Charge-transfer-based Gas Sensing Using Atomic-layer MoS$_2$

Byungjin Cho*, Myung Gwan Hahm*, Minseok Choi, Jongwon Yoon, Ah Ra Kim, Young-Joo Lee, Sung-Gyu Park, Jung-Dae Kwon, Chang Su Kim, Myungkwan Song, Kee-Seok Nam, Sangchul Lee, Tae Jin Yoo, Chang Goo Kang, Byoung Hun Lee, Heung Cho Ko, Pulickel M. Ajayan† & Dong-Ho Kim

1Advanced Functional Thin Films Department, Surface Technology Division, Korea Institute of Materials Science (KIMS), 797 Changwondaero, Changwon, Gyeongnam 642-831, Republic of Korea, 2Advanced Characterization and Analysis Group, Korea Institute of Materials Science (KIMS), 797 Changwondaero, Sungsan-Gu, Changwon, Gyeongnam 642-831, Republic of Korea, 3School of Materials Science and Engineering, Gwangju Institute of Science and Technology (GIST), 261 Cheonmodang-wongi, Buk-Gu, Gwangju 500-712, Republic of Korea, 4Electrochemistry Department, Korea Institute of Materials Science (KIMS), 797 Changwondaero, Sungsan-Gu, Changwon, Gyeongnam 642-831, Republic of Korea, 5Department of Chemical Engineering and Materials Science, Stevens Institute of Technology, Hoboken, New Jersey 07030, United States, 6Cambridge Graphene Center, University of Cambridge, 9 JJ Thomson Avenue, Cambridge, United Kingdom, 7Department of Materials Science and NanoEngineering, Rice University, 6100 Main Street, Houston, Texas 77005, USA.

Over the past few decades, metal oxide semiconductors have been applied as conventional chemical sensing materials because of their high sensitivity and relatively low cost. However, intrinsic synthesis challenges have made this task difficult. In addition, the detection mechanisms for gas molecules are not fully understood. Here, we report a high-performance gas sensor constructed using atomic-layered MoS$_2$ synthesised by chemical vapour deposition (CVD). A highly sensitive and selective gas sensor based on the CVD-synthesised MoS$_2$ was developed. In situ photoluminescence characterisation revealed the charge transfer mechanism between the gas molecules and MoS$_2$, which was validated by theoretical calculations. First-principles density functional theory calculations indicated that NO$_2$ and NH$_3$ molecules have negative adsorption energies (i.e., the adsorption processes are exothermic). Thus, NO$_2$ and NH$_3$ molecules are likely to adsorb onto the surface of the MoS$_2$. The in situ PL characterisation of the changes in the peaks corresponding to charged trions and neutral excitons via gas adsorption processes was used to elucidate the mechanisms of charge transfer between the MoS$_2$ and the gas molecules.
charge transfer between the MoS$_2$ and the gas molecules. These findings will help to implement future gas sensing technologies using diverse two dimensional TMDs nanomaterials.

Results

Wafer-scale synthesis of atomic-layered MoS$_2$. Most approaches use direct/indirect sulphurisation of Mo-containing thin films to synthesise atomic-layered MoS$_2$ thin films. The precursor is a key factor in the synthesis of MoS$_2$. In previous studies, most authors adopted one of three precursors: molybdenum thin films$^{16}$; molybdenum trioxide$^{17}$; or ammonium thiomolybdate$^{18}$. However, previous methods have involved complex precursor preparations, yielding films with inconsistent quality. In our search for strategies for synthesising uniform wafer-scale MoS$_2$ (see schematic in Fig. 1a), we have focused on the development of a thermal CVD system and process. Atomic-layered MoS$_2$ was grown using molybdenum trioxide (MoO$_3$) deposited onto a sapphire substrate and a sulphur powder source. The sublimated sulphur served as a precursor to sulphurise the MoO$_3$ film. To achieve our overall goal of preparing MoS$_2$ films of consistent quality on the desired substrates, we turned our attention to pressure control during the CVD reaction. A recent report indicated that an increase in the amount of either Mo or S atoms results in increased formation of energetically favourable defects on the MoS$_2$ surface during film growth$^{19}$. Thus, we systematically controlled the reaction pressure to provide sufficient sublimated sulphur using a custom-made automatic pressure control system (Supplementary Fig. S1).

