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High-Performance Atomically-Thin Room-Temperature NO$_2$ Sensor

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Abstract:

The development of room-temperature sensing devices for detecting small concentrations of molecular species is imperative for a wide range of low-power sensor applications. We demonstrate a room-temperature, highly sensitive, selective, and reversible chemical sensor based on a monolayer of the transition metal dichalcogenide Re$_{0.5}$Nb$_{0.5}$S$_2$. The sensing device exhibits thickness dependent carrier type, and upon exposure to NO$_2$ molecules, its electrical resistance considerably increases or decreases depending on the layer number. The sensor is selective to NO$_2$ with only minimal response to other gases such as NH$_3$, CH$_2$O, and CO$_2$. In the presence of humidity, not only are the sensing properties not deteriorated, but also the monolayer sensor shows complete reversibility with fast recovery at room temperature. We present a theoretical analysis of the sensing platform and identify the atomically-sensitive transduction mechanism.
Chemical sensing devices are crucial to monitoring environmental pollution, health conditions, and industrial processes. In particular, the detection of nitrogen dioxide (NO₂), a toxic gas emitted from power plants, vehicles, and industrial sources, is of significant importance. NO₂ can have major environmental effects such as contributing to the creation of acid rain, the formation of ground-level ozone, and catalyzing small particles that trigger a range of health problems. For example, exposure to a high concentration of NO₂ can worsen respiratory diseases¹. In addition to monitoring applications, ultrasensitive chemical sensors can be used for medical diagnoses, such as identifying asthma². Thus, there is a need for more sensitive NO₂ sensors (at the parts per billion (ppb) level) that are both selective and reversible. Common sensor materials are metal oxides³–⁵, conducting polymers⁶,⁷, and low-dimensional materials⁸–¹¹. Semiconducting metal oxides have been extensively used for detecting NO₂. However, they usually must operate at high temperatures to achieve an acceptable level of sensitivity⁴,⁵ and satisfactory response and recovery kinetics¹². This hinders their application due to the increased power consumption.

Two-dimensional (2D) materials¹³–²⁰ offer extremely high surface-to-volume ratio, layer-dependent electronic structure, and tunable active sites for redox reactions, making them attractive candidates for gas sensing applications¹¹,²¹–²⁵. Graphene²¹ and MoS₂²²,²³ have shown excellent sensitivities toward NO₂, but they are not selective and suffer from slow recovery kinetics. Black phosphorus has also been used for gas sensing with an excellent sensitivity for NO₂ down to the ppb level²⁴. However, its poor stability and selectivity limit its practical application²⁴. 2D tin disulfide (SnS₂) has been shown to be highly sensitive to NO₂ with superior selectivity²⁵. The SnS₂ sensor also offers excellent reversibility at 120 °C, but unfortunately does not exhibit acceptable response and recovery times at temperatures below 80 °C²⁵. Furthermore,
practical sensors should operate not only at room temperature, but also under conditions of high relative humidity. Humidity greatly deteriorates the sensing properties of metal oxide sensors\textsuperscript{26,27} and, to a lesser degree, graphene-based sensors\textsuperscript{28}. Therefore, the realization of an ultrasensitive, selective, and reversible NO\textsubscript{2} sensor that can operate in ambient condition (\textit{i.e.} at room temperature and under substantial relative humidity) remains elusive.

Here, we explore the NO\textsubscript{2} sensing behavior of atomically-thin specimens of the transition metal dichalcogenide Re\textsubscript{0.5}Nb\textsubscript{0.5}S\textsubscript{2}. We find that the sensing properties depend sensitively on layer number, with monolayers giving the best overall performance. The monolayer is capable of detecting ultralow concentrations of NO\textsubscript{2} while showing excellent selectivity. Critically, in the presence of humidity, the sensor is highly reversible at room temperature with fast response and recovery times. We explore theoretically the sensor operation for different gas species using density functional theory (DFT), and identify the underlying sensing mechanism.

