Ultrasensitive reversible oxygen sensing by using liquid-exfoliated MoS$_2$ nanoparticles$^\dagger$

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Two-dimensional (2D) molybdenum disulfide (MoS$_2$) has been attracting rapidly increasing interest for application in chemoresistive gas sensors owing to its moderate band gap energy and high specific surface area. However, the mechanism of chemoresistive sensing via the adsorption and desorption of gas molecules and the influence of the shape of 2D materials are not well understood yet. Herein we investigate the oxygen sensing behavior of MoS$_2$ microflakes and nanoparticles prepared by mechanical and liquid exfoliation, respectively. Liquid-exfoliated MoS$_2$ nanoparticles with an increased number of edge sites present high and linear responses to a broad range of oxygen concentrations (1–100%). The energetically favorable oxygen adsorption sites, which are responsible for reversible oxygen sensing, are identified by first-principles calculations based on density functional theory. This study serves as a proof-of-concept for the gas sensing mechanism depending on the surface configuration of 2D materials and broadens the potential of 2D MoS$_2$ in gas sensing applications.

Introduction

In modern society, managing air quality is essential for enhancing the quality of human life. The high concentrations of fine dust, CO, NO$_2$, SO$_2$, and CO$_2$ cause complex respiratory diseases and hamper the productivity and learning ability in work places.$^1$ Furthermore, as the Internet of Things (IoT), interconnected devices capable of exchanging their own information about the internal state and the external environment with users or other devices, attracts attention, monitoring air quality becomes a requisite function for next-generation electronics.$^2$

Until now, the concentrations of CO, NO$_2$, SO$_2$, and CO$_2$ have been measured at the parts-per-million (ppm) level for monitoring air quality, because exposure to small portions of these gases can have a detrimental effect on human health. Detecting the oxygen concentration in percentage terms is also important because low levels of oxygen can produce negative symptoms in humans. The symptoms of increased heart and breathing rates and impaired attention are caused by oxygen concentrations >16%. In a harsh environment, workers can become asphyxiated at oxygen concentrations below 12% (Table S1$^†$).$^3$ Moreover, the oxygen concentration should be maintained at a certain level for particular applications like incubators for premature infants, and cell culture media. The development of oxygen gas sensors that can detect oxygen over a broad concentration range is desired for varied applications.

Chemoresistive gas sensors based on semiconducting materials are considered promising candidates for emerging applications such as IoT and flexible electronics due to their facile fabrication processes, small sizes, low costs, and easy integration into integrated circuits. However, commercialized oxygen sensors are mostly based on electrochemical gas sensors. These sensors have complex structures and hardly provide high reliability and linearity over a wide range of oxygen concentrations, which limit their applicability in IoT and flexible electronics.$^4$

2D materials are gaining increasing attention in this field as prospective sensing materials because surfaces without bulk offer high surface-to-volume ratios, and surface configurations including dangling bonds on the edge sites and basal planes can be easily modified. Moreover, facile surface modification with charge-transfer doping effects readily improves the gas sensing properties.$^5$–$^7$ In particular, MoS$_2$, a layered semiconducting transition metal dichalcogenide, has shown interesting gas sensing properties owing to its high surface-to-volume ratio, semiconducting nature, and numerous active edge sites.$^8$–$^{11}$ However, despite the increasing attention and the
diverse research studies, studies on the relationship between the gas sensing mechanism and the edge sites of 2D MoS$_2$ have not been achieved yet.

Herein, we report the comparative oxygen sensing behaviours of liquid-exfoliated MoS$_2$ nanoparticles and mechanically exfoliated MoS$_2$ microflakes. The sensors prepared by drop-casting methods on Pt interdigitated electrodes (IDES) exhibit a high and linear response to a wide range of oxygen concentrations due to the increased number of active edge sites. The adsorbed oxygen promotes the interaction kinetics between the reducing gases and the sensing materials, resulting in high sensitivity to ethanol at a parts-per-billion (ppb) level under ambient conditions. First-principles calculations were conducted to estimate the oxygen adsorption energies based on the surface configuration of the 2D materials. The calculations reveal the critical role played by the specific adsorption sites in the reversible and high oxygen response.