The new CVD system design was very effective for the uniform synthesis of MoS$_2$ films on 2-inch sapphire substrates, as illustrated in Fig. 1b. Cross-sectional transmission electron microscopy (TEM) was used to examine the number of layers formed by CVD (Fig. 1c). The MoS$_2$ films contained double, triple, and, in some cases, more than three layers (additional TEM images, TEM energy-dispersive X-ray spectroscopy (EDS) maps, TEM EDS point spectra, atomic force microscopy images, X-ray photoelectron spectra, and absorption spectra are provided in Supplementary Figs. S2–7). The Raman spectrum in Fig. 1d shows the in-plane vibrational mode of the Mo and S atoms (E$_{2g}$) and the out-of-plane vibrational mode of S atoms (A$_{1g}$) in the as-synthesised MoS$_2$ films$^{20}$. The difference in peak position ($\Delta$) between the E$_{2g}$ and A$_{1g}$ bands, which is a strong indicator of the number of layers, was approximately 22.9. This result indicates that the as-synthesised MoS$_2$ was mainly composed of three layers$^{18,21,22}$.

To confirm the wafer-scale synthesis of MoS$_2$, we conducted a large-scale structural analysis using Raman mapping and an imaging technique. The Raman mapping area was 50 $\times$ 50 $\mu$m$^2$ with 0.3 $\mu$m steps (the original Raman mapping spectra are shown in Supplementary Fig. S8). The corresponding Raman images revealed the spatial distribution of MoS$_2$ over a 250-$\mu$m$^2$ area of the substrate (Figs. 1e and f). The blue and red models show the spatial distributions of the E$_{2g}$ and A$_{1g}$ bands, respectively. The as-synthesised MoS$_2$ was highly uniform over a large area of the surface (Figs. 1e and f). Thus, systematic pressure control during the CVD process resulted in highly uniform MoS$_2$ films on the wafer scale.

Gas detection characteristics of the MoS$_2$ gas sensor. The uniform atomic-layered MoS$_2$ films were used for gas molecule detection (Fig. 2a). Transient resistance responses were investigated using two analyte gases (NO$_2$ or NH$_3$ at concentrations from 1.2 to 50 ppm). The gas sensitivity was calculated using \[ R_s = \frac{R_a - R_g}{R_a} \]

where $R_s$, $R_a$, and $R_g$ represent the resistance of the device to air, MoS$_2$ film, and analyte gas, respectively. In the NO$_2$ gas mode, the resistance increased (positive sensitivity) (Fig. 2b). The NO$_2$...
sensitivity values were comparable to those in a previous report. NO2 acts as an electron acceptor, resulting in p-doping (Supplementary Fig. S12). The NO2 molecules on the surface of MoS2 bring the Fermi level closer to the valence-band edge. During the desorption process, thermal energy (heating to 100 °C) enhances the rate of desorption of the NO2 molecules from the MoS2 film (Fig. 2b, red line). We next compared the gas sensing characteristics for NH3 to those for NO2 (Fig. 2c). In contrast to the resistance recorded for NO2 molecules, the resistance of the MoS2 sensing device decreased with the adsorption of NH3 gas molecules, i.e., negative sensitivity was observed. NH3 acts as an electron donor (i.e., n-doping) such that it shifts the Fermi level of the MoS2 to the conduction-band edge. However, theoretical calculations indicated that the Fermi-level shift induced by the NH3 molecules is negligible (Supplementary Fig. S12). The measured overall NH3 sensitivities were lower than those of NO2 (Figs. 2b and c) because of the smaller charge transfer of NH3 compared to that of NO2. The dependence of the gas response on the gas concentration at different operating temperatures is plotted in Fig. 2d. The surface chemical reaction between the MoS2 channel and the NO2 molecules saturated at approximately 20 ppm, irrespective of the operating temperature (Fig. 2c, red and blue lines). By contrast, in the case of NH3, the sensitivity at RT gradually increased from 5 to 50 ppm and the sensitivity under 5 ppm was undetectable. However, the sensing signal at 100 °C was imperceptible at all concentrations (Supplementary Fig. S9). Thus, the recovery rate of NO2 at 100 °C is clearly superior to that of NH3, which is closely related to the faster desorption process of NO2 molecules as a result of the thermal energy. At 20 ppm and 100 °C, we obtained the best selectivity for NO2 relative to NH3 (~400% increase compared to that at RT).