Bulk crystals of Re\textsubscript{0.5}Nb\textsubscript{0.5}S\textsubscript{2} are synthesized using chemical vapor transport. The samples are mechanically cleaved to atomic thinness. The cleaved samples remain air stable. Figure 1a shows an annular dark-field scanning transmission electron microscope (ADF-STEM) image of the monolayer Re\textsubscript{0.5}Nb\textsubscript{0.5}S\textsubscript{2}. Owing to the Z (atomic number) contrast of the atomic-resolution image, Re atoms (heavier) show a brighter contrast while Nb atoms (lighter) appear dimmer. In addition, the ADF-STEM image in Fig. 1b reveals an AA’ stacking sequence for bilayer and trilayer regions. Chemical composition of the flake is confirmed from the atomically-resolved ADF-STEM image and complementary energy-dispersive X-ray spectroscopy (EDS) measurements (Fig. 1c and Fig. S1), with near-equal concentration of Re and Nb, as expected for Re\textsubscript{0.5}Nb\textsubscript{0.5}S\textsubscript{2}. 
Re$_{0.5}$Nb$_{0.5}$S$_2$ offers a broad range of bandgap energies, ranging from $\sim$1.03 eV to $\sim$0.36 eV as the thickness increases from monolayer to bulk\textsuperscript{29}. This can result in striking layer-dependent electrical properties. For our sensor platform, different layer number field-effect transistor (FET) devices are fabricated with a two-terminal back-gate configuration (see Fig. 1d and Fig. S2). Prior to sensing measurements, we measure the transport behavior of the FET devices in vacuum. Fig. 1e demonstrates the change in the drain current ($I_{ds}$) as a function of source-drain bias ($V_{ds}$) for the monolayer, six-layer (6L), and 30-layer (30L) devices. The linear characteristic of the $I_{ds}$-\(V_{ds}\) curves implies Ohmic contacts. Sweeping the gate voltage, a distinct layer-dependent transport behavior is seen (Fig. 1f). Interestingly, the carrier type of the Re$_{0.5}$Nb$_{0.5}$S$_2$ FET devices changes with the layer number, e.g. n-type for the monolayer device and p-type for the 6L device. In addition, as the flakes become thicker, the gate control becomes weaker. For instance, the on/off ratio decreases from $\sim$1.4*10\textsuperscript{4}, for the monolayer to $\sim$4 for 6L. The 30L device displays a quasi-metallic behavior with negligible gate control. This can be attributed to the large modification of the Re$_{0.5}$Nb$_{0.5}$S$_2$ electronic structure with thickness\textsuperscript{29}.

For the sensing measurements, we apply a constant source-drain bias ($V_{ds}$) of 1V to the two-terminal FET devices and monitor the changes in their electrical resistances upon exposure to different concentrations of gas species. The NO$_2$ molecule, with an unpaired electron, is a strong oxidizer that withdraws electrons from the conduction band of the sensing material, in contrast to electron donor gases (e.g. NH$_3$, CH$_2$O) which donate electrons to the sensing material. Consistent with the electrical transport measurements, we observe that the electrical resistance of the monolayer (1L) sensor increases, while that of the 6L sensor decreases, upon the exposure to NO$_2$. Since the monolayer Re$_{0.5}$Nb$_{0.5}$S$_2$ is an n-type semiconductor, the electron transfer from the Re$_{0.5}$Nb$_{0.5}$S$_2$ to NO$_2$ decreases the carrier concentration and hence increases its electrical
resistivity. The 6L device, on the other hand, is a p-type semiconductor and its electrical resistivity decreases upon exposure to NO\textsubscript{2}. Figure 2a-b show the responses of the monolayer, 6L, and 30L devices to different NO\textsubscript{2} concentrations ranging from 50 ppb to 15 ppm in dry air. We observe a thickness-dependent response for the Re\textsubscript{0.5}Nb\textsubscript{0.5}S\textsubscript{2} sensors. While monolayer and 6L devices show excellent responses to NO\textsubscript{2} even at ultra-low concentrations, the 30L sensor is not very sensitive to NO\textsubscript{2}. This highlights the importance of surface-to-volume ratio of low-dimensional materials for gas sensing applications. In addition to the surface-to-volume ratio, the drastic change in the electronic structure of Re\textsubscript{0.5}Nb\textsubscript{0.5}S\textsubscript{2} with the layer number can be another cause of this behavior\textsuperscript{29}. We note that metallic single-walled carbon nanotubes (SWNTs) typically show small resistance changes upon exposure to NO\textsubscript{2}, while semiconducting SWNTs are capable of detecting small concentrations of NO\textsubscript{2}\textsuperscript{30}. For the monolayer and 6L Re\textsubscript{0.5}Nb\textsubscript{0.5}S\textsubscript{2}, the response of the sensors almost linearly increases with the NO\textsubscript{2} concentration, as more electrons transfer from Re\textsubscript{0.5}Nb\textsubscript{0.5}S\textsubscript{2} to NO\textsubscript{2} when the NO\textsubscript{2} concentration is increased.

