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Physisorption Based Charge Transfer in Two-Dimensional SnS₂ for Selective and Reversible NO₂ Gas Sensing

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ABSTRACT

Nitrogen dioxide (NO_2) is a gas species that plays an important role in certain industrial, farming and healthcare sectors. However, there are still significant challenges for NO_2 sensing at low detection limits, especially in the presence of other interfering gases. The NO_2 selectivity of current gas sensing technologies is significantly traded-off with their sensitivity and reversibility as well as fabrication and operating costs. In this work, we present an important progress for selective and reversible NO_2 sensing by demonstrating an economical sensing platform based on the charge transfer between physisorbed NO_2 gas molecules and two-dimensional (2D) tin disulfide (SnS_2) flakes at low operating temperatures. The device shows high sensitivity and superior selectivity to NO_2 at operating temperatures of less than 160°C which are well below those of chemisorptive and ion conductive NO_2 sensors with much poorer selectivity. At the same time, excellent reversibility of the sensor is demonstrated which has rarely been observed in other 2D material counterparts. Such impressive features originate from the planar morphology of 2D SnS_2 as well as unique physical affinity and favorable electronic band positions of this material that facilitate the NO_2 physisorption and charge transfer at parts per billion (ppb) levels. The 2D SnS_2 based sensor provides a real solution for low-cost and selective NO_2 gas sensing.

KEYWORDS: Two dimensional materials; post transition metal dichalcogenide; SnS_2 ; gas sensor; nanosheet; physisorption

Nitrogen dioxide (NO_2) is an industrially and biologically important gas species, which can be particularly dangerous to humans at levels greater than 1 parts per million (ppm), causing damage to the respiration system and worsening respiratory diseases.^{1, 2} The US environmental protection agency recognizes NO_2 as an air pollutant that is co-released during many types of fuel combustions.³ It plays an important role in the chemistry of the atmosphere producing acid rain and contributing to the formation of ozone (O_3), which is the major cause of photochemical smog.⁴ NO_2 is also an important material for the synthesis of nitric acid that is used in the production of fertilizers for agriculture and explosives for both military and mining uses.⁵ Furthermore, NO_2 is an essential gas for many bio-systems. Nitrogen monoxide (NO) appears as a gasotransmitter in many cell signaling pathways,⁶ which can convert to NO_2 rapidly when exposed to an environmental disturbance in the presence of oxygen. The sensing of nitrogen oxides (NO_x , a group mainly consists of NO_2 and NO) can be potentially implemented in diagnostic processes. For instance, the detection of NO_x in exhaled breath (at parts per billion (ppb) levels) is helpful for identifying infections of lung tissues.⁷ In addition, the NO_x can possibly be used as a biomarker for some of the gastrointestinal disorder symptoms such as irritable bowel disease.⁶

It is important to consider that in many of the aforementioned sensing scenarios, NO_2 gas should be measured in the presence of other interfering gas species. Therefore, the realization of accurate, highly selective and low detection limit NO_2 gas sensors, which can operate in a wide range of ambient conditions, is a critical step in environmental monitoring and surveillance in many industries as well as healthcare and clinical practices.

Based on the sensing mechanism, the current NO_2 gas sensor technologies can be mainly categorized into optical, electrochemical and chemiresistor types.⁸ Optical methods predominately rely on the unique optical fingerprints of NO_2 gas molecules including their chemiluminescent emission and infrared light absorption wavelengths, which result in high selectivity NO_2 sensing. Such optical sensing methods need sophisticated instruments or system configurations to achieve a high NO_2 sensitivity, which significantly increase their sizes and costs.⁸⁻¹² Instead, electrochemical

sensing of NO₂, which relies on the electrochemical reduction of NO₂ in the presence of noble catalysts, is a low-cost approach.¹³ Nevertheless, such sensors have cross-talk with active gas species such as hydrogen and their operation lifetime are relatively short.¹⁴ These drawbacks can be increasingly eliminated by using zirconia-based solid electrolytes.¹⁵ However, their high operation temperatures (in the range of 500-900 °C) result in significant operation costs and limit their applications mostly to combustion and automotive monitoring systems. Another economical method of NO₂ sensing is based on chemiresistor transducing platforms, relying on the charge transfer between metal oxides and surface chemisorbed NO₂.^{16, 17} However, the pristine or modified surface of these metal oxides shows weak discrimination to different gas species, making them poorly selective. Furthermore, the presence of oxygen is crucial for the operation of chemiresistive metal oxide compounds, which is not suitable for some particular anaerobic applications. Finally high operation temperature of above 200°C is needed in order to improve the response and recovery kinetics of these sensors.

Therefore, considering the trade-offs between sensitivity, selectivity and cost, there still exists an on-going quest for the ideal NO₂ sensing platform. The paramagnetic nature of NO₂ can be utilized to realize a different class of highly selective NO₂ gas sensors, as it can produce a magnetic dipole in addition to a surface electric dipole generated by the mirror charge when it is physisorbed onto the surface of a sensitive layer, resulting in a much stronger affinity compared to other non-magnetic gases such as CO₂, H₂, H₂S and CH₄.¹⁸ Upon the NO₂ molecule adsorption, a charge transfer can occur depending on the relative band positions of sensitive material and NO₂ as well as possible hybridization of gas molecule states with sensitive material orbitals.^{19, 20} Such a charge transfer affects the electrical resistance of the sensitive material, which can be easily measured using the low-cost resistive transducing platform. More importantly, the physisorption of gas molecules can be occurred at low temperatures and the corresponding charge transfer mechanism does not rely on the breakdown of the adsorbed gas, presenting an ideal NO₂ sensing platform that can operate reliably at relatively low temperatures, regardless of the presence of ambient oxygen.

So far, the search for exploring suitable sensitive materials for selective NO₂ physisorptive sensing with high adsorption/desorption kinetics has resulted in limited success. Low-dimensional carbon-based materials, including carbon nanotube and graphene, have been investigated as possible candidates.²¹⁻²⁴ Although excellent sensitivities toward NO₂ have been demonstrated, these sensors exhibit low selectivity and slow recovery kinetics.²⁵ The emergence of two-dimensional (2D) transition metal dichalcogenides (TMDs)²⁶⁻³⁰ and phosphorene^{31, 32} as the alternatives have alleviated some of these drawbacks but the outcomes are still far from sufficient practical values. Especially the most prominent candidate to date, 2D molybdenum disulfide (MoS₂), despite presenting a good selectivity to NO₂ it does not show sufficiently fast recovery kinetics. Therefore, the realization of a low-cost sensing platform with strong potentials of excellent NO₂ physisorptive selectivity, sensitivity and reversibility, which can operate at relatively low temperatures at a small development cost, is pending to the discovery of an appropriate candidate material with a favorable surface energy value for NO₂ adsorption as well as optimum electronic band structure facilitating the charge transfer.