**In situ photoluminescence of the MoS2-based gas sensor.** To explore the gas adsorption characteristics of the MoS2, we adopted theoretical and experimental approaches. First-principles density functional theory (DFT) calculations were conducted using the screened hybrid functional of Heyd-Scuseria-Ernzerhof with the D2 correction for van der Waals interactions (see the detailed methods in the Supplementary Information). To simulate NO2 and NH3 adsorption onto the MoS2 monolayer, supercells containing 16 Mo and 32 S atoms with NO2 and NH3 were employed using a 2 × 2 × 1 k-point grid. The most stable configurations of NO2 and NH3 reported in a recent study that compared the total energy between different adsorption configurations were considered. The NO2 and NH3 molecules were preferentially adsorbed onto the top of the hexagon of the MoS2 (Figs. 3a and b). The adsorption energies of the NO2 and NH3 gas molecules were evaluated using 

\[ E_a = E_{(\text{MoS}_2 - \text{molecule})} - [E_{(\text{MoS}_2)} + E_{(\text{molecule})}] \]

where \( E_{(\text{MoS}_2 - \text{molecule})} \) is the total energy of a supercell containing both an MoS2 monolayer and a gas molecule (NO2 or NH3), \( E_{(\text{MoS}_2)} \) is the total energy of the host MoS2 supercell, and \( E_{(\text{molecule})} \) is the total energy of a supercell containing a gas molecule. The calculated adsorption energies of NO2 and NH3 were −0.14 eV and −0.16 eV, respectively. These values were ~0.1 eV smaller than the values obtained using the local density approximation (LDA) because the LDA functional overestimates the adsorption energy. The negative adsorption energies indicate that the adsorption process is exothermic. Thus,
NO2 and NH3 molecules are likely to be adsorbed onto the surface of MoS2.

Next, we turned our attention to the in situ characterisation of PL to study the sensing mechanism in depth. The high temperature during film growth can induce unintentional defects on the substrate/MoS2 interface. To prevent defects, we transferred the as-grown MoS2 from the sapphire substrate to a SiO2/p+Si substrate. Interestingly, the atomic-layered MoS2 transferred onto the SiO2/p+Si substrate exhibited opposite gas sensitivity (i.e., p-type behaviour) compared to the n-type behaviour of MoS2 on the sapphire substrate (see Supplementary Fig. S13 for details). Dangling bonds at the semiconductor/substrate interface can redefine the effective Fermi levels within gap states, modulating the conductive properties of the MoS2. The dangling oxygen bonds on the SiO2 surface can result in a p-type MoS2 semiconductor. In the in situ PL characterisation with the two analyte gases (see Supplementary Fig. S10 for details), we observed various intensity changes in the PL spectra for NO2 and NH3 molecules (Figs. 3c and d). The atomic-layered MoS2 had two main PL peaks associated with the A and B excitons (Supplementary Figs. S11). Spin-orbit coupling-induced valence-band splitting can give rise to A and B excitons. After the gas molecules are adsorbed, the PL intensities of the A and B excitons can either be suppressed or increased by changes in the concentrations of the charge carriers. We here focused on the signal peak of the A exciton. The relatively low-energy A exciton signal expands to two features: a trion of A–/1+ (two electrons to a hole, resulting in a negatively charged exciton, or an electron to two holes, resulting in a positively charged exciton) and a neutral exciton of A0. With the emergence of the trion, we assumed that the exciton is coupled to either another electron or to a hole at the Fermi level. In the case of MoS2, the A– and A0 peaks correspond to the trions (1.8413 eV) and to the neutral excitons (1.8424 eV), respectively. The bare MoS2 notwithstanding, the positive trion (in this case, an electron to two holes, resulting in positively charged excitons) emission dominates the PL spectra because the bare MoS2 on the SiO2 substrate exhibits p-type characteristics, as previously mentioned. By adsorption of the gas molecules, the PL spectra change in the presence of NO2 and NH3 molecules. NO2 molecules on the surface of MoS2 act as electron acceptors, whereas NH3 molecules act as electron donors. The in situ PL spectra recorded from the MoS2 with NO2 (c) and NH3 (d) molecules. The overall intensity of the PL spectra changes in the presence of NO2 and NH3 molecules. The PL intensities of the A– trions and A0 excitons are either suppressed or increased by changes in the concentrations of the charge carriers. (e, f) Schematics of the charge density differences for MoS2 in the presence of NO2 (e) and NH3 (f) gas molecules. NO2 molecules on the surface of MoS2 act as electron acceptors, whereas NH3 molecules act as electron donors.