In order to identify the origin of the carrier type dependence on the Re\textsubscript{0.5}Nb\textsubscript{0.5}S\textsubscript{2} thickness, we compute the alignments of the energy levels with respect to the vacuum level up to 4 layers. Among several possible low-energy stackings of highly ordered model Re\textsubscript{0.5}Nb\textsubscript{0.5}S\textsubscript{2}, we focus on the three lowest-energy AA´-type stackings (see Fig. S4). The alignment of the valence band and the conduction band edges with respect to the vacuum level for all three stackings is presented in Fig. 2c (see the energy level alignments with the adsorbed NO\textsubscript{2} molecule in Fig. S5). Additionally, we can assume that defect states exist inside the gap in the experimental set up. They can act both as donors and acceptors depending on the chemical potential\textsuperscript{31}, which is determined by the work function of the metal contacts. In a simplified model, we can assume that all the defect states below the Fermi level of the metal contacts are occupied, and all the defect
states above that level are unoccupied. Since our metal contacts have a work function of ~5 eV, these levels would promote n-type (p-type) behavior in the thinner (thicker) cases, because the change in the conduction band edge is smaller than that in the valence band edge as the thickness increases. This effect of the carrier type change with increasing thickness has been also observed in other 2D materials, such as WSe$_2^{18,19}$.

One of the most important characteristics of a chemical sensor is its selectivity to specific molecular species. Fig. 3a shows the responses of the monolayer and 6L sensors to NO$_2$, NH$_3$, CH$_2$O, and CO$_2$ gases in dry air. Both the 1L and 6L sensors are strongly selective to NO$_2$ with only minimal responses to the other gases. For instance, responses of the monolayer sensor to NH$_3$ (1 ppm) and CH$_2$O (2 ppm) are found to be ~1.25% and ~2.86%, respectively, while it shows a response of ~34.04% for NO$_2$ (1 ppm). We also tested the sensitivity of the sensors to 5000 ppm CO$_2$ and found a negligible response to CO$_2$ (~0.57%).

To understand the selectivity of the Re$_{0.5}$Nb$_{0.5}$S$_2$ sensors toward NO$_2$, we computationally investigate the adsorption of various molecules on the monolayer crystal. We start with 16 random initial configurations for each of the NH$_3$, CO$_2$, CH$_2$O, and NO$_2$ molecules on Re$_{0.5}$Nb$_{0.5}$S$_2$ and allow them to relax to minimize the forces. We find that each molecule is physisorbed, as shown in Fig. 3b-e. The resulting adsorption energies are 0.22, 0.16, 0.19, 0.29 eV for the NH$_3$, CO$_2$, CH$_2$O, and NO$_2$ molecules, respectively (see details in Supplementary Information and table S1). Since the adsorption energies of the molecules are within the same order of magnitude, the difference in the sensors’ response to NO$_2$ compared to the other molecules is not due to potential differences in coverage. To illuminate the origin of this behavior, we analyze the electronic structure of Re$_{0.5}$Nb$_{0.5}$S$_2$ with the adsorbed molecules. In Fig. 3f-i, we present the densities of states for the Re$_{0.5}$Nb$_{0.5}$S$_2$ + adsorbed molecule systems. We
observe that NH$_3$, CO$_2$ and CH$_2$O molecules contribute states that are deep in the valence and conduction bands of Re$_{0.5}$Nb$_{0.5}$S$_2$, whereas the NO$_2$ molecule contributes an unoccupied state 0.5 eV above the valence band edge. If Re$_{0.5}$Nb$_{0.5}$S$_2$ were an ambipolar semiconductor experimentally, we would expect this state to act as an acceptor state and lead to p-type behavior. However, because of the observed n-type behavior of the monolayer device, we can assume that there are defect states in the gap that are filled up to a level closer to the conduction band edge. In this case, the NO$_2$ defect state in the gap would accept electrons from these states, reducing the n-type conduction, as experimentally observed. On the other hand, because the other molecules do not generate any gap states, they do not significantly modify the conduction of the system. The unoccupied NO$_2$ defect state remains close to the valence band edge for the thicker films that we computed (up to 4 layers). Therefore, we expect it to weaken conduction by electrons and strengthen conduction by holes for all thicknesses, as observed. The charge transfer from Re$_{0.5}$Nb$_{0.5}$S$_2$ to the molecule is also apparent in the projected densities of state (PDOS) plot in Fig. 3i, as the unoccupied in-gap state has non-zero projection onto the Re$_{0.5}$Nb$_{0.5}$S$_2$ states. This can also be observed in the real-space charge transfer plot (Fig. 3j-k).