Although tin (Sn) does not belong to the transition metal family, tin disulfide (SnS₂) exists in a layered crystal phase,³³ which is similar to TMDs in various aspects.^{34, 35} This phase is composed of Sn atoms sandwiched between two layers of hexagonally disposed close packed sulfur (S) atoms, the adjacent S layers are connected by the weak van der Waal's forces (Figure 1a). Compared to 2D MoS₂, SnS₂ has a larger electronegativity, potentially enhancing gas adsorption sites.³⁶ Furthermore, the relatively stronger temperature dependency on the electronic band structure of SnS₂ can possibly enable the optimization of sensing response and be used for enhancing recovery kinetics at a range of moderately elevated temperatures, advantageous for practical gas sensing applications.^{37,}

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In this work, we present a novel approach for selective and reversible NO₂ gas sensing based on 2D SnS₂ flakes. Many of the current synthesis methods of 2D SnS₂ are based on exfoliation, wet chemical and vapor deposition techniques.³⁹⁻⁴⁵ Here, the planar 2D SnS₂ flakes are synthesized *via* a

facile wet chemical route. The planar few-layered 2D structure is selected as it both provides large active surface area for more efficient adsorption of NO₂ gas molecules and also facilitates their accommodation into the van der Waal' spacing due to small SnS₂ interlayer binding energy (~10-20 meV/Å²).⁴⁶ We shows that these 2D SnS₂ flakes are integrated onto low-cost resistive transducing platforms for highly selective and excellent sensitive NO₂ gas sensing at ppb levels, which relies on the physisorption based charge transfer.

RESULTS AND DISCUSSION

The 2D SnS₂ flakes were prepared by a wet chemical synthesis technique (details are presented in Materials and Method section). In brief, upon the mixture of Sn precursor and sulfurization reagents at elevated temperatures, the preferential crystal nucleation occurs at the lateral planes due to the strong coupling along them. The existence of excessive dangling bonds at the edges causes the growth of SnS₂ crystals to be continued with a high anisotropic nature, resulting in the planar 2D morphology. Atomic force microscopy (AFM) verifies the presence of 2D hexagonal flakes with the thicknesses in the order of multiple SnS₂ unit cells in the as-synthesized flakes. A typical example is the AFM image shown in Figure 1b, which is a ~6 nm thick 2D flake corresponding to 10 monolayers of SnS₂, as the thickness of a monolayer SnS₂ is ~0.59 nm.^{39, 41} [ENREF 35](#) A statistical analysis based on AFM measurements indicates that the 2D flakes have different thicknesses with the majority lying in the range of 7 to 11 monolayers (Figure S1a). The obtained hexagonal 2D flakes demonstrate some polydispersity in lateral dimensions mainly ranging from 80 to 200 nm according to the transmission electron microscopy (TEM) imaging and dynamic light scattering (DLS) pattern shown in Figures 1c and S1b, respectively. Figure 1d shows the high resolution TEM (HRTEM) image of a 2D SnS₂ flake, in which a lattice fringe spacing of 0.319 nm is identified and corresponds to both the ($\bar{1}100$) and ($01\bar{1}0$) lattice planes of hexagonal SnS₂. The inset in Figure 1d presents the fast Fourier transform (FFT) pattern of this region, showing the faceted edges with an angle of 120°, which corresponds to the hexagonal symmetry of crystalline

SnS₂ projected along the *c*-axis. The cross-sectional HRTEM image illustrated in Figure 1e confirms that these 2D SnS₂ flakes consist of average 9 ± 2 layers with the interlayer distance of 0.587 nm (Figure 1f).

X-ray diffraction (XRD) assessment was utilized to further investigate the crystal phase of 2D hexagonal SnS₂ flakes. From Figure 2a, the primary diffraction peaks of 2D flakes at 15.04°, 28.27°, 32.17°, 41.95°, 50.05°, 52.45° and 60.62° are ascribed to the (001), (100), (101), (102), (110), (111), (201) planes, respectively, which are in accordance with hexagonal 2H SnS₂ structure (ICDD 23-0677). 2H SnS₂ belongs to space group of $P\bar{3}m1$ and has three atoms in the unit cell, which extends over only one monolayer.⁴⁷ However, the additional appearance of a small diffraction peak at ~58° and the relatively intensified peak at 50.05° suggest the co-existence of another SnS₂ crystal phase, which can be identified as 4H structure (ICDD 21-1231). Although it is still within the hexagonal domain, the space group of 4H SnS₂ is changed to $P6_3mc$, which contains six atoms in a single unit cell and extends over two monolayers.⁴⁷ It is found that its composition is almost equal to that of 2H phase when the reaction time is shortened (Figure S2), suggesting that this additional phase might be an intermediate phase during the chemical reaction.

The concurrent phase phenomenon can also be investigated by Raman spectroscopy. From Figure 2b, two distinguished Raman peaks can be found at ~205 and ~314 cm⁻¹ and there is a broad peak centered at ~288 cm⁻¹ for the 2D SnS₂ flakes. The 314 cm⁻¹ peak can be ascribed to the vertical plane vibration mode (A_{1g}) of Sn–S bonds of 2H SnS₂.^{39, 47} Nevertheless, this peak can also be contributed to the A_1+E vertical vibration Raman mode of 4H structure due to the close position between these two structures (~313.5 cm⁻¹ for 4H structure vs. ~314 cm⁻¹ for 2H structure^{39, 47}). Instead, the in-plane vibrational *E* mode allows a facile discrimination between 2H and 4H structures. The E_g mode of 2H structure appears as a single and intense band at 205 cm⁻¹, whereas the *E* mode of 4H structure gives rise to a doublet at 200 and 214 cm⁻¹ according to previous literature.^{39, 47} Therefore, the composition of 4H structure in the 2D SnS₂ flakes is minor. The broad peak centered at 288 cm⁻¹ may also be ascribed to the A_{1g} Raman mode of 2H SnS₂ as a previous

report shows that it is merged in the prominent A_{1g} mode centered at 314 cm^{-1} .³⁹ However, the position of this peak is overlapped with that of B_{2g} Raman mode of SnS.^{48, 49} The XPS results in Figure S3a show that there is no Sn^{2+} signature in the 2D SnS_2 flakes, indicating that the amount of SnS in the flake is negligible.