**Experimental section**

**Materials**

The procedures for exfoliating MoS$_2$ into nanoparticles were adapted from a previous report and slightly modified. Briefly, natural molybdenum sulfide powder (MoS$_2$, Sigma-Aldrich) was immersed into N,N-dimethylformamide (DMF, Sigma-Aldrich) at an initial concentration of 10 mg mL$^{-1}$ followed by ultrasonication at 60 Hz for 12 hours. The mixture was washed by centrifugation at 14 000 rpm for 15 minutes 4 times, changing DMF into distilled water. The obtained solution was centrifuged at 2000 rpm for 30 minutes, and the top 2/3 of the supernatant was collected. The precipitated solid was re-dispersed in distilled water at a concentration of $\sim$2 mg mL$^{-1}$.

**Sensor fabrication**

IDES of 4 $\mu$m interspacing were prepared on a SiO$_2$/Si substrate using photolithography followed by metal (Pt/Ti) deposition by e-beam evaporation. A 2 $\mu$L drop of 2 mg mL$^{-1}$ MoS$_2$ nanoparticle solution was cast onto a Pt IDE/SiO$_2$/Si substrate and was then dried for 30 minutes at 100 $^\circ$C. The fabricated sensors were annealed at 300 $^\circ$C for 20 minutes. To prepare SnO$_2$ nanosphere sensors, an aqueous suspension of 300 nm-diameter polystyrene (PS) beads was used. The PS beads were spin-coated on an O$_2$ plasma treated Pt IDE/SiO$_2$/Si substrate. A 70 nm-thick SnO$_2$ film was deposited onto the PS template by room-temperature radio frequency sputtering. The sample was calcined in air at 500 $^\circ$C for 1 hour to burn out the polymer beads and simultaneously crystallize the SnO$_2$ film, resulting in a nanosphere film on the substrate.

**Characterization**

MoS$_2$ nanoparticles on a Si substrate were characterized by using a scanning electron microscope (FE-SEM, MERLIN Compact, ZEISS) using 1 kV. For the TEM study, MoS$_2$ nanoparticles were deposited on quantifoil Cu grids (300 mesh holey carbon). The TEM experiments were performed by using a JEM-2100F. The AFM image (NANO Station II, Surface Imaging system) was obtained in the non-contact mode. Raman scattering was performed on a Raman spectrometer with excitation by 640 nm laser light. XPS was carried out at 4D beamlines at Pohang Accelerator Laboratory (PAL).

**Results and discussion**

For comparative analysis of the gas sensors prepared by different exfoliation methods, two types of MoS$_2$ gas sensors were fabricated by mechanical and liquid exfoliation methods from the same MoS$_2$ single crystal (Fig. 1a). Over the entire fabrication process, any chemicals which could modify the chemical sensing properties of MoS$_2$ were not added. Fig. 1b and c show the scanning electron microscopy (SEM) and atomic force microscopy (AFM) images of the mechanically exfoliated MoS$_2$ microflakes and Fig. 1d and e show the images of the liquid-exfoliated MoS$_2$ nanoparticles deposited between the Pt IDEs. The mechanically exfoliated MoS$_2$ sensor was prepared by the Scotch tape method, in which the MoS$_2$ microflakes with an average size of 5 $\mu$m were sparsely attached to the substrate (Fig. S2†). On the other hand, the liquid-exfoliated MoS$_2$ nanoparticles were deposited on the Pt IDEs by the drop-casting method and the nanoparticles were uniformly distributed with smaller sizes ($\sim$100 nm wide and $\sim$15 nm high). These particle shapes imply a higher ratio of edge sites for the liquid-exfoliated MoS$_2$ nanoparticles. Raman scattering was performed on...
a Raman spectrometer with excitation by 640 nm laser light. Fig. 2a shows the Raman spectrum of the liquid-exfoliated MoS₂ nanoparticles, which reveals the in-plane vibrational modes of the Mo and S atoms ($E_{1g}^{2}$) and the out-of-plane vibrational mode of the S atoms ($A_{1g}$). Transmission electron microscopy (TEM) images were taken from different liquid-exfoliated MoS₂ nanoparticles (Fig. 2b–d). The upper inset in each TEM image shows the corresponding electron diffraction pattern and the lower inset in Fig. 1c is a high-resolution transmission electron microscopy (HRTEM) image of the liquid-exfoliated MoS₂ nanoparticles. The electron diffraction pattern obtained from the liquid-exfoliated MoS₂ nanoparticles reveals their single-crystalline nature. X-ray photoemission spectroscopy (XPS) was performed on the as-deposited MoS₂ nanoparticles and the particles after heat treatment at 300 °C under ambient conditions (21% O₂ and 79% N₂). A MoO₃ peak is observed after the heat treatment, which demonstrates the adsorption of oxygen on MoS₂ surfaces (Fig. S3†).