Figure 3 | Adsorption configurations and in situ PL. (a, b) Top views of the most favourable configurations for NO2 (a) and NH3 (b) on the MoS2. The calculated adsorption energies were −0.14 eV for NO2 and −0.16 eV for NH3. The negative adsorption energies indicate that the adsorption process is exothermic, indicating that NO2 and NH3 molecules are likely to be adsorbed onto the surface of the MoS2. (c, d) In situ PL spectra recorded from the MoS2 with NO2 (c) and NH3 (d) molecules. The overall intensity of the PL spectra changes in the presence of NO2 and NH3 molecules. The PL intensities of the A– trions and A0 excitons are either suppressed or increased by changes in the concentrations of the charge carriers. (e, f) Schematics of the charge density differences for MoS2 in the presence of NO2 (e) and NH3 (f) gas molecules. NO2 molecules on the surface of MoS2 act as electron acceptors, whereas NH3 molecules act as electron donors.
tion of NO₂ gas molecules, a neutral exciton (A') can be converted into a quasi-particle (A'A) because of excessive holes generated by electron extraction from the MoS₂. As a result, the A' peak in the PL spectrum increases in intensity and the A' peak is suppressed (Fig. 3c). By contrast, when additional electrons are introduced from the NH₃ molecules, the intensity of the A' peak in the PL spectrum is suppressed because of dissociation of the positive trions from the neutral excitons, resulting in increased neutral excitons (A'A') as shown in Fig. 3d. The in situ PL characterisation clarifies the mechanisms of charge transfer between the MoS₂ and the gas molecules.

Discussion

The gas sensing characteristics of wafer-scale layered MoS₂ fabricated by CVD were determined. The gas sensor based on the CVD-fabricated MoS₂ exhibited excellent sensitivity and high selectivity. The in situ PL characterisation and theoretical studies elucidated the charge-transfer mechanism between the gas molecules and the MoS₂. In-depth PL studies verified that the electron depletion of the MoS₂ by NO₂ adsorption increased the intensity of the A’ peak and suppressed that of the Ap peak, whereas electron accumulation by NH₃ adsorption suppressed the intensity of the A’ peak and increased that of the Ap peak. Intensive PL characterisation clarified the charge transfer phenomena between the MoS₂ and the gas molecules. The results of this study will enable more extensive applications of gas sensing using two dimensional transition metal dichalcogenides nanomaterials.

Methods

CVD synthesis of the MoS₂ nanofilms. MoS₂ nanofilms were synthesised using chemical vapour deposition (CVD) (Teraleader Co., Ltd., South Korea) (Supplementary Fig. S1). First, C-plane sapphire substrates were prepared using a typical cleaning process (sonication in acetone, isopropyl alcohol, and deionised water for 10 min each). MoO₃ films (5 nm) were deposited onto the clean substrates using a thermal evaporator. The pre-deposited MoO₃ films were placed at the centre of the furnace, and ~1 g of sulphur powder, which was used as a sulphur precursor, was subsequently loaded into a quartz boat in an independently temperature-controllable flange heater located near the inlet of the furnace. The furnace and the flange heater were heated to ~850°C and ~180°C respectively, for 1 h. The process was maintained for an additional 1 h under flowing Ar:H₂ gas (voltage ratio: Ar / H₂ = 85:15%) at a chamber pressure of 760 torr. The MoO₃ film was converted into a MoS₂ nanofilm via a two-step reaction (the reduction of MoO₃ by hydrogen gas, followed by sulphurisation of the reduced MoO₃ with sublimated sulphur gases). Finally, the furnace was rapidly cooled to room temperature by opening the chamber box after the furnace was turned off.

Fabrication of the MoS₂ sensing device. The SiO₂ (300 nm)/C-plane sapphire was cleaned using a typical cleaning process (sequential sonication in acetone, isopropyl alcohol, and deionised water for 10 min each). A MoO₃ film (~5 nm thick) was patterned with an active shadow mask using a thermal evaporator. The patterned MoO₃ film was converted into a MoS₂ nanofilm by CVD. Using a thermal evaporator and a shadow mask with an interrogated electrode array structure consisting of two opposing comb-shaped electrodes with a width of 400 µm and a gap of 100 µm, we deposited an Ag film (100 nm; used for the electrodes) onto the MoS₂ nanofilm. Detailed fabrication schemes are provided in Supplementary Fig. S14.

Characterisation of CVD-synthesised MoS₂ gas sensing, DFT calculations, in situ PL tests. See the detailed methods in the Supplementary Information.
calculations for the MoS₂ with gas molecules. B.C., M.G.H., M.C., S.-G.P., J.-D.K., C.S.K., M.S., Y.J., K.-S.N., B.H.K., H.C.K., P.M.A. and D.-H.K. analysed the data. B.C., M.G.H. and D.-H.K. co-wrote the paper. All authors discussed the results and commented on the manuscript.

Additional information
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