Photo-enhanced gas sensing of SnS2 with nanoscale defects†

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Recently a SnS2 based NO2 gas sensor with a 30 ppb detection limit was demonstrated but this required high operation temperatures. Concurrently, SnS2 grown by chemical vapor deposition is known to naturally contain nanoscale defects, which could be exploited. Here, we significantly enhance the performance of a NO2 gas sensor based on SnS2 with nanoscale defects by photon illumination, and a detection limit of 2.5 ppb is achieved at room temperature. Using a classical Langmuir model and density functional theory simulations, we show S vacancies work as additional adsorption sites with fast adsorption times, higher adsorption energies, and an order of magnitude higher resistance change compared with pristine SnS2. More interestingly, when electron–hole pairs are excited by photon illumination, the average adsorption time first increases and then decreases with NO2 concentration, while the average desorption time always decreases with NO2 concentration. Our results give a deep understanding of photo-enhanced gas sensing of SnS2 with nanoscale defects, and thus open an interesting window for the design of high performance gas sensing devices based on 2D materials.

Nitrogen dioxide (NO2) is one of the most common hazardous gas pollutants produced as a by-product of industry. 1,4,6 Notably, NO2 is also a product yielded from the thermal decomposition of organic nitrates, such as TNT, which is a useful fingerprint for controlling these substances and combating international terrorism. 5 An issue of global concern, serious respiratory diseases can be caused by chronic environmental exposure to as little as 53 ppb NO2. 1,4,6 Therefore, the research and development of gas sensors with high sensitivities is always of high priority. 2,7–19 Recently, 2D materials have been used for gas sensing owing to their large surface-to-volume ratios. 13,20 A wide variety of 2D materials, such as graphene, 9,10,14 black phosphorus, 2,22 metal dichalcogenides, 4,12,15,18,19,22–24 have been studied as high performance gas sensors. 16,20,23,25,26

As a member of the wide class 2D materials, tin disulfide (SnS2) displays many intriguing properties in electronics, 2,21 photonics and optoelectronics, 27–29 as well as gas monitoring. 24,26–42 It was reported recently by Kalantar-zadeh et al. that a SnS2-based NO2 gas sensor with a sensitivity of 0.5 ppm could be improved to 30 ppb when heated to 120 °C. 24 However, an elevated operating temperature typically increases power consumption and thus a more intricate setup is required. 1,10,16,20,24,27,43 Furthermore, the high operating temperature might pose the risk of ignition when detecting in flammable or explosive atmospheres which would limit sensor’s application. 41–46 Concurrently, it is known that 2D materials produced by chemical vapor deposition (CVD) usually contain nanoscale defects, such as vacancies, grain boundaries, etc. and in particular CVD grown SnS2 is reported to naturally contain S vacancies. 47 It is well known that nanoscale defects can significantly affect gas sensing performance. 48 Thus it is important to investigate how S vacancies in SnS2 affect the gas sensing performance. Furthermore, it should be also noted that compared with thermally assisted gas sensing, a photon assisted arrangement can not only improve the detection limit of gas sensor but also can accelerate the desorption ratio. 15,19,49–51 It is reported that SnS2 nanosheets exhibit excellent optoelectronics properties, 27–30 making it feasible to improve the gas sensing performance of SnS2 with photon illumination.
In this work, we demonstrate that photon illumination can significantly enhance the performance of NO$_2$ gas sensors based on SnS$_2$, and an ultra-low concentration sensitivity of 2.5 ppb is achieved at room temperature. The results also show that gas sensitivity increases linearly with decreasing SnS$_2$ nanosheet thickness. In combination with a classical Langmuir model and density functional theory simulations, we show that S vacancies also characterized by Raman spectroscopy, as shown in Fig. 2(a). Only a single Raman peak (A$_{1g}$ mode at 314 cm$^{-1}$) can be clearly observed for an 8 nm thick SnS$_2$ nanosheet, and an additional Raman peak, the E$_g$ mode at 205 cm$^{-1}$, appears for a thicker 60 nm SnS$_2$ nanosheet, which is consistent with literature.\cite{28,32} The E$_g$ mode is due to the scattering centers for in-plane scattering. When the thickness drops below 8 nm the intensity decreases and effectively becomes undetectable.\cite{29} The crystal structure of few-layer SnS$_2$ was further characterized by high-resolution transmission electronic microscopy (HRTEM), indicating the single-crystalline structure of the SnS$_2$ (Fig. 2(c)).