The response curves of the mechanically and liquid-exfoliated MoS₂ sensors were measured for O₂ concentrations up to 100% at elevated temperatures of 200, 300, and 400 °C (Fig. 3a and b). The responses of the sensors were accurately determined by the ratio of the fully saturated resistances after exposure to the test gas (O₂) to the base resistances in nitrogen (N₂). The response is defined as $R_O/R_N$, where $R_O$ and $R_N$ denote resistances of the sensor in O₂ and in N₂, respectively. For the mechanically exfoliated MoS₂ sensor, the response to O₂ increased with increasing temperature but the response is as low as 1.5 at 400 °C and the sensor shows irreversible and retarded gas sensing behaviours. In addition, the sensor exhibits a high electrical noise level with unstable base resistance. In contrast, the liquid-exfoliated MoS₂ sensor shows a response as high as ~5700 at 400 °C. The liquid-exfoliated MoS₂ sensor exhibits higher responses to O₂ at all the elevated temperatures (Fig. 3c). The sensors show huge differences in sensing properties according to their fabrication methods. It may be attributed to the modified surface-to-volume ratio and the consequent change in the number of edge sites. Additional measurements were performed at 300 °C because the base resistance is unstable at the elevated temperature of 400 °C. Fig. 4a shows a dynamic sensing transient of the liquid-exfoliated MoS₂ sensor to four consecutive pulses of 100% O₂ at 300 °C. The device shows high stability and full recovery to the four pulses of O₂ without shifting the base resistance or responses. The responses of the sensor to 2–100% of O₂ at 300 °C as shown in Fig. 4b were measured. The responses of the liquid-exfoliated MoS₂ sensor were 8.69, 10.83, 12.25, 17.4, 23.98, 29.96, 50.28, and 63.73 to 2, 5, 7, 10, 15, 25, 50, 75, and 100% O₂, respectively. The linear relationship between the response and O₂ gas concentration indicates that the operational capabilities of the sensor are reliable over a wide concentration range up to 100%. The slope of the plotted line, calculated to be 5453.6 ppm⁻¹, represents the sensitivity of the sensor (Fig. 4c). The plotted line does not seem to meet the zero point when the O₂ concentration goes to zero. However, the response will finally reach the zero point because the response–concentration curve will not be in a linear relationship for very
low oxygen concentrations such as ppm levels. This extremely high sensitivity and linearity to \( \text{O}_2 \) concentrations are great merits of 2D MoS\(_2\) with an increased number of edge sites. As far as we are aware, oxygen gas sensors with these outstanding sensing characteristics have never been achieved before this by the chemoresistive method (Table S2†).

The experimental results suggest that the surface configurations of MoS\(_2\) particles prepared by using different exfoliation techniques are critical for gas-sensing properties, i.e., edge sites attract more \( \text{O}_2 \) molecules than clean surfaces. To confirm this, the adsorption energies of \( \text{O}_2 \) on MoS\(_2\) were investigated using first-principles calculations based on density functional theory (see Calculations).