The optical properties of the 2D flakes were studied by measuring their absorption spectrum (Figure 2c). An absorption peak at $\sim 580\text{ nm}$ with the shoulder centered at $\sim 660\text{ nm}$ can be observed, which are ascribed to the indirect excitonic transition from Γ to M point of the Brillouin zone in 2H and 4H SnS_2 structures, respectively.⁵⁰ The broad peak centered at $\sim 490\text{ nm}$ can be the convoluted peak of the direct excitonic transition at the M point for both 2H and 4H structures according to a previous measurement ($\sim 484\text{ nm}$ for 2H and $\sim 510\text{ nm}$ for 4H)⁵¹ and theoretical calculation values ($\sim 443\text{ nm}$ for 2H and $\sim 454\text{ nm}$ for 4H).⁵⁰ The corresponding photoluminescence (PL) spectrum of 2D SnS_2 flakes was investigated at the excitation wavelength of 532 nm . From Figure 2d, a relatively sharp peak at $\sim 580\text{ nm}$ is observed, which is consistent with the position of indirect excitonic peak of 2H SnS_2 . It should be noted that the position is also close to that of SnO_x .⁵² However, the XPS analysis presented in Figure S3 indicates that there is no observable co-existing SnO_x in the 2D SnS_2 flakes. The broad peak centered at $\sim 660\text{ nm}$ can be ascribed to the hot PL of the indirect exciton recombination of 4H SnS_2 . Although such a broad peak has been ascribed to the PL originated from the structural impurities by a number of researchers,^{53, 54} the energy dispersive X-ray (EDX) survey spectrum in Figure S4a together with the XRD pattern in Figure 2a show no observable structural impurities in 2D SnS_2 flakes. In addition, the measured Sn/S composition ratio is $\sim 1:2$, matching the theoretical value of SnS_2 , implying that the influence of substoichiometric levels and sulfur vacancies toward the electronic and optical properties of the flakes can be neglected. The mapping images of Sn and S elements displayed in Figure S4b demonstrate that both Sn and S distribute uniformly along the flake.

The 2D SnS_2 gas sensors were fabricated by drop-casting of the solution containing 2D SnS_2 flakes on the resistive transducing substrates which were made of alumina with surface

interdigitated electrode (IDE) patterns (Specification was presented in Materials and Method section). The IDE metal is chosen to assure that Ohmic contacts were formed with drop-casted SnS₂. The electrical resistance of the device was measured for calculating the gas response factor using R_g/R_a for $R_g > R_a$, or R_a/R_g for $R_g < R_a$, where R_a and R_g represent the resistance of the device to air and the analyte gas, respectively. The sensor response and recovery time are defined as the time required for a 90% change in the full magnitude change of the gas response factor.

We tested the operation temperature of sensors from room to 160°C. For the temperatures lower than 80°C, the device did not show acceptable response/recovery time and additionally R_g was relatively large and beyond the measurement range of the Ohm-meter. There is an observable transition from SnS₂ to tin oxide compounds (SnO_x) when the operation temperature exceeds 160°C (Figure S5) and therefore operation at such elevated temperatures is ruled out.

From Figure 3a and Table S1, after the exposure to 10 ppm NO₂ in synthetic air balance at the operation temperature of 80°C, the sensor's resistance is impressively ~28 times larger than that of only synthetic air (translates into the initial response factor of ~28). As will be fully discussed later, the surface adsorbed NO₂ gas molecules act as electron acceptors to receive electrons from 2D SnS₂ flakes. Such charge transfers reduce the number of free electrons in the flakes, increasing the resistance. With the increase of the operating temperature, the response factor is enhanced while the response and recovery time are decreased, suggesting that the increase of the temperature facilitates the adsorption of NO₂ gas molecules onto the 2D SnS₂ surface and enhances the charge transfer. The optimal sensing takes place at 120°C with a maximum response factor of ~36 with the shortest response and recovery time of ~170 and ~140 s, respectively. By further increasing the operating temperature beyond 120°C, the response factor is dramatically dropped and the response time is slightly increased, implying that the surface desorption process of NO₂ gas becomes a more dominant effect at such temperatures.

The dynamic performance of the sensor towards NO₂ gas with concentrations ranged from 0.6 to 10 ppm at the optimum operation temperature of 120°C was shown in Figure 3b. With the increase

in the concentration of NO₂, more surface dipoles are formed before the NO₂ coverage reaches its maximum, resulting in more electron transfer from SnS₂ to NO₂. The measured response factor of the sensor is observed to be almost linear with the exposure concentrations of NO₂ gas, while the response time is greatly decreased when increasing the NO₂ concentration from 0.6 to 1.2 ppm and reaches the saturation stage afterwards (Table S2). Excellent sensor reversibility is observed (Figure 3b and Figure S6) with the recovery time of less than 180 s at the optimum operating temperature regardless of the NO₂ concentration. This remarkable reversibility is not commonly seen in physisorptive charge transfer based sensors and the recovery time of such systems can be up to several orders of magnitude longer due to their slow recovery kinetics.²² Based on the NO₂ dynamic responses, the NO₂ detection limit of our sensor is estimated to be ~20-30 ppb at a noise level of ±5%. Such a low detection limit is superior in comparison to those of low-cost NO₂ optical and electrochemical sensors, which are both only in the ppm ranges^{9, 12, 13, 15} and comparable to those of best-reported metal oxide based chemisorptive gas sensors (10-50 ppb)¹⁶ which are not NO₂ selective. The value is also close to those of 2D MoS₂²⁸ and carbon²² based physisorptive gas sensors which show poor reversibility.

The 2D SnS₂ flakes are very strongly selective to NO₂ as only minimal responses toward other gases under investigation in this work are observed. At 120°C, which is the near optimal operating temperature for all those gases, response factors at industrially meaningful concentrations for H₂ (1%), CH₄ (10%), CO₂ (10%) and H₂S (56 ppm) are found to be ~1.0, ~1.1, ~1.1 and ~1.3, respectively, in comparison to ~36 for NO₂ (10 ppm) (Figure 3c). The particular selected concentrations of toxic NO₂ (10 ppm) and H₂S (56 ppm) gases are well below the immediately dangerous to life or health (IDLH) values defined by US national institute for occupational safety and health (NIOSH), which are 20 and 100 ppm, respectively.⁵⁵ The exposure limit of NO₂ defined by NIOSH is recommended to be 1 ppm.⁵⁵ If taking this into account, the NO₂ selectivity of this sensor is still superior as its response factor is ~10 at 1.2 ppm NO₂ which is almost an order magnitude higher than other aforementioned gases. In addition, the humidity plays a negligible role

in the NO₂ gas sensing performance of the sensor (Figure S7). It has also been previously shown that the response of nanostructured SnS₂ towards several other gases are relatively smaller than that of shown to NO₂ here. For instance, NH₃ has only a response of ~1.5 at a concentration of 100 ppm.⁵⁶

To understand the selectivity of 2D SnS₂ flakes toward NO₂ gas, we calculated the molecule-surface binding energies using density functional theory (DFT) to assess the dispersion forces. The outcomes are shown in Figure 3d and Table S3. The closest distance between the molecules and the surface, for the bound gas species, range from 2.17 to 2.87 Å which is within the typical range for physisorbed molecules. The values of the binding energies also indicate the physisorption occurs between the molecule and the surface for CH₄, CO₂, H₂S, NH₃ and NO₂, with NO₂ being the most strongly bound species. The binding energy for NO₂ is approximately 140 meV greater than that of the next most bound species (NH₃), while H₂ and O₂ are non-binding due to its small adsorption energy (~50 meV) and positive adsorption energy (Table S3), respectively. The repelling of O₂ molecules on the SnS₂ surface possibly indicates that the charge transfer to the physisorbed NO₂ molecules does not rely on the presence of O₂ gas, which is distinctly different from those of metal oxides based chemisorptive NO₂ sensors.^{16, 17} The calculated surface binding energies toward different gas molecules are in accordance with the measurement results, confirming that the impressive selective NO₂ gas response of 2D SnS₂ flakes originates from its unique physical surface affinity to the gas molecules.

