Chemical Vapor Sensing with Monolayer MoS₂


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Supporting Information

ABSTRACT: Two-dimensional materials such as graphene show great potential for future nanoscale electronic devices. The high surface-to-volume ratio is a natural asset for applications such as chemical sensing, where perturbations to the surface resulting in charge redistribution are readily manifested in the transport characteristics. Here we show that single monolayer MoS₂ functions effectively as a chemical sensor, exhibiting highly selective reactivity to a range of analytes and providing sensitive transduction of transient surface physisorption events to the conductance of the monolayer channel. We find strong response upon exposure to triethylamine, a decomposition product of the V-series nerve gas agents. We discuss these results in the context of analyte/sensor interaction in which the analyte serves as either an electron donor or acceptor, producing a temporary charge perturbation of the sensor material. We find highly selective response to electron donors and little response to electron acceptors, consistent with the weak n-type character of our MoS₂. The MoS₂ sensor exhibits a much higher selectivity than carbon nanotube-based sensors.

KEYWORDS: Chemical sensor, MoS₂, molybdenum disulfide, two-dimensional materials, vapor sensing

The planar habit of two-dimensional (2D) materials is attractive for the ultimate size scaling envisioned by Moore’s Law and beyond, and offers relative ease of fabrication, the requisite large-scale integration, and exceedingly low power consumption. The very high surface-to-volume ratio of such single or few monolayer materials enables highly efficient gating of charge transport via surface gates, obviating the need for the more complex growth and fabrication procedures required for wrapped-gate nanowire transistors.

Graphene has captivated attention since the first measurements of high mobility transport were reported in single layer flakes. Progress toward monolithic graphene circuits was recently demonstrated by the fabrication of wafer-scale inductor/transistor circuits, vertically integrated graphene/graphite transistor arrays, and transistors with improved on/off ratios. Recent effort has focused on other 2D materials such as the transition metal dichalcogenides, and field effect transistors with a monolayer of MoS₂ as the active channel were shown to exhibit high on/off ratios at room temperature, ultralow standby power dissipation, and well-defined photoreponse. Very recent work has demonstrated fabrication of complex integrated logic circuits based on bilayer MoS₂ transistors, and significant advances have been made in large area growth of MoS₂ on several substrates. The high surface-to-volume ratio is also important for new sensor materials which must exhibit selective reactivity upon exposure to a range of analytes (determined by the character of surface physisorption sites), rapid response and recovery, and sensitive transduction of the perturbation to the output parameter measured. The conductivity of graphene near the charge neutrality point has been shown to change with adsorption of a variety of analytes, but annealing to 150 °C was required to restore the conductivity to its original value, suggesting the analytes were strongly bound. Other work has shown that graphene’s intrinsic response to physisorption of analytes such as ammonia is very small. The sensitivity can be enhanced by functionalizing the graphene surface, for example, by oxidation, but these devices showed little selectivity, and functionalization introduces additional complexity to the fabrication process. Recent work has shown that the selectivity of graphene sensors can be enhanced by measuring analyte-dependent changes in the low frequency noise spectrum, although degassing in vacuum at room temperature for several hours between measurements was needed to obtain good reproducibility. Other 2D materials are likely to offer selective surface reactivity to physisorbed species, and if semiconducting in character, can provide both lower background carrier densities and the possibility of photomodulated sensing mechanisms.

We have fabricated planar sensor structures consisting of a monolayer MoS₂ channel on SiO₂/Si wafers, as shown in Figure 1a and b. The change in channel conductance was measured during exposure to a variety of analytes, including standard laboratory chemicals, solvents, and simulants/byproducts for explosives, nerve agents, or precursors thereof. The conductance increases rapidly with exposure to triethylamine (TEA, a decomposition product of the V-series of nerve gas agents) and acetone, and is unaffected by exposure to many agents.

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other analytes or gases, including dichlorobenzene, dichloro- 
opentane, nitromethane, nitrotoluene, and water vapor. We 
directly compare the MoS2 sensor response with that of similar 
planar sensors fabricated from monolayer graphene and carbon 
nanotube networks, and from these data obtain consistent 
evidence for a charge transfer mechanism involving transient 
doping of the sensor channel.

