to traditional gas sensors, CNT gas sensors show higher sensitivity, faster response time, and a wider range of detectable concentrations. However, carbon nanotube gas sensors for measuring the common organic contaminants that are present in our environment still lack study. Therefore, in this study, I am going to develop a multi-walled carbon nanotubes (MWCNTs) paper gas sensor and observe its adsorption behavior when it is exposed to the vapor of polar and non-polar organic solvents, and explore the mechanism behind its adsorption behavior.

Firstly, a preliminary study of the adsorption of polar organic chemicals is discussed. In this study, I developed multi-walled carbon nanotubes (MWCNTs) gas sensor with multi-walled carbon nanotubes (MWCNTs) paper. It can stand freely without substrate, it is flexible and foldable, and two sides of MWCNT paper can work to adsorb gases. For this study, I selected methanol, ethanol, water vapor, and acetone as the target polar organic chemicals to detect. I then examined the fitting of the adsorption isotherm and the sensing parameters of sensitivity, response and recovery time, and reproducibility of the gas sensor based on the Langmuir isotherm model. The results showed that the Langmuir adsorption model fits well with the experimental data for the target gases, with equilibrium constants of 2.409×10^{-3} Pa^{-1} for acetone, 8.459×10^{-4} Pa^{-1} for methanol, 9.287×10^{-4} Pa^{-1} for ethanol, and 2.246×10^{-4} Pa^{-1} for water vapor. The MWCNT paper gas sensor was most sensitive to acetone, with a response time of no more than 20 s, followed by methanol and water vapor (30 s) and ethanol (40 s). For all types of polar organic chemicals, this sensor showed good reproducibility and stability.

Secondly, I investigated the adsorption behavior of non-polar organic chemicals to carbon nanotubes. In 2018, it was found that the electric conductance of the nanotube thin film showed a sudden change when adsorbing non-polar molecules, indicating excess adsorption. This excess adsorption of non-polar molecules has not yet been fully explained in the study. To better understand this, I selected benzene and hexane as the target non-polar organic chemicals in this study. I observed step-like sensitivity behavior when I used the MWCNT paper gas sensor to detect the vapors of these chemicals, which is distinct from the behavior observed for polar molecules. Based on the IUPAC isotherm model and the relatively weak interaction between the surface of the MWCNT paper gas sensor and the non-polar gas molecules, I infer that this adsorption behavior can be fit by Type VI isotherm model.

Finally, I discussed the mechanism behind the different adsorption behavior of polar and non-polar molecules. Based on my model results, I proposed two hypotheses for the adsorption mechanism of these molecules: a line parallel structure, in which the molecules are arranged in the same plane parallel to the graphene, and a sandwich structure, in which the second layer of molecules is located on top of the first layer that has been adsorbed onto the surface of graphene. To prove these hypotheses, I used Gaussian 16 software to calculate the total energy of each possible structure. It's determined that the structure with the lowest adsorption energy consumption is the one most likely to be adopted by the molecules due to its chemical stability. The results showed that for benzene molecules, the lowest total energy was 9.87 fJ in a sandwich structure with a distance of 60 pm between Benzene molecules and a distance of 43.56 pm between two layers of graphene. For methanol molecules, the lowest total energy was 9.00 fJ in a parallel structure with a distance of 220 pm between methanol molecules and a distance of 284.6 pm between two layers of graphene. This indicates that non-polar molecules are adsorbed by graphene in a sandwich structure, with the second layer of molecules located on top of one another, while polar molecules showed one-layer adsorption in a parallel structure.

In conclusion, this research includes the fabrication of a gas sensor using MWCNT paper and the analysis of the different behavior towards various vapors of polar and non-polar organic chemicals. It shows that the Langmuir adsorption isotherm model fits well with polar molecules, while the Type VI isotherm fits well with non-polar molecules. In addition, the total energy calculated by Gaussian 16 indicates different adsorption mechanisms for polar and non-polar molecules, one-layer adsorption and two-layer adsorption, respectively.