Another possible reason can be attributed to the influence of different gas molecules on SnS₂ electronic band structure. Figure 4 shows the spin resolved electronic Density of States (eDOS) plots for the clean SnS₂ surface and for surfaces onto which aforementioned gas molecules are physisorbed. For the most weakly bound gas species (CO₂ and CH₄), the total eDOS and the projected eDOS of the nearest neighbor surface S atoms are almost the same as for the clean surface near the Fermi level, suggesting there is negligible charge transfer between the molecules and surface. The next most bound species, H₂S and NH₃, display similar features in the eDOS. In both

cases, molecular physisorption introduces states in the gap, and the projected eDOS indicates that both molecule and surface atom states contribute to this state in the band gap. In addition, the bands near the valance band maximum (VBM) is shifted down by nearly 0.1 eV compared to that of clean surface. However, these generated gap states are relatively far away from the Fermi level (~ 0.5 -1 eV), resulting in inefficient charge transfer between the physisorbed gas molecules and SnS₂ surface. In contrast, the eDOS for NO₂ physisorption is different from the other species. Firstly, the DOS is asymmetric when comparing spin-up and spin-down, possibly due to the formation of surface magnetic moment upon the physisorption of NO₂ gas molecules. More importantly, while the energy bands near the conduction band minimum (CBM) are lowered by ~ 60 meV, the band states close to the Fermi level are raised in energy by approximately 20 meV compared to the clean surface, indicating significant charge transfer from SnS₂ to the physisorbed NO₂ gas molecules.

In comparison to other 2D semiconductors, it is noted that the response factor of 2D SnS₂ toward NO₂ is at least one order larger than that of exfoliated 2D MoS₂ at similar exposure concentration and operation temperature.²⁸ This can be mainly ascribed to the larger NO₂ adsorption energy of SnS₂ compared to MoS₂ (~ 150 meV),⁵⁷ resulting in more adsorption of NO₂ gas molecules either on the surface or possibly within the van der Waal's gap of SnS₂ through efficient intercalation as few-layered SnS₂ has a much weaker interlayer binding energy than that of MoS₂.⁴⁶ In addition, the Mulliken population analysis of the charge density for the NO₂ physisorption indicates a transfer in charge density of $0.048 e^-$ from SnS₂ surface to the NO₂ molecule, while only $0.034 e^-$ is observed for that of MoS₂.⁵⁷ Such an improvement can be possibly due to a more favorable Fermi energy of SnS₂ related to partially occupied molecular orbitals (POMO) of NO₂ (Figure 4), which is also another key factor for the strength of physisorption based charge transfer.

We observed that our 2D SnS₂ sensor demonstrates a much higher rate of NO₂ recovery kinetics compared to those of previously physisorption based sensors made of 2D materials (*e.g.* 2D MoS₂) at elevated temperatures.²⁶⁻²⁸ It is found that NO₂ gas molecules are favorably absorbed on the S atoms of SnS₂ with a calculated bond length of 2.41 Å, while the NO₂ gas molecules are adsorbed

onto Mo atoms of MoS₂ between two sandwiched S layers with a much shorter bond length of 1.21 Å.⁵⁷ Therefore, the thermal vibration energy available at an elevated temperature causes a more efficient NO₂ gas desorption from SnS₂ compared to MoS₂. The stronger temperature dependence of SnS₂ Fermi level can also result in a more favorable position related to that of NO₂ POMO at elevated temperatures.^{37, 38} The temperature effect, together with its strong physical NO₂ affinity, ensures the domination of charge transfer from SnS₂ to NO₂ despite the large NO₂ gas desorption at relatively high temperatures.

The charge transfer phenomenon from the surface of 2D SnS₂ to the physisorbed NO₂ gas molecules is partially evidenced by Raman spectroscopy before and after the NO₂ exposure at 120°C. From Figure 5a, there is no observable Raman peak shift associated with stiffening, confirming no chemical bond modification upon the physisorption of NO₂ gas molecules. The intensity of A_{1g} Raman mode is found to be significantly reduced, while the Raman E_g mode seems to remain unchanged after the NO₂ exposure and their intensity ratio $I(A_{1g}/E_g)$ is decreased from 1.05 to 0.8. The NO₂ adsorption may affect the equilibrium lattice parameter in SnS₂. Additionally, the NO₂ molecules on the surface act as electron acceptors, modifying the electron-phonon interaction in SnS₂. Similar to the cases of charge-transfer doping observed in graphene and TMDs,⁵⁸⁻⁶⁰ such a modification leads to the phonon self-energy renormalization and consequently weakening of the phonons, causing the intensity decrease of the A_{1g} mode that is more sensitive to the free electron density of the material.

The PL spectrum can be a good indicator in the charge transfer phenomenon as well. As SnS₂ is an *n*-type semiconductor,⁴⁰ its PL peak can be theoretically decomposed into the portions of neutral exciton and the negative trion.⁶¹ A negative trion consists of two electrons to a hole, resulting in a negatively charged exciton, while the neutral exciton is coupled to the extra electron at the Fermi level.⁵⁸ Upon the adsorption of NO₂ gas molecules, the negative trion is converted back into the neutral exciton as the free electrons are depleted from SnS₂. At the same time, the generated surface dipoles between the gas molecules and SnS₂ surface are strong enough to split the neutral excitons,

leading to a significant reduction in their recombination and subsequently a strongly quenched PL (Figure 5b), which is analogous to the PL modulation in MoS₂-WS₂ heterostacks or electrical gating of MoS₂.^{61, 62} In addition, it seems that such gas molecules induced charge transfers show no difference on the crystal polytypes of SnS₂ as the quenched degrees of the 2H and 4H PL peaks are similar.