First, we calculated the adsorption free energy (\( G_{\text{ad}} \)) of the \( \text{O}_2 \) molecule on a clean surface at temperature \( T \) and partial pressure \( P \) as follows:

\[
G_{\text{ad}}(T, P) = G(\text{MoS}_2 + \text{O}_2) - G(\text{MoS}_2) - \mu_{\text{O}_2}(T, P)
\]

where \( G(\text{MoS}_2 + \text{O}_2) \) and \( G(\text{MoS}_2) \) indicate the free energies of the MoS\(_2\) surface with an \( \text{O}_2 \) molecule adsorbed on clean MoS\(_2\), respectively, and \( \mu_{\text{O}_2}(T, P) \) is the gas-phase chemical potential of the \( \text{O}_2 \) molecule. The experimental conditions are considered in \( \mu_{\text{O}_2}(T, P) \) as follows:

\[
\mu_{\text{O}_2}(T, P) = \mu_{\text{O}_2}(T, P^0) + k_B T \ln \left( \frac{P}{P^0} \right),
\]

where \( P^0 \) is 1 atm. In addition,

\[
\mu_{\text{O}_2}(T, P^0) = \Delta H + T \Delta S_{\text{O}_2}(T, P^0) + \mu_{\text{O}_2}(0 \text{ K}, P^0)
\]

where \( \Delta H \) and \( \Delta S \) correspond to the enthalpy and entropy changes per molecule between \( T \) and 0 K at the standard pressure, respectively, and are obtained from thermodynamical tables. In eqn (3), \( \mu_{\text{O}_2}(0 \text{ K}, P^0) \) is equal to the total energy of the \( \text{O}_2 \) molecule. Because of the well-known overbinding of the \( \text{O}_2 \) molecule in density functional theory, we determined this value using the experimental binding energy of 5.23 eV.

For the clean MoS\(_2\) surface, the \( \text{O}_2 \) molecule was locally stable only at the top of S atoms. However, \( G_{\text{ad}}(300 \text{ °C}, 1 \text{ atm}) \) on this site is 1.72–3.21 eV, meaning that the \( \text{O}_2 \) molecule would not bind to the clean MoS\(_2\) surface (Fig. S4 and Table S3†). Next, we investigated the energetics of \( \text{O}_2 \) adsorption on a semi-infinite stripe model of MoS\(_2\). For the termination of the MoS\(_2\) edge, we considered clean Mo-edges (Fig. 5a–c) and Mo-edges with S monomers (Fig. 5d and e). We exclude the S-edge model because the \( \text{O}_2 \) adsorption is locally unstable. The stable sites of \( \text{O}_2 \) adsorption on each MoS\(_2\) edge are displayed in Fig. 5a–e with respective \( G_{\text{ad}}(300 \text{ °C}, 1 \text{ atm}) \) values shown under each figure.

![Fig. 4](image-url) (a) Response curves of the liquid-exfoliated MoS\(_2\) gas sensor to four pulses of 100% of \( \text{O}_2 \) at 300 °C. (b) Response curves to different \( \text{O}_2 \) concentrations at 300 °C. (c) Linear fit of the responses as a function of \( \text{O}_2 \) at 300 °C.
The $G_{\text{ad}}$ values for Mo-edges ($-3.30$ to $-2.51$ eV) are much lower than those for Mo-edges with S monomers ($-0.57$ to $1.30$ eV) due to the strong affinity of oxygen to Mo. To consider the experimental conditions more explicitly, we investigated the effect of oxygen partial pressure on $G_{\text{ad}}$ values at each temperature. Fig. 6a and b show the $G_{\text{ad}}$ values of O$_2$ molecules on the Mo–S bridges (Fig. 5d) and the S monomers (Fig. 5e) of Mo-edges with S monomers, respectively. In Fig. 6a, the $G_{\text{ad}}$ of O$_2$ molecules on the Mo–S bridges increases with decreasing $P$, crossing the zero point at low pressure. This indicates that O$_2$ desorbs from the Mo–S bridge sites. At lower temperatures of 200 and 300 °C, the crossing of the zero point occurs at much lower partial pressures. This is in qualitative agreement with the above experiment, in which the sensitivity of O$_2$ sensing improves at high temperatures. On the other hand, Fig. 6b indicates that O$_2$ does not bind on the S monomers of Mo-edges with S monomers. The $G_{\text{ad}}$ values of O$_2$ molecules on Mo-edges (not shown) confirm that O$_2$ binds at these edges too strongly to show reversible adsorption/desorption. Therefore, it is clear that only the Mo–S bridges in Fig. 5d allow for reversible O$_2$ adsorption/desorption among the considered binding sites. We have also investigated the dependence of O$_2$ adsorption energies for Mo–S bridge sites on O$_2$ coverage to explain the linear relationship at high oxygen concentrations (Fig. S5†).