MoS2 is a layered compound with weak interaction between 
the layers, similar to graphite, and is widely used as a lubricant. 
Each layer consists of a plane of molybdenum atoms 
sandwiched between layers of sulfur atoms (Figure 1a). It is 
relatively nonreactive at moderate temperatures (<350 °C)—it is 
difficult to oxidize and unaffected by dilute acids. In contrast 
with graphite/graphene, it is a semiconductor with an indirect 
bandgap (∼1.2 eV) and exhibits catalytic properties useful for 
hydrodesulfurization.18 Recent work has shown that a single 
monolayer of MoS2 exhibits properties markedly different from 
the bulk: it transitions from an indirect to direct gap 
semiconductor (∼1.9 eV) with high luminescence efficiency19,20 
and can be used as the transport channel in a field 
effect transistor with high on/off ratio and pronounced 
photoresponse.8,9 The resistivity of exfoliated MoS2 flakes 2–
4 layers thick was shown to slowly increase (over 30 s) upon 
exposure to NO molecules followed by a 2 min approach to 
saturation, attributed to strong chemisorption, with a similarly 
slow decrease when the NO was removed.21 The behavior of 
single monolayer MoS2 showed an unstable response.21

Our sensor devices were fabricated from monolayer flakes of 
MoS2 that were exfoliated from bulk samples using the “Scotch 
tape” method and deposited onto a 270 nm thick thermal SiO2 
film on Si wafers. Electrical contacts were placed on the MoS2 
flake by liftoff processes using electron beam lithography 
followed by electron beam evaporation of Au and Ti/Au. An 
image of a typical sensor device is shown in Figure 1b. The bulk 
samples were obtained from three different sources, and the 
responsivity of the sensor flakes showed some variability that 
we attribute to variations in the purity of the original bulk 
samples. Further details appear in the Methods section and the 
Supporting Information file.

The electrical response to vapor exposure of a selected 
analyte was evaluated in a combined probe station/gas bubbler 
dosing system described elsewhere.22 The gas flow, analyte 
concentration, and analyte pulse sequence are controlled by 
computer via appropriate mass flow controllers and valves. The 
analyte concentration is recorded as a percent of its equilibrium 
vapor pressure at 20 °C, \( P_0 \). The sample conductivity is 
continuously measured using standard lock-in amplifier 
techniques while a timed sequence of analyte pulses of selected 
concentration are introduced into the 5 lpm \( N_2 \) carrier gas 
stream. The data are presented as a change in conductivity, 
\( \Delta G/G_0 \) versus time, where \( G_0 \) is the initial conductivity when 
the pulse sequence is begun. All data are obtained at room 
temperature and ambient pressure.

The sensor response was measured for a variety of analytes, 
including those considered to be electron donors, acceptors, or 
highly polar molecules. The MoS2 monolayer sensor exhibits a 
pronounced response to triethylamine (TEA—\( N(CH_2 - CH_3)_3 \)) 
exposure, a laboratory-safe decomposition product from the V-
series nerve gas agents. The response to a sequence of 10 TEA 
pulses, each with a concentration of 0.002% \( P_0 \) (∼1 ppm), is 
shown in Figure 2a. The timing of the pulse sequence is shown 
as a dashed line—the TEA is on for 15 s and off for 30 s 
(within the constant 5 lpm \( N_2 \) carrier flow). Upon exposure to 
TEA, the MoS2 conductivity increases abruptly, with an initially 
rapid rise (∼5 s) followed by a slower approach to saturation. 
This initial response is much more rapid than the 30 s reported 
previously for multilayer MoS2.21 Single pulse measurements at 
0.02% \( P_0 \) (10 ppm) show that the response saturates at 
concentration is summarized in Figure 2c, and the error bars 

Figure 1. Schematic and image of the MoS2 monolayer sensor. (a) A 
single monolayer of MoS2 is supported on an SiO2/Si substrate and 
contacted with Au contact pads. Transient physisorption of molecules 
duces temporary changes in the conductivity of the monolayer 
channel. (b) An optical image of the processed devices showing the 
monolayer MoS2 flakes electrically contacted by multiple Au leads.