CONCLUSIONS

We successfully developed a novel gas sensor based on 2D SnS₂ flakes with a very strong selectivity to NO₂ molecules. The 2D SnS₂ flakes were synthesized using a facile wet chemical route with a great potential for production scalability. The 2D structure of SnS₂ hexagonal planes were made of a few layers of unit cell thickness, which provided plenty of room for NO₂ molecule adsorption either on the surface or in-between the van der Waals's spacings. The NO₂ adsorption mechanism was theoretically and experimentally shown to be dominated by physisorption with a concurrent charge transfer into 2D SnS₂ flakes that could occur at relatively low operating temperatures. Our theoretical calculations also suggested no oxygen was involved in the NO₂ adsorption/desorption process, possibly indicating the sensor could also operate in anaerobic environments. The best NO₂ gas sensing performance of 2D SnS₂ was achieved at the optimum temperature of 120°C, reaching the detection limits of <30 ppb and showing an impressive response factor of ~36 when exposed to a NO₂ concentration of 10 ppm. Excellent NO₂ selectivity was demonstrated with reference to other gas species, which had not been previously exhibited for NO₂ gas sensors that operate based on a physisorptive charge transfer mechanism. Such a unique selectivity was ascribed to the strong physical affinity of paramagnetic NO₂ gas molecules towards SnS₂ surfaces as well as the relatively favorable position between Fermi level of SnS₂ and NO₂ POMO. Our 2D SnS₂ based NO₂ gas sensor was also highly reversible, showing excellent recovery to the baseline in contrast to 2D TMDs, such as 2D MoS₂.

The realization of the presented economical, exceptionally selective and highly sensitive NO₂ gas sensing platform, which operates at relatively low temperatures without the presence of oxygen, provides a feasible approach to allow high performance NO₂ sensing for a wide range of applications in environmental monitoring, industry, clinical practices and healthcare.

MATERIALS AND METHODS

Synthesis of 2D SnS₂ flakes: Tin (IV) chloride (SnCl₄•5H₂O, >99.9%, Sigma Aldrich, 0.5 mM) was added to a mixture of 5 mL oleic acid (OAc, >90.0%, Sigma Aldrich) and 10 mL octadecene (ODE, >90.0%, Sigma Aldrich) in a 100 mL three-neck flask to produce tin precursor. A standard Schlenk line was used to protect the reaction from oxygen and moisture under a flow of high-purity N₂. The mixed solution was degassed at 120°C for 1 h to remove the moisture and the oxygen. Subsequently, the solution was heated to 280°C within 15 min with a vigorous stir (700 rpm). Sulfide powder (1 mM) was dispersed into 5 mL oleylamine (OAm, >90.0%, Sigma Aldrich) to produce the sulfide precursor which was subsequently injected into the reaction system. The reaction was maintained at 280 °C for 30 min. After cooling the solution to room temperature, the 2D SnS₂ flakes (in powder form) were collected and separated from the solution by centrifugation. The powder was further washed two times by ethanol and hexane (1/1, V/V) and finally dispersed in ethanol. The powder was stable in air without further protection for characterizations.

Morphological, structural and optical characterizations: Lateral dimensions and thickness of 2D SnS₂ flakes were measured using DLS (ALV fast DLS particle sizing spectrometer) and AFM (Bruker Multimode 8 with PF TUNA), respectively. Their crystal structure was characterized using XRD (Philips PANanalytical) with CuKα radiation at 45 kV and 40 mA, HRTEM (TEM, Tecnai F20, FEI) at an accelerating voltage of 200 kV and Raman spectroscopy (Craic 20-30 microspectrophotometer) under the excitation wavelength of 785 nm at 1 mW power. The EDX spectrum and mapping of the flakes were carried out by scanning electron microscopy (JEOL

JSM6700F) equipped with an EDX spectroscopy. The optical absorption spectra of the 2D flakes were examined using a Varian Cary 500 spectrometer in dual beam mode using quartz cuvettes. PL spectroscopy was carried out on a Princeton Instruments SP2500i with a PIXIS100 ExCelon CCD camera detector using a Monochromatic 532 nm laser delivering approximately 200 μ W average power to the sample.

Gas sensor fabrication and characterization: The transducing substrates were made of alumina pattern with 8 pairs of IDE Pt electrodes. The spacing between each IDE pair was 200 μ m. 5 μ L of suspension containing 1 mg/mL 2D SnS₂ flakes was drop-casted on the transducing substrate within the exposed area of 0.5 cm $\times$ 0.5 cm at a temperature of 50°C. The resistance of the sensor was measured using Agilent 34410A digital multimeter. The gas sensing measurements were conducted in a LINKAM (Scientific Instruments) customized gas testing chamber with the capability to control the operation temperature for up to 600°C. A computerized mass flow control (MFC) multi-channel gas calibration system was used to regulate the incoming gas stream at a total constant flow rate of 200 standard cubic centimeters per minute (sccm) to the LINKAM chamber. For the investigation of NO₂ gas sensing performance in the humidified environment, the humidification of the gas was realized by a simple unheated bubble humidifier, in which the gas was forced down a tube into the bottom of a bottle containing 100 mL of water. The gas then escaped from the distal end of the tube under water surface forming bubbles, which gained humidity as they rose to the water surface. Given the relatively smaller gas flow rate (200 sccm or 0.2 L/min), the relative humidity (RH) of the incoming gas stream towards the sensor reached approximately 100%,^{63, 64} which was also confirmed by a commercial humidity sensor.

Theoretical calculation on the surface adsorption energy and total density of states: Spin-dependent Hybrid DFT calculations were carried out in Gaussian basis set *ab initio* package CRYSTAL14.^{65, 66} The B3LYP hybrid exchange-correlation functional was used⁶⁷ that was augmented with an empirical London-type correction to the energy in order to incorporate dispersion contributions to the overall energy. The correction term used in these calculations is the

one proposed by Grimme,⁶⁸ which has been successfully used with B3LYP to calculate cohesive energies in dispersion bonded molecular crystals.⁶⁹ For all atoms (other than Sn) a triple zeta valence (TZV) basis set, with polarization functions, was used for modeling the electrons.⁷⁰ In contrast, a fully relativistic effective core potential was used for Sn, accounting for the 28 core electrons ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$) and a 411(51d) basis set for the valence electrons.⁷¹ A periodic $3\times 3\times 1$ or $5\times 5\times 1$ slab of SnS_2 was used for representing the SnS_2 surface. Initially, each target gas molecule was placed ~ 1.5 Å from the S surface layer of SnS_2 and the molecule/slab configuration was geometry optimized prior to calculating the molecule-slab binding energy.

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SUPPORTING INFORMATION

AFM statistical analysis and DLS measurements of 2D SnS_2 flakes; XRD pattern of flakes synthesized by shorter reaction time; XPS analysis of 2D SnS_2 flakes; EDX spectrum and mapping of 2D SnS_2 flakes; Raman spectra of 2D SnS_2 flakes at different temperatures; The recovery kinetics of 2D SnS_2 flakes after NO_2 gas exposure; NO_2 gas sensing performance of 2D SnS_2 flakes in the humidified environment.