All the sensing measurements so far described are performed in dry air. Since real-life sensors need to operate under typical atmospheric conditions, we test the monolayer sensor in the presence of humidity. Figure 4a exhibits the dynamic response of the monolayer Re$_{0.5}$Nb$_{0.5}$S$_2$ sensor to NO$_2$ with concentrations ranging from 50 ppb to 15 ppm. Humidity not only does not deteriorate sensing properties of the monolayer device, but also is extremely beneficial for improving its recovery and response to NO$_2$ at room temperature.

For example, the recovery of the monolayer sensor after exposure to NO$_2$ (0.5 ppm) is incomplete after being exposed to dry air for 360 s (Fig. S6). However, a complete recovery is
achieved when the sensor is exposed to air with 40% relative humidity (RH) in the same timeframe (Fig. 4a). The response and recovery times, defined as the time required to reach 90% of the resistance change upon exposure to and removal of NO₂ (15 ppm), are approximately ∼245 s and ∼504 s, respectively, under 40% RH at room temperature. For comparison, an NO₂ sensor based on semiconducting SWNTs was demonstrated to detect 200 ppm of NO₂ with a recovery time of 12 hours at room temperature and 1 hour at 200°C³⁰. A metal oxide sensor based on WO₃ detected 500 ppb of NO₂ with recovery times of 270 s and 1350 s at 300 and 150°C, respectively¹². An NO₂ sensor based on monolayer MoS₂ was recovered to its initial state by leaving it in air for 12 hours at room temperature²³.

In addition to improving the recovery of the Re₀.₅Nb₀.₅S₂ sensor at room temperature, humidity also largely enhances its response to NO₂. For example, the monolayer Re₀.₅Nb₀.₅S₂ sensor shows a response of ∼195.53% for NO₂ (1 ppm) in the presence of humidity (40% RH), compared to a response of ∼34.04% in dry air. Testing the monolayer sensor under different humidity conditions, we see a decrease in the resistance of the device as the relative humidity increases from 0 to 80% (Fig. 4b). This is in contrast to the MoS₂ sensor where an increase in the resistance with humidity was observed²². Despite the fact that both the monolayer Re₀.₅Nb₀.₅S₂ and MoS₂ are n-type semiconductors, they interact with humidity very differently, analogous to the behavior of semiconducting metal oxide sensors. For instance, while a decrease in the resistance with humidity has been observed in n-type gas sensors such as SnO₂ ³² and ZnO ³³, WO₃, also n-type, has shown an opposite behavior³⁴.

In order to determine whether the monolayer sensor retains its selectivity to NO₂ in the presence of humidity, we test its response to other gas molecules in air with 40% RH. Fig. 4c displays the responses of the monolayer device to NO₂, NH₃, and CH₂O gases. Even in the
presence of humidity (40% RH), the monolayer sensor is still highly selective to NO\textsubscript{2} with insignificant responses to the other gases. The responses of the monolayer sensor to NH\textsubscript{3} (8ppm) and CH\textsubscript{2}O (20ppm) are \(\sim 8.77\%\) and \(\sim 23.56\%\), respectively, compared to a response of \(\sim 401.86\%\) for NO\textsubscript{2} (5 ppm).

