Abstract

Rapid industrialization and transportation have severely degraded air quality, creating an urgent need for efficient gas sensors capable of detecting harmful gases such as CO_2, CO, NO_x, and SO_2. Among existing technologies, resistive and field-effect transistor (FET)-based sensors are particularly attractive due to their simple fabrication and CMOS compatibility. Conventional metal oxide sensors, though widely used, require high operating temperatures (200-400 °C), suffer from poor selectivity, and are highly sensitive to humidity. In contrast, two-dimensional (2D) materials such as reduced graphene oxide (rGO) offer tunable electronic properties, low-temperature operation, and facile functionalization. Surface modification strategies, including chemical functionalization, metal nanoparticle decoration, and defect engineering, can further enhance sensitivity, selectivity, and recovery by tuning charge transfer and adsorption behavior. However, theoretical studies that examine these effects on an atomistic scale remain limited. Insights from density functional theory (DFT) therefore provide a deeper understanding of the sensing mechanisms and guide the rational design of high-performance 2D-material-based gas sensors. This thesis focuses on the development of graphene-derivative-based gas sensors through combined experimental and DFT investigations.

The first study reports an L-glutathione-functionalized rGO (ATcf-rGO) sensor that is highly selective toward formaldehyde and exhibits rapid response and recovery. DFT calculations confirmed the thiol binding of L-glutathione on rGO and the interaction of the amine group with HCHO, as supported by adsorption energy and interaction analyses. *The second study* used two approaches: (i) introduce defects in rGO via oxygen plasma treatment and (ii) functionalize rGO with gold particles of different sizes (rGO-AuNP and rGO-AuμP). All systems showed selectivity toward NH_3; however, plasma-treated rGO exhibited poor recovery, while Au-functionalized rGO demonstrated size-dependent response and recovery characteristics. Electrical characterization revealed that Au particles modulated

the flat-band voltage without inducing significant doping, which was suppressed by the metal-induced gap states (MIGS) effect. The DFT analysis also showed that the NH_3 molecules interacted more strongly with the Au surfaces, consistent with the calculations of the adsorption energy and the work function.

In *the third study*, this thesis investigates the fabrication of an AuNP functionalized CO_2 sensor based on rGO driven by the polarity of the electric-field. The experimental results revealed an enhanced CO_2 response under an applied electric field. DFT simulations showed that under a positive field, CO_2 molecules adsorb through their oxygen end, with adsorption decreasing as field strength increases, whereas under a negative field, adsorption occurs through the carbon end and increases with field strength. The overall response was higher under a positive electric field. The proposed sensing mechanism was further supported by electron difference density (EDD) and Mulliken population analyses.

The fourth study modeled GO and rGO to investigate the role of oxygen functional groups. The results showed that epoxy groups strongly modulate the bandgap (0-3.26 eV), whereas hydroxyl groups have a minor effect. Their combined presence leads to stronger modulation than either group alone. Moreover, the bandgap was found to vary non-monotonically with epoxy concentration and depended critically on the spatial arrangement and orientation of functional groups at a given concentration.

Together, the experimental findings of this thesis, complemented by theoretical insights, demonstrate that functionalization, nanoparticle decoration, and electric-field modulation govern adsorption and charge transfer, thereby providing design principles for next-generation, low-power, and selective rGO-based gas sensors.