REFERENCES

1. Guarnieri, M.; Balmes, J. R. Outdoor Air Pollution and Asthma. *Lancet* 2014, 383, 1581-1592.
2. Schwela, D. Air Pollution and Health in Urban Areas. *Rev. Environ. Health* 2000, 15, 13-42.
3. EPA, U. S. Air Pollution. www.epa.gov/air/nitrogenoxides/ (accessed 30/06/2015).
4. Atkinson, R. Atmospheric Chemistry of VOCs and NOx. *Atmos. Environ.* 2000, 34, 2063-2101.
5. Hodge, C. A. *Pollution Control in Fertilizer Production*. CRC Press: 1994.
6. Ou, J. Z.; Yao, C.; Rotbart, A.; Muir, J. G.; Gibson, P. R.; Kalantar-zadeh, K. Human Intestinal Gas Measurement Systems: *In Vitro* Fermentation and Gas Capsules. *Trends in biotechnol.* 2015, 33, 208-213.
7. Puckett, J. L.; George, S. C. Partitioned Exhaled Nitric Oxide to Non-Invasively Assess Asthma. *Resp. Physiol. Neurobi.* 2008, 163, 166-177.
8. Andringa, A.-M.; Piliago, C.; Katsouras, I.; Blom, P. W. M.; Leeuw, D. M. d. NO₂ Detection and Real-Time Sensing with Field-Effect Transistors. *Chem. Mater.* 2014, 26, 773-785.
9. Swanson, J. J.; Watts, W. F.; Newman, R. A.; Ziebarth, R. R.; Kittelson, D. B. Simultaneous Reduction of Particulate Matter and NOx Emissions Using 4-Way Catalyzed Filtration Systems. *Environ. Sci. Technol.* 2013, 47, 4521-4527.
10. De Castro, A. J.; Meneses, J.; Briz, S.; López, F. Nondispersive Infrared Monitoring of NO Emissions in Exhaust Gases of Vehicles. *Rev. Sci. Instrum.* 1999, 70, 3156-3159.
11. Jimenez, J. L.; McRae, G. J.; Nelson, D. D.; Zahniser, M. S.; Kolb, C. E. Remote Sensing of NO and NO₂ Emissions from Heavy-Duty Diesel Trucks Using Tunable Diode Lasers. *Environ. Sci. Technol.* 2000, 34, 2380-2387.

12. Wang, X.-D.; Wolfbeis, O. S. Fiber-Optic Chemical Sensors and Biosensors. *Anal. Chem.* 2013, 85, 487-508.
13. Chang, S.-C.; Stetter, J. R. Electrochemical NO₂ Gas Sensors: Model and Mechanism for the Electroreduction of NO₂. *Electroanal.* 1990, 2, 359-365.
14. Privett, B. J.; Shin, J. H.; Schoenfish, M. H. Electrochemical Sensors. *Anal. chem.* 2008, 80, 4499-4517.
15. Zhuiykov, S.; Miura, N. Development of Zirconia-Based Potentiometric NO_x Sensors for Automotive and Energy Industries in the Early 21st Century: What are the Prospects for Sensors? *Sensor Actuat. B-Chem.* 2007, 121, 639-651.
16. Afzal, A.; Cioffi, N.; Sabbatini, L.; Torsi, L. NO_x Sensors based on Semiconducting Metal Oxide Nanostructures: Progress and Perspectives. *Sensor Actuat. B-Chem.* 2012, 171–172, 25-42.
17. Fine, G. F.; Cavanagh, L. M.; Afonja, A.; Binions, R. Metal Oxide Semiconductor Gas Sensors in Environmental Monitoring. *Sensors* 2010, 10, 5469.
18. Wehling, T. O.; Novoselov, K. S.; Morozov, S. V.; Vdovin, E. E.; Katsnelson, M. I.; Geim, A. K.; Lichtenstein, A. I. Molecular Doping of Graphene. *Nano Lett.* 2008, 8, 173-177.
19. Leenaerts, O.; Partoens, B.; Peeters, F. M. Adsorption of H₂O, NH₃, CO, NO₂, and NO on Graphene: A First-Principles Study. *Phys. Rev. B* 2008, 77, 125416.
20. Hu, T.; Gerber, I. C. Theoretical Study of the Interaction of Electron Donor and Acceptor Molecules with Graphene. *J. Phys. Chem. C* 2013, 117, 2411-2420.
21. Llobet, E. Gas Sensors Using Carbon Nanomaterials: A Review. *Sensor Actuat. B-Chem.* 2013, 179, 32-45.
22. Iqbal, N.; Afzal, A.; Cioffi, N.; Sabbatini, L.; Torsi, L. NO_x Sensing One- and Two-Dimensional Carbon Nanostructures and Nanohybrids: Progress and Perspectives. *Sensor Actuat. B-Chem.* 2013, 181, 9-21.

23. Li, H.; Wu, J.; Qi, X.; He, Q.; Liusman, C.; Lu, G.; Zhou, X.; Zhang, H. Graphene Oxide Scrolls on Hydrophobic Substrates Fabricated by Molecular Combing and Their Application in Gas Sensing. *Small* 2013, 9, 382-386.
24. He, Q.; Wu, S.; Yin, Z.; Zhang, H. Graphene-based Electronic Sensors. *Chem. Sci.* 2012, 3, 1764-1772.
25. Schedin, F.; Geim, A. K.; Morozov, S. V.; Hill, E. W.; Blake, P.; Katsnelson, M. I.; Novoselov, K. S. Detection of Individual Gas Molecules Adsorbed on Graphene. *Nat. Mater.* 2007, 6, 652-655.
26. Cho, B.; Hahm, M. G.; Choi, M.; Yoon, J.; Kim, A. R.; Lee, Y.-J.; Park, S.-G.; Kwon, J.-D.; Kim, C. S.; Song, M., *et al.* Charge-Transfer-Based Gas Sensing Using Atomic-Layer MoS₂. *Sci. Rep.* 2015, 5, 8052.
27. Late, D. J.; Huang, Y.-K.; Liu, B.; Acharya, J.; Shirodkar, S. N.; Luo, J.; Yan, A.; Charles, D.; Waghmare, U. V.; Dravid, V. P., *et al.* Sensing Behavior of Atomically Thin-Layered MoS₂ Transistors. *ACS Nano* 2013, 7, 4879-4891.
28. Donarelli, M.; Prezioso, S.; Perrozzi, F.; Bisti, F.; Nardone, M.; Giancaterini, L.; Cantalini, C.; Ottaviano, L. Response to NO₂ and Other Gases of Resistive Chemically Exfoliated MoS₂-Based Gas Sensors. *Sensor Actuat. B-Chem.* 2015, 207, 602-613.
29. He, Q.; Zeng, Z.; Yin, Z.; Li, H.; Wu, S.; Huang, X.; Zhang, H. Fabrication of Flexible MoS₂ Thin-Film Transistor Arrays for Practical Gas-Sensing Applications. *Small* 2012, 8, 2994-2999.
30. Li, H.; Yin, Z.; He, Q.; Li, H.; Huang, X.; Lu, G.; Fam, D. W. H.; Tok, A. I. Y.; Zhang, Q.; Zhang, H. Fabrication of Single- and Multilayer MoS₂ Film-Based Field-Effect Transistors for Sensing NO at Room Temperature. *Small* 2012, 8, 63-67.