To understand the origins of the improved response and recovery of the monolayer Re\textsubscript{0.5}Nb\textsubscript{0.5}S\textsubscript{2} sensor in the presence of humidity, we turn to additional theoretical investigations. First, we compute the optimal position of the H\textsubscript{2}O molecule to adsorb onto Re\textsubscript{0.5}Nb\textsubscript{0.5}S\textsubscript{2} (Fig. 4d-e). We then repeat the procedure to find the optimal configurations of higher H\textsubscript{2}O coverages (2, 3 and 4 molecules per 4\times4 supercell). The adsorption energy per molecule for each coverage is given in Table 1. These calculations suggest that the energetic drive for the water molecules to adsorb onto Re\textsubscript{0.5}Nb\textsubscript{0.5}S\textsubscript{2} does not diminish even at very high coverage values. For each H\textsubscript{2}O coverage, we conduct a further search to find the lowest-energy configuration of the NO\textsubscript{2} adsorption (Fig. 4F-g). To elucidate the energetic drive for NO\textsubscript{2} on the H\textsubscript{2}O-covered surface, we compute the adsorption energies as

\[
E_{\text{ad}} = E_{\text{substrate}} + E_{\text{molecule}} - E_{\text{substrate+molecule}},
\]

where the substrate is defined as the combination of Re\textsubscript{0.5}Nb\textsubscript{0.5}S\textsubscript{2} and the already adsorbed H\textsubscript{2}O molecules (Table 1). We find that the NO\textsubscript{2} molecules lower their energy by adsorbing near the H\textsubscript{2}O molecules (by 0.05 eV for the lowest coverage), indicating a nonzero attraction between the adsorbed molecules. This attraction is due to the intrinsic and induced dipole moments of the molecules and the intermolecular charge transfer. The increase in the NO\textsubscript{2} adsorption energies with H\textsubscript{2}O coverage suggests that more NO\textsubscript{2} molecules adsorb onto Re\textsubscript{0.5}Nb\textsubscript{0.5}S\textsubscript{2} when there are more water molecules available.
The depletion of the Re$_{0.5}$Nb$_{0.5}$S$_2$’s charge also increases with H$_2$O coverage, as listed in Table 1 ($\Delta \rho$ is defined as the total charge transfer from the alloy to the adsorbed molecules). When a water molecule adsorbs onto Re$_{0.5}$Nb$_{0.5}$S$_2$, a small amount of charge transfer to the alloy occurs ($\Delta \rho = +0.01e$), as visualized in Fig. 4d-e. However, when the NO$_2$ molecule adsorbs at a nearby location on Re$_{0.5}$Nb$_{0.5}$S$_2$, the charge transfer between the alloy and the molecules is significantly modified (Fig. 4f-g), and Re$_{0.5}$Nb$_{0.5}$S$_2$ ends up losing more electrons ($\Delta \rho = -0.12e$) than it does due to the NO$_2$ molecule alone ($\Delta \rho = -0.10e$). The fact that the charge depletion of the alloy increases with higher H$_2$O coverage can be visually observed by comparing the PDOS plots in Fig. 3i and Fig. 4h-i, as the projection of the unoccupied in-gap state onto the Re$_{0.5}$Nb$_{0.5}$S$_2$ states increases. The fact that both adsorption energy and charge transfer increase with humidity explains the improved response of the monolayer sensor to NO$_2$ in the presence of humidity.

Regarding the improved recovery rate, we propose a potential mechanism for the desorption of the NO$_2$ molecules in the presence of humidity driven by the intermolecular dipole-dipole interaction. First, we observe that both NO$_2$ and H$_2$O are polar molecules due to their geometry, as opposed to the other molecules prominent in air, i.e. N$_2$ and O$_2$. By computing electronic structure of the two molecules in isolation, we find $p_{H_2O} = 1.81$ Debye and $p_{NO_2} = 0.23$ Debye. If dipole-dipole interaction were the dominant cause of attraction between molecules, this qualitative difference between H$_2$O and the other atmospheric gases would suggest that the H$_2$O molecules attract the adsorbed NO$_2$ molecules while passing close to the alloy’s surface, and “sweep” them away, whereas N$_2$ and O$_2$ do not. To test this hypothesis, we compute the interaction energies between the molecular pairs. For NO$_2$ and H$_2$O, this interaction energy ($\Delta E$), defined as
\[ \Delta E = E_{\text{NO}_2 + \text{H}_2\text{O}} - E_{\text{NO}_2} - E_{\text{H}_2\text{O}}, \]  