The dependence of the change in conductivity on TEA 
concentration is summarized in Figure 2c, and the error bars

The amplitude of the conductivity change increases with 
increasing TEA concentration. Figure 2b shows the device 
response to a sequence of pulses in which the TEA 
concentration increases from 0.002% \( P_0 \) (1 ppm) to 0.2% \( P_0 \) 
(100 ppm) over a total pulse sequence of 450 s. The 
conductivity change with each TEA pulse exhibits similar 
characteristics as noted above, with an initially rapid rise and fall 
and a positively sloped background (removed in the figure).

The dependence of the change in conductivity on TEA 
concentration is summarized in Figure 2c, and the error bars
illustrate the differences in relative sensitivity observed. These differences could not simply be attributed to geometric factors, but we cannot exclude variations in inadvertent residual contamination during device fabrication. The strong response and excellent signal-to-noise provide a TEA detection threshold of 10 ppb.

For comparison, similar data were acquired for planar sensors fabricated from (a) monolayer graphene grown by chemical vapor deposition on copper and (b) a carbon nanotube (CNT) network consisting of a dense array of CNTs forming an electrically continuous thin film, as the transport/sensor channel. These data are shown in Figure 2d, where ΔG/G₀ is plotted for a sequence of TEA pulses (10s on, 20 s off) of 0.025% P₀ (12 ppm) concentration. The CNT response amplitude to a single pulse is comparable to that of the MoS₂ monolayer, while that of the graphene sensor is much smaller. However, in marked contrast with the response exhibited by the MoS₂, the graphene and CNT conductivity both decrease with TEA exposure, and the data are superposed on a negatively sloped background.

Figure 2. Response of sensors to triethylamine (TEA) exposure. (a) Change in conductivity of the monolayer MoS₂ sensor channel upon exposure to a sequence of 0.002% P₀ TEA pulses (black line). The dashed blue lines show the pulse timing (15 s on/30 s off) and concentration. The solid red line shows the response to exposure of nitrogen only and serves as a control experiment. The solid green and purple lines show the response of the MoS₂ and graphene sensors to water vapor pulses (0.025% P₀), respectively. (b) Same as part a, but for a series of exposure pulses in which the TEA concentration increases from 0.002% P₀ to 0.2% P₀. A positive slope background has been removed. The inset shows a model of the TEA molecule, in which the nitrogen atom is blue, the carbon atoms are black, and the hydrogen atoms are light gray. (c) The amplitude of the conductivity change increases with TEA concentration. The vertical axis is the response to each individual pulse (not the time integrated response). (d) Change in conductivity of a CVD graphene monolayer (red) and CNT-network sensor (black) upon exposure to a sequence of 0.025% P₀ TEA pulses (10 s on/20 s off).

The opposite response of the MoS₂ and graphene/CNT sensors can be understood to first order by considering the transient charge perturbation to the sensor material upon interaction with the TEA molecule. Our MoS₂ monolayer samples are n-type, while the air-exposed CNT networks exhibit a p-type character, and the graphene device as fabricated possesses a Dirac point at a substantial positive substrate bias indicating that the dominant carriers are holes. TEA is a strong electron donor, and thus transient physisorption will enhance the majority carrier density and conductivity for MoS₂ but decreases these parameters on graphene and the CNT network. The opposite response of the MoS₂ and graphene/CNT devices to TEA exposure provides a strong indicator of TEA presence with high confidence. In the following paragraphs, we make comparison to the CNT network devices, because they have been shown to be highly sensitive to a wide variety of analytes.
exposure to dimethylformamide, \((\text{CH}_3)_2\text{NC(O)H}\), produced no response above the noise level.

The response and sensitivity of the MoS\(_2\) monolayer to other classes of analytes was determined in a similar fashion. The response to a pulse sequence of acetone \((\text{CH}_3)_2\text{CO}\), a highly polar molecule, is shown in Figure 3a, where the acetone concentration increases from 0.02\% \(P_0\) to 2\% \(P_0\) (black line). The dashed blue lines show the pulse timing (20 s on/40 s off) and concentration. (b) Same as part a, but for a CNT-network sensor, and the acetone concentration increases from 0.01\% \(P_0\) to 1\% \(P_0\) with a pulse sequence of 10 s on/20 s off. The inset shows a model of the acetone molecule, in which the oxygen atom is red, the carbon atoms are black, and the hydrogen atoms are light gray.