31. Abbas, A. N.; Liu, B.; Chen, L.; Ma, Y.; Cong, S.; Aroonyadet, N.; Köpf, M.; Nilges, T.; Zhou, C. Black Phosphorus Gas Sensors. *ACS Nano* 2015, 9, 5618-5624.
32. Kou, L.; Frauenheim, T.; Chen, C. Phosphorene as a Superior Gas Sensor: Selective Adsorption and Distinct I – V Response. *J. Phys. Chem. Lett.* 2014, 5, 2675-2681.
33. Julien, C.; Eddrief, M.; Samaras, I.; Balkanski, M. Optical and Electrical Characterizations of SnSe, SnS₂ and SnSe₂ Single Crystals. *Mat. Sci. Eng. B-Solid* 1992, 15, 70-72.
34. Chhowalla, M.; Shin, H. S.; Eda, G.; Li, L. J.; Loh, K. P.; Zhang, H. The Chemistry of Two-Dimensional Layered Transition Metal Dichalcogenide Nanosheets. *Nat. Chem.* 2013, 5, 263-275.
35. Varrla, E.; Backes, C.; Paton, K. R.; Harvey, A.; Gholamvand, Z.; McCauley, J.; Coleman, J. N. Large-Scale Production of Size-Controlled MoS₂ Nanosheets by Shear Exfoliation. *Chem. Mater.* 2015, 27, 1129-1139.
36. Xu, Y.; Schoonen, M. A. A. The Absolute Energy Positions of Conduction and Valence Bands of Selected Semiconducting Minerals. *Am. Mineral.* 2000, 85, 543-556.
37. Patil, S. G.; Tredgold, R. H. Electrical and Photoconductive Properties of SnS₂ Crystals. *J. Phys. D Appl. Phys.* 1971, 4, 718.
38. El-Mahalawy, S. H.; Evans, B. L. Temperature Dependence of the Electrical Conductivity and Hall Coefficient in 2H-MoS₂, MoSe₂, WSe₂, and MoTe₂. *physica status solidi B* 1977, 79, 713-722.
39. Huang, Y.; Sutter, E.; Sadowski, J. T.; Cotlet, M.; Monti, O. L. A.; Racke, D. A.; Neupane, M. R.; Wickramaratne, D.; Lake, R. K.; Parkinson, B. A., *et al.* Tin Disulfide—An Emerging Layered Metal Dichalcogenide Semiconductor: Materials Properties and Device Characteristics. *ACS Nano* 2014, 8, 10743-10755.

40. Ahn, J.-H.; Lee, M.-J.; Heo, H.; Sung, J. H.; Kim, K.; Hwang, H.; Jo, M.-H. Deterministic Two-Dimensional Polymorphism Growth of Hexagonal *n*-Type SnS₂ and Orthorhombic *p*-Type SnS Crystals. *Nano Lett.* 2015, 15, 3703-3708.
41. Su, G.; Hadjiev, V. G.; Loya, P. E.; Zhang, J.; Lei, S.; Maharjan, S.; Dong, P.; M. Ajayan, P.; Lou, J.; Peng, H. Chemical Vapor Deposition of Thin Crystals of Layered Semiconductor SnS₂ for Fast Photodetection Application. *Nano Lett.* 2015, 15, 506-513.
42. Du, Y.; Yin, Z.; Rui, X.; Zeng, Z.; Wu, X.-J.; Liu, J.; Zhu, Y.; Zhu, J.; Huang, X.; Yan, Q., *et al.* A Facile, Relative Green, and Inexpensive Synthetic Approach toward Large-Scale Production of SnS₂ Nanoplates for High-Performance Lithium-Ion Batteries. *Nanoscale* 2013, 5, 1456-1459.
43. Kim, T.-J.; Kim, C.; Son, D.; Choi, M.; Park, B. Novel SnS₂-Nanosheet Anodes for Lithium-Ion Batteries. *J. Power Sources* 2007, 167, 529-535.
44. Seo, J.-w.; Jang, J.-t.; Park, S.-w.; Kim, C.; Park, B.; Cheon, J. Two-Dimensional SnS₂ Nanoplates with Extraordinary High Discharge Capacity for Lithium Ion Batteries. *Adv. Mater.* 2008, 20, 4269-4273.
45. Zhang, Y. C.; Du, Z. N.; Li, S. Y.; Zhang, M. Novel Synthesis and High Visible Light Photocatalytic Activity of SnS₂ Nanoflakes from SnCl₂·2H₂O and S Powders. *Appl. Catal. B-Environ* 2010, 95, 153-159.
46. Björkman, T.; Gulans, A.; Krasheninnikov, A. V.; Nieminen, R. M. Van Der Waals Bonding in Layered Compounds from Advanced Density-Functional First-Principles Calculations. *Phys. Rev. Lett.* 2012, 108, 235502.
47. Smith, A. J.; Meek, P. E.; Liang, W. Y. Raman Scattering Studies of SnS₂ and SnSe₂. *J. Phys. C Solid State* 1977, 10, 1321.

48. Chandrasekhar, H. R.; Humphreys, R. G.; Zwick, U.; Cardona, M. Infrared and Raman Spectra of the IV-VI Compounds SnS and SnSe. *Phys. Rev. B* 1977, 15, 2177-2183.
49. Price, L. S.; Parkin, I. P.; Hardy, A. M. E.; Clark, R. J. H.; Hibbert, T. G.; Molloy, K. C. Atmospheric Pressure Chemical Vapor Deposition of Tin Sulfides (SnS, Sn₂S₃, and SnS₂) on Glass. *Chem. Mater.* 1999, 11, 1792-1799.
50. Seminovski, Y.; Palacios, P.; Wahnón, P. Effect of Van Der Waals Interaction on the Properties of SnS₂ Layered Semiconductor. *Thin Solid Films* 2013, 535, 387-389.
51. Domingo, G.; Itoga, R. S.; Kannewurf, C. R. Fundamental Optical Absorption in SnS₂ and SnSe₂. *Phys. Rev.* 1966, 143, 536-541.
52. Faglia, G.; Baratto, C.; Sberveglieri, G.; Zha, M.; Zappettini, A. Adsorption Effects of NO₂ at ppm Level on Visible Photoluminescence Response of SnO₂ Nanobelts. *App. Phys. Lett.* 2005, 86, 011923.
53. Shibata, T.; Kambe, N.; Muranushi, Y.; Miura, T.; Kishi, T. Optical Characterisation of Single Crystal 2H-SnS₂ Synthesised by the Chemical Vapour Transport Method at Low Temperatures. *J. Phys. D Appl. Phys.* 1990, 23, 719.
54. Deshpande, N. G.; Sagade, A. A.; Gudage, Y. G.; Lokhande, C. D.; Sharma, R. Growth and Characterization of Tin Disulfide (SnS₂) Thin Film Deposited by Successive Ionic Layer Adsorption and Reaction (SILAR) Technique. *J. Alloy Comd.* 2007, 436, 421-426.
55. NIOSH. NIOSH Pocket Guide to Chemical Hazards. <http://www.cdc.gov/niosh/npg/npgd0454.html> (accessed 23/09/2015).
56. Shi, W.; Huo, L.; Wang, H.; Zhang, H.; Yang, J.; Wei, P. Hydrothermal Growth and Gas Sensing Property of Flower-Shaped SnS₂ Nanostructures. *Nanotechnology* 2006, 17, 2918.
57. Zhao, S.; Xue, J.; Kang, W. Gas Adsorption on MoS₂ Monolayer from First-Principles Calculations. *Chem. Phys. Lett.* 2014, 595–596, 35-42.