(2)

is -0.046 eV and -0.029 eV when their dipole moments are aligned and anti-aligned, respectively. In the absence of induced dipole moments, the difference between the two values would be equal to twice the dipole-dipole interaction energy \( E_{d-d} = -0.008 \text{ eV} \). From basic electrostatics, this energy can be estimated using the dipole moments of the molecules and the intermolecular distance \( \Delta z = 3.45 \text{ Å} \), which yields \( E_{d-d,\text{estimated}} = -0.012 \text{ eV} \). The difference between the two \( E_{d-d} \) values suggests that the induced dipole moments are non-negligible and may cause similar levels of attraction between NO\(_2\) and non-polar molecules. In Table 2, we list the \( \Delta E \) and \( p_{\text{induced}} \) values for the interaction between NO\(_2\) and all three atmospheric gases. We find that both the attraction and the induced dipole moment of H\(_2\)O is significantly greater than N\(_2\) and O\(_2\). Repeating these calculations on Re\(_{0.5}\)Nb\(_{0.5}\)S\(_2\), where the NO\(_2\) molecule is adsorbed optimally with its dipole moment points away from the alloy, yields the same comparison between the three atmospheric gases. Therefore, we suggest that the significant improvement of the recovery rate may be due to the attraction between the polar H\(_2\)O molecules and the adsorbed NO\(_2\) molecules, which is significantly greater than those for N\(_2\) and O\(_2\).

In summary, we have demonstrated an NO\(_2\) sensor based on a monolayer semiconducting alloy that has the advantage of room-temperature finite-humidity operation and ppb sensitivity. The monolayer sensor is highly selective to NO\(_2\) with only minimal responses to other gases. In the presence of humidity, the monolayer sensor is highly reversible at room temperature with fast recovery time. Humidity also largely enhances the response of the sensor to NO\(_2\) due to the increased charge transfer by the co-adsorption of the NO\(_2\) and H\(_2\)O molecules onto the monolayer crystal. Furthermore, our atomically-thin Re\(_{0.5}\)Nb\(_{0.5}\)S\(_2\) sensor is flexible and optically...
transparent, making it attractive for a wide range of low-power sensor applications, such as in wearable electronics.

**Fig. 1** | Atomic structure, chemistry, and electrical characteristics of Re$_{0.5}$Nb$_{0.5}$S$_2$. a, An ADF-STEM image of the monolayer Re$_{0.5}$Nb$_{0.5}$S$_2$ with the corresponding FFT (inset). b, An atomic-resolution ADF-STEM image of the bilayer and trilayer regions of Re$_{0.5}$Nb$_{0.5}$S$_2$ revealing its stacking order. c, EDS spectrum from a few-layer Re$_{0.5}$Nb$_{0.5}$S$_2$ crystal (see Fig. S1) showing peaks of Re, Nb, S, and Si (from the silicon nitride TEM grid). d, Schematic of the NO$_2$ sensors based on an FET device with a two-terminal back-gate configuration. e, Drain current ($I_{ds}$) as a function of source-drain bias ($V_{ds}$) for the monolayer, 6L, and 30L devices. f, Conductance ($G$) of the monolayer, and 6L devices as a function of the gate voltage ($V_{bg}$).

**Fig. 2** | Layer-dependent behavior of Re$_{0.5}$Nb$_{0.5}$S$_2$ NO$_2$ sensors. The responses of the monolayer, 6L, and 30L devices to different NO$_2$ concentrations raging from a, 50 ppb to 1 ppm and b, 1 to
15 ppm in dry air. Response is defined as 

\[ S = \frac{R_g - R_{\text{air}}}{R_{\text{air}}} \]

with \( R_g \) and \( R_{\text{air}} \) being the resistance of the device in target gas and air, respectively. 

**c.** The alignment of the valence band and the conduction band edges with respect to the vacuum level for three AA’-type stackings (see Fig. S4).

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**Fig. 3 | Selectivity of the Re\(_{0.5}\)Nb\(_{0.5}\)S\(_2\) sensors toward NO\(_2\).** 

**a.** The responses of the 1L and 6L sensors to NO\(_2\), NH\(_3\), CH\(_2\)O, and CO\(_2\) gases in dry air. 

**b-e.** NH\(_3\), CO\(_2\), CH\(_2\)O, and NO\(_2\) molecules being physisorbed on the monolayer crystal. 

**f-i.** The densities of states for the Re\(_{0.5}\)Nb\(_{0.5}\)S\(_2\) and the adsorbed NH\(_3\), CO\(_2\), CH\(_2\)O, and NO\(_2\) molecule systems. Projections onto the atomic orbitals are used to distinguish between the molecular states and the states in the substrate. The NO\(_2\) molecule causes spin polarization in the system, and hence the two spins are plotted separately. 