Figure 3. Response of sensors to acetone. (a) Change in conductivity of the monolayer MoS\(_2\) sensor channel upon exposure to a sequence of pulses in which the acetone concentration increases from 0.02\% \(P_0\) to 2\% \(P_0\) (black line). The dashed blue lines show the pulse timing (20 s on/40 s off) and concentration. (b) Same as part a, but for a CNT-network sensor, and the acetone concentration increases from 0.01\% \(P_0\) to 1\% \(P_0\) with a pulse sequence of 10 s on/20 s off. The inset shows a model of the acetone molecule, in which the oxygen atom is red, the carbon atoms are black, and the hydrogen atoms are light gray.

The conductivity again increases upon exposure, with temporal characteristics similar to those observed for TEA—the incremental change in conductivity is strongly correlated with the exposure pulse sequence, the amplitude of \(\Delta G/G_0\) is comparable for a given concentration, and the background exhibits a positive slope over the total duration of the exposure. The sensitivity to acetone is much lower than for TEA, with a detection threshold of \(~500\) ppm. The corresponding response of a CNT network sensor is shown in Figure 3b and exhibits a complementary response consistent with the transient charge perturbation model discussed above: the incremental conductivity decreases with acetone exposure, and the background exhibits a negative slope.

In contrast with the relatively strong responses described above, the MoS\(_2\) sensor exhibited no measurable change in conductivity upon exposure to analytes considered to be electron acceptors, including \(o\)-dichlorobenzene, \(1,5\)-dichloropentane, \(o\)-nitrotoluene, and nitromethane at concentrations as high as 2\% \(P_0\) \((P_0 = 1350, 960, 136, \text{ and } 37\,400\) ppm, respectively), although the CNT devices respond to all. We note, however, that transport in CNTs is also affected by dipole-induced scattering, a mechanism that would only decrease conductivity, and may not be relevant for 2D materials such as MoS\(_2\). Thus the MoS\(_2\) sensor exhibits a much higher degree of selectivity than the CNT-based sensors, a desirable sensor characteristic. As an example, the response to a sequence of nitrotoluene (NT) pulses, a laboratory-safe simulant for the explosive trinitrotoluene (TNT), is shown in Figure 4. As the NT concentration increases from 0.01\% \(P_0\) to 1\% \(P_0\), no change in conductivity of the MoS\(_2\) monolayer is visible. The corresponding response of the CNT network sensor is shown for comparison, with the CNT conductivity increasing significantly upon exposure.

A histogram summarizing the sensitivity and selectivity of both the monolayer MoS\(_2\) and CNT network sensors to these various analytes appears in Figure 5. The MoS\(_2\) monolayer sensor displays good sensitivity, high selectivity, and a response that is typically opposite in polarity to that of CNT networks. While the states responsible for the MoS\(_2\) in-plane conductivity derive from the sulfur—molybdenum hybridized orbitals, we hypothesize that the interaction mechanism with the analyte is mediated by the localized lone pair orbitals of the sulfur end units. Zonnevylle et al. modeled the atomic orbital configuration for planar MoS\(_2\) sheets to understand the process of hydrodesulfurization. They found that the Mo 3d\(_x\) orbitals are used to form the Mo—S bond. The Mo 3d\(_x\) orbitals and S 2p orbitals extend above the surface plane and are free to interact—the charge density distributions make the Mo 3d\(_x\) slightly reduced (negatively charged) and the S 2p slightly oxidized (positively charged). This is a polarized surface that
and metal evaporation and lift-off were formed by e-beam lithography using MMA/PMMA resist.

Optical contrast and Raman spectroscopy were used to identify accurate monolayer selection (1 ML).

Microscope and isolation of suspected monolayers, atomic force microscopy measurements were performed to ensure method unambiguous identification of a wide range of analytes in a very compact and low power package.