58. Liu, J.; Li, Q.; Zou, Y.; Qian, Q.; Jin, Y.; Li, G.; Jiang, K.; Fan, S. The Dependence of Graphene Raman D-Band on Carrier Density. *Nano Lett.* 2013, 13, 6170-6175.
59. Rakesh, V.; Barun, D.; Chandra Sekhar, R.; Rao, C. N. R. Effects of Charge Transfer Interaction of Graphene with Electron Donor and Acceptor Molecules Examined Using Raman Spectroscopy and Cognate Techniques. *J. Phys. Condens. Mat.* 2008, 20, 472204.
60. Shi, Y.; Huang, J.-K.; Jin, L.; Hsu, Y.-T.; Yu, S. F.; Li, L.-J.; Yang, H. Y. Selective Decoration of Au Nanoparticles on Monolayer MoS₂ Single Crystals. *Sci. Rep.* 2013, 3, 1839.
61. Yuan, J.; Najmaei, S.; Zhang, Z.; Zhang, J.; Lei, S.; M. Ajayan, P.; Yakobson, B. I.; Lou, J. Photoluminescence Quenching and Charge Transfer in Artificial Heterostacks of Monolayer Transition Metal Dichalcogenides and Few-Layer Black Phosphorus. *ACS Nano* 2015, 9, 555-563.
62. Newaz, A. K. M.; Prasai, D.; Ziegler, J. I.; Caudel, D.; Robinson, S.; Haglund Jr, R. F.; Bolotin, K. I. Electrical Control of Optical Properties of Monolayer MoS₂. *Solid State Commun.* 2013, 155, 49-52.
63. Al Ashry, H. S.; Modrykamien, A. M. Humidification during Mechanical Ventilation in the Adult Patient. *BioMed Res. Int.* 2014, 2014, 12.
64. Kacmarek, R. M.; Stoller, J. K.; Heuer, A. *Egan's Fundamentals of Respiratory Care*. Elsevier: 2013.
65. Dovesi, R.; Orlando, R.; Erba, A.; Zicovich-Wilson, C. M.; Civalleri, B.; Casassa, S.; Maschio, L.; Ferrabone, M.; De La Pierre, M.; D'Arco, P., *et al.* CRYSTAL14: A Program for the *Ab Initio* Investigation of Crystalline Solids. *Int. J. Quantum Chem.* 2014, 114, 1287-1317.
66. Dovesi, R.; Saunders, V. R.; Roetti, C.; Orlando, R.; Zicovich-Wilson, C. M.; Pascale, F.; Civalleri, B.; Doll, K.; Harrison, N. M.; Bush, I. J., *et al.* *CRYSTAL14 User's Manual* University of Torino: Torino, 2014.

67. Becke, A. D. Density-Functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* 1993, 98, 5648-5652.
68. Grimme, S. Semiempirical GGA-Type Density Functional Constructed with A Long-Range Dispersion Correction. *J. Comput. Chem.* 2006, 27, 1787-1799.
69. Civalleri, B.; Zicovich-Wilson, C. M.; Valenzano, L.; Ugliengo, P. B3LYP Augmented with An Empirical Dispersion Term (B3LYP-D*) as Applied to Molecular Crystals. *CrystEngComm* 2008, 10, 405-410.
70. Peintinger, M. F.; Oliveira, D. V.; Bredow, T. Consistent Gaussian Basis Sets of Triple-Zeta Valence with Polarization Quality for Solid-State Calculations. *J. Comput. Chem.* 2013, 34, 451-459.
71. Crystal - Basis Sets Library. <http://www.crystal.unito.it/basis-sets.php>.

Figure 1. Morphological and structural characterization of 2D SnS₂ flakes. **a.** Top and cross-sectional schematics of SnS₂; **b.** Height profile of a typical 2D SnS₂ flake along the green line in the AFM image inset; **c.** TEM image of 2D SnS₂ flakes; **d.** HRTEM image of a typical 2D SnS₂ flake; **e.** Cross-sectional HRTEM of 2D SnS₂ flakes; **f.** The zoomed in HRTEM figure indicating the interlayer spacing for hexagonal SnS₂ is 0.587 nm.

Figure 2. Crystal structure and optical properties of 2D SnS₂ flakes. **a.** XRD pattern of 2D SnS₂ flakes; **b.** Raman spectrum of 2D SnS₂ flakes at the laser excitation wavelength of 785 nm with schematics of E_g and A_{1g} Raman vibrational modes; **c.** The optical absorption spectrum of 2D flakes at the wavelengths between 400 to 800 nm; **d.** The PL spectrum of 2D flakes at the excitation wavelength of 532 nm.

Figure 3. Gas sensing performance of 2D SnS₂ flakes. **a.** Response factor and response time of sensors made of 2D SnS₂ flakes in the presence of 10 ppm NO₂ in synthetic air balance as a function of operation temperatures; **b.** Dynamic sensing performance of 2D SnS₂ flakes toward NO₂ gas at the concentrations ranged from 0.6 to 10 ppm under the operation temperature of 120°C; **c.** Measured cross-talk of 2D SnS₂ flakes towards H₂ (1%), CH₄ (10%), CO₂ (10%), H₂S (56 ppm) and NO₂ (10 ppm); **d.** Calculated molecule-surface adsorption energies of 2D SnS₂ flakes towards the aforementioned gases together with NH₃.

Figure 4. eDOS of NO₂, NH₃, H₂S, CO₂ and CH₄ adsorbed on SnS₂ in a 5×5×1 supercell, in which the clean surface of SnS₂ is utilized as the reference. The Fermi level (0 eV along the energy scale) is aligned to that of SnS₂ clean surface (E_F) and the total eDOS is also scaled, so that the shape of the DOS can be visible on the same axis as the projected eDOS results.

Figure 5. Physisorption based charge transfer in 2D SnS₂ flakes upon NO₂ gas exposure. a. Raman spectra of 2D SnS₂ flakes before and after NO₂ gas exposure at 120°C. The corresponding intensity ratio of A_{1g} and E_g modes is shown in the inset. The error bar represents the standard deviation based on the analysis of 100 samples; **b.** PL spectra of 2D SnS₂ flakes before and after NO₂ gas exposure at 120°C.

ToC Figure