**j-k.** The real-space charge transfer plot showing the charge transfer from Re\(_{0.5}\)Nb\(_{0.5}\)S\(_2\) to the NO\(_2\) molecule. 

Re: navy, Nb: violet, S: yellow, N: green, H: grey, O: blue, C: red.
Fig. 4 | Humidity impacts on the monolayer sensor. a, Dynamic response of the monolayer Re$_{0.5}$Nb$_{0.5}$S$_2$ sensor to NO$_2$ with concentrations ranging from 50 ppb to 15 ppm under 40% RH condition at room temperature. b, Change in the resistance of the monolayer sensor as a function of the relative humidity. c, Responses of the monolayer device to NO$_2$, NH$_3$, and CH$_2$O gases in presence of humidity (40% RH). d-e, The optimal position of the H$_2$O molecule to adsorb onto the monolayer Re$_{0.5}$Nb$_{0.5}$S$_2$. f-g, The lowest-energy configuration of the NO$_2$ adsorption on the alloy for each H$_2$O coverage. h-i, The PDOS plots for the Re$_{0.5}$Nb$_{0.5}$S$_2$ and the adsorbed NO$_2$ and H$_2$O molecules, showing an increase in the charge depletion of Re$_{0.5}$Nb$_{0.5}$S$_2$ with higher H$_2$O coverage. Re: navy, Nb: violet, S: yellow, N: green, H: grey, O: blue.

| H$_2$O coverage per 4×4 cell | 0 | 1 | 2 | 3 | 4 |
|-----------------------------|---|---|---|---|---|
| $E_{ad}$(H$_2$O) (eV)       | | 0.16 | 0.16 | 0.15 | 0.14 |
| $E_{ad}$(NO$_2$) (eV)       | 0.29 | 0.34 | 0.41 | 0.42 | 0.51 |
| $\Delta \rho$               | -0.10e | -0.12e | -0.14e | -0.14e | -0.16e |

Table 1 | Computed adsorption energies of H$_2$O and NO$_2$ molecules on the Re$_{0.5}$Nb$_{0.5}$S$_2$ alloy, under various H$_2$O coverages, and the charge transfer from the alloy to the adsorbed molecules. The first (top) row lists the number of adsorbed H$_2$O molecules in the 4×4 cell. The second row lists the adsorption energy of the $n^{th}$ H$_2$O molecule in the cell. The third row lists the adsorption energy of the NO$_2$ molecule with $n$ H$_2$O molecules already adsorbed onto Re$_{0.5}$Nb$_{0.5}$S$_2$. The entries in the fourth row correspond to the configurations in the third row, and list the charge transfer from the alloy to the adsorbed molecules, after the adsorption of all the molecules (NO$_2$ + $n$ × H$_2$O).
Table 2 | Computed interaction energies of H₂O, N₂ and O₂ with NO₂ and the induced dipole moment in each case. The second row of the table lists the interaction energies, defined as $\Delta E = E_{\text{NO}_2+\text{H}_2\text{O}} - E_{\text{NO}_2} - E_{\text{H}_2\text{O}}$ for H₂O, and similarly for the other molecules. The third row of the table lists the induced dipole moment for each of these configurations. The fourth row is analogous to the second, but with the initial NO₂ molecule adsorbed onto Re₀.₅Nb₀.₅S₂, as shown in Fig. 3j-k. To compute $\Delta E$, the additional molecule (H₂O, N₂ or O₂) is placed on top of the already-adsorbed NO₂ molecule and the atoms are allowed to relax. Here, $\Delta E = E_{\text{alloy+NO}_2+\text{H}_2\text{O}} - E_{\text{alloy+NO}_2} - E_{\text{H}_2\text{O}}$ for H₂O, and similar for the other molecules. The fifth row lists the induced dipole moment for each of these configurations.

| Molecule interacting with NO₂ | H₂O  | N₂  | O₂  |
|------------------------------|------|-----|-----|
| $\Delta E$ in vacuum (eV)    | -0.046 | -0.014 | -0.021 |
| $p_{\text{induced}}$ in vacuum (D) | 0.34 | 0.04 | 0.10 |
| $\Delta E$ on alloy (eV)     | -0.012 | -0.004 | -0.007 |
| $p_{\text{induced}}$ on alloy (D) | 0.23 | 0.03 | 0.08 |

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