Methods. Planar devices were fabricated from MoS 2 exfoliated monolayer flakes using the "Scotch tape" method deposited onto a 270 nm thermal SiO 2 film on n-type Si wafers. Optical contrast and Raman spectroscopy were used to identify and confirm the monolayer areas used for subsequent processing. After optical inspection of the wafers in a microscope and isolation of suspected monolayers, atomic force microscopy measurements were performed to ensure accurate monolayer selection (1 ML ~ 0.7 nm). Raman data and photoluminescence spectra analysis also confirm that the samples were single monolayer.

− Ti/Au bond-pad contacts were formed by e-beam lithography using MMA/PMMA resist and metal evaporation and lift-off in acetone. A second e-beam lithography step/metal evaporation/lift-off is performed to connect the MoS 2 to the bond pads with an Au contact line. Excess MoS 2 near the device is removed by defining a mesa level with another electron beam lithography step and then reactive ion etching in SF 6/O 2.

A combined electrical probe station–gas bubbler system was used to determine the electrical response of the sensor samples to controlled exposures of various analytes. Briefly, dry N 2 is bubbled at low flow rates (milliliters per minute) by means of a glass frit through a container of liquid analyte with an equilibrium vapor pressure P 0 (at 20 °C). It is expected that the N 2 stream leaving the bubbler is saturated with analyte vapor. This vapor stream is diluted by mixing with a constant flow of 200 mlpm dry N 2. Actual concentration of analyte is checked in a residual gas analyzer equipped with a capillary and differential pumping to achieve operation at atmospheric pressure (Hiden Analytical Inc. HPR-20 QIC). This diluted vapor stream is switched into a much larger 5 lpm N 2 flow by means of a solenoid-activated valve to create a gas of controlled high dilution. This gas stream is directed at the sample under test from a separation of a few millimeters.

Electrical contact to the sample pads is provided through Au-coated tungsten probe tips, and the conductivity between two contacts on the MoS 2 is measured by applying a small AC voltage (~100 mVAC RMS, 1 kHz) to one electrode while observing the voltage drop across a bias resistor between another electrode and ground with a lock-in amplifier. The value of the bias resistor is selected to approximately match the nominal impedance of the MoS 2 channel. In this way we can measure resistance with a high signal-to-noise ratio.

ASSOCIATED CONTENT

Supporting Information

Description of the sample fabrication and measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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MoS₂ was mechanically exfoliated using the Scotch Tape method onto 275 nm SiO₂ on Si. Suitable flakes were first identified by optical contrast using a compound light microscope. Atomic force microscopy (AFM) was then performed to confirm monolayer thickness. As an example, an AFM image of a flake is shown in Figure S1. The thickness of monolayer MoS₂ was found to be 6.5-8 Angstroms, consistent with what has been reported in the literature¹,²,³.

![AFM image and step height of monolayer MoS₂.](image)

**Figure S1**: AFM image and step height of monolayer MoS₂.

We also used Raman spectra and photoluminescence (PL) spectroscopy measurements to further confirm the thickness. Raman spectroscopy studies of MoS₂ are widely available in the literature and show that the distinguishing characteristic of a monolayer is an $E_{2g}$-$A_{1g}$ peak to peak separation of approximately 18 cm⁻¹.⁴,⁵ As the number of layers increases, the $E_{2g}$-$A_{1g}$ peak separation increases. **Figure S2a** shows an example of Raman spectroscopy on one of our monolayer films. **Figure S2b** shows an example of PL spectrum taken with a 532nm green CW laser line at T=5K. The PL measurements show a distinctive increase in intensity for a monolayer and an A-exciton peak at ~1.86eV, similar to what is reported in the literature⁴,⁵.
Figure S2: a) Raman spectroscopy of a monolayer of MoS$_2$ showing an E$_{2g}$-A$_{1g}$ peak separation of $\sim$18 cm$^{-1}$. Inset shows the E$_{2g}$-A$_{1g}$ peak separation as a function of the number of layers. b) PL measurement of a monolayer of MoS$_2$.