To understand how O$_2$ adsorption influences the conductivity of a MoS$_2$ film, we examined the electronic structure of the clean Mo-edges with S monomers both with and without O$_2$ adsorption. Fig. 7a and b show the band structure (left) and density of states projected on the edge atoms (right) for each model, respectively. The charge distribution near the Fermi level is shown in the bottom figures. In the band structure of the clean Mo–S bridges, the energy band crosses the Fermi level, indicating the metallic character. The colour intensity of the crossing band indicates that the metallic states are localized along the edges. The charge density distribution in the bottom figure shows that the metallic states originate mainly from the d orbitals of Mo atoms on the edges. This was also reported in previous theoretical studies. On the other hand, with O$_2$ adsorption on the Mo–S bridge sites, the electronic structure undergoes substantial changes (Fig. 7b). The metallic band in Fig. 7a is significantly flattened, meaning that the effective electron mass becomes much higher than that for the clean edges. The large effective electron mass would directly lower the electrical conductivity according to the semiclassical Drude model. The charge distribution at the bottom of Fig. 7b also shows that the electronic states are more localized along the edges in comparison with Fig. 7a.
Fig. 8a shows dynamic sensing transients of the liquid-exfoliated MoS2 sensor and SnO2 nanosphere sensor to 50 ppm of C2H5OH, CH3COCH3, C3H8, C6H6, CH3CHO, CO, NH3, and H2, 3% of CO2, 2 ppm of H2S, and 5 ppm of NO2 at 300 °C. The SnO2 sensor was fabricated using sputtering, the experimental details of which are mentioned in our previous report.14 Their responses are shown in Fig. 8b. In previous studies, it has been demonstrated that pre-adsorbed O2 molecules on semiconducting metal oxides play a major role in the sensing reaction to reducing gases.14–28 Similarly, the liquid-exfoliated MoS2 sensor exhibits high selectivity for C2H5OH because of a large number of pre-adsorbed O2 molecules on the MoS2. On the other hand, the response of the liquid-exfoliated MoS2 sensor to NO2, 5, is lower than that of the SnO2 sensor, 215. Direct adsorption is proposed for NO2 without any interaction with pre-adsorbed molecules [NO2 + e− → NO2].22 Since the liquid-exfoliated MoS2 exhibits extremely high oxygen sensitivity, most adsorption sites may have been occupied with pre-adsorbed O2 molecules. Accordingly, no unoccupied adsorption sites were left for NO2. Thus, the liquid-exfoliated MoS2 sensor has comparatively higher selectivity to C2H5OH and a lower response to NO2 than the SnO2 sensor. Furthermore, to evaluate the detection limit for C2H5OH, the response of the MoS2 sensor was measured over the 3–50 ppm concentration range. The minimum detection limit of the proposed sensor for C2H5OH is determined to be 49.96 ppb at 300 °C (Fig. S6†).14,15

Conclusions

In conclusion, we have reported the high oxygen sensitivity of a liquid-exfoliated MoS2 gas sensor prepared by facile fabrication steps. The liquid-exfoliated MoS2 gas sensor demonstrates high responses with wide concentration range stability to O2. The high response of liquid-exfoliated MoS2 nanoparticles to O2 molecules is attributed to the semiconducting nature of MoS2 and the increased number of edge sites developed by liquid exfoliation. First-principles calculations revealed the critical role of the edge sites, which can be easily modified by fabrication procedures, in O2 sensing. We believe that the outstanding device performance demonstrated in this study has proven the potential of MoS2-based oxygen gas sensors in practical applications.

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Notes and references