For the devices in this study, 3 bulk sources of MoS$_2$ were used. One piece was obtained from a colleague’s tribology research project (called the Wahl sample). A second piece of MoS$_2$ was obtained from SPI Supplies/Structure Probe, Inc. from a mine in Otter Lake, Ontario, Canada. A third piece was obtained from Wolfram Camp mine in Queensland, Australia. X-ray photoelectron spectroscopy (XPS), shown in Figure S3, reveals various levels of contaminants in the 3 sources. XPS was acquired using a monochromatic Al x-ray anode, operated at 300W, and a hemispherical electron analyzer. Wide-scan spectra were obtained with an 80 eV pass energy and elemental-specific high resolution scans were obtained with a 20 eV pass energy. Data was collected quantitatively from a 0.5 mm diameter spot in the center of the sample to avoid any edge effects. In Figure S3, we can see that the Wahl and SPI samples have a significant amount of oxygen, while the Wahl sample also has a significant amount of carbon. The Wolfram Camp sample is the cleanest. The Wahl sample produced no reproducible sensing data. Most of our devices were fabricated from the SPI sample, and the chemical sensing data from the SPI and Wolfram Camp samples were very similar.
Figure S3: XPS of 3 different MoS$_2$ crystals. The Wahl sample (green) is the dirtiest containing both oxygen and carbon impurities. The SPI sample (black) has some oxygen. The cleanest sample is the Wolfram Camp sample (red).

Most of the flakes identified were approximately 10 microns long at their longest point, enabling the placement of 4-6 electrical contacts. Electron beam lithography with MMA/PMMA was used to pattern the contacts. Ti/Au was deposited by electron-beam evaporation for the large wire-bonding contacts, while electron-beam deposited Au alone made contact to the MoS$_2$. Previous studies have shown that higher MoS$_2$ mobilities can be obtained with sample annealing with Au as the sole contact metal\textsuperscript{6}. We found that annealing a Ti/Au contacted device resulted in the device failing to conduct. We hypothesize that oxygen in the MoS$_2$, which XPS studies show exists, reacts with the Ti during annealing and produces a non-conducting TiO$_2$ layer, thus destroying the device. We also tried to use Pt contacts to the MoS$_2$, which resulted in no appreciable difference in electrical signal or chemical sensing. A final electron beam lithography step was done to cover only the active part of the device with a PMMA mask. A light SF$_6$/O$_2$ RIE plasma etch (40/10 SCCM, 100mTorr, 150 Watts) was used to clean any excess MoS$_2$ away from the device. The device was then rinsed in acetone and isopropyl alcohol. We annealed our samples at temperatures between 150-200 °C in H$_2$/Ar prior to measurement to remove any excess processing residue, and a similar anneal was done occasionally (~ weekly) to remove any adsorbed chemicals.
For this study, approximately 20 devices were made using the methods described above and tested. All showed approximately the same electrical and chemical sensing behavior, although there were some minor variations from device to device, such as resistance, turn-on gate voltage, signal to noise ratio, and amplitude of sensing response. The devices were also highly susceptible to electrostatic discharge damage. Preliminary electrical data were taken in order to determine the quality of the electrical contacts and the function of the back gate. A typical gate voltage sweep is shown in Figure S4. FET mobilities for the devices were \(~20\) cm\(^2\)/Vs. Although the conductance of our monolayer MoS\(_2\) devices can be increased significantly by application of a back gate voltage to increase the electron density, the sensitivity of the device to analytes did not change appreciably. The gate-voltage induced increase in conductivity tends to dilute the increase in conductivity produced by electron donor analytes such as TEA. Therefore, all measurements presented were obtained with the back gate grounded.

![Gate voltage sweeps done at constant voltage bias for one of our devices.](image)

**Figure S4:** Gate voltage sweeps done at constant voltage bias for one of our devices.
The equilibrium vapor pressure at 20°C, $P_0$, is calculated for each analyte from literature data. These values are summarized in Table I.

**Table I. Equilibrium vapor pressure $P_0$ at 20°C of selected analytes in ppm**

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**References**

6. See, for instance, the supplementary material for ref. 3.