Fig. 1(a) shows a schematic of the chemical vapor deposition (CVD) arrangement for the SnS$_2$ nanosheet growth. A sulfur powder source was placed upstream in the furnace. Sn granules were smashed into pieces and were placed at the center of the furnace. Several pieces of a diced 300 nm SiO$_2$/Si (1 cm $\times$ 1 cm) wafer were placed downstream as substrates for SnS$_2$ growth. Further details of the SnS$_2$ growth can be found in the Experimental section. After the reaction, SnS$_2$ nanosheets were formed on the SiO$_2$/Si substrates. Fig. 1(b) shows a scanning electron microscopy (SEM) image of a SnS$_2$ flake grown on a SiO$_2$/Si substrate. The flakes typically have a semi-hexagonal structure with lateral dimensions ranging from 10 $\mu$m to 228 $\mu$m (Fig. S1$^\dagger$). Fig. 1(c) gives the structure of SnS$_2$ with the purple and yellow spheres representing Sn and S atoms, respectively.

Atomic force microscopy (AFM) was used to determine the thicknesses of the nanosheets. Fig. 2(a) shows the height profile of an ultrathin SnS$_2$ nanosheet with a thickness $\approx$ 6 nm ($\approx$ 10 layers, 0.6 nm per layer), as measured along the red dotted line in the inset image, (more examples in Fig. S2$^\dagger$). The SnS$_2$ was also characterized by Raman spectroscopy, as shown in Fig. 2(b). The 2D Raman peak of pure SnS$_2$ at 285 cm$^{-1}$ can be clearly observed at 13 ppb NO$_2$. To confirm this, Fig. 4(d) plotted $I_{DS}$-$V_{DS}$ curves of the same device under

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**Fig. 1** (a) A schematic of CVD growth setup. (b) A SEM image of a semi-hexagonal nanosheet of SnS$_2$. (c) Schematic of SnS$_2$ structure with purple and yellow spheres representing Sn and S atoms, respectively.

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different NO₂ concentrations. It is apparent that in the dark environment, the \( I_{DS}-V_{DS} \) curves for 0 ppb, 26 ppb and 52 ppb NO₂ merge together. In contrast with this, clear distinctions can be observed between 0 ppb, 26 ppb and 52 ppb NO₂ with 405 nm laser illumination. A similar effect was observed with 650 nm (26 ppb) and 785 nm (52 ppb) lasers (Fig. S3†). Thus, laser illumination can improve the gas sensing capabilities of such devices.

The stability of a sensor is critical for practical applications. Multi-cycle dynamic sensing responses of the SnS₂-based sensor against to 13, 39 and 78 ppb NO₂ are used here to demonstrate the good repeatability and reproducibility of such SnS₂-based sensors (Fig. 4(e)). Moreover, the response to varied concentrations of NO₂ with a relative humidity 64% is also shown in Fig. S5(d).† These indicate the reliability of the illuminated SnS₂-based sensor and that the presence of water does not degrade performance.

To probe the function of sensitivity versus the thickness of SnS₂, we also tested more than 10 samples with different thicknesses, ranging from 17 nm to 370 nm (Fig. S4–S9†). It is found that the sensitivity increases linearly as the thickness of the SnS₂-nanosheets is reduced, as shown in Fig. 4(f). Remarkably, a significant response is unmistakably observed at 2.5 ppb NO₂ for a 22 nm thick SnS₂ based gas sensor (Fig. S8(d)†), suggesting that SnS₂ based gas sensor can achieve a NO₂ detection limit better than 2.5 ppb. To the best of our knowledge, this is the lowest detection limit for NO₂ achieved using SnS₂ devices to date, which is an improvement by a factor greater than ten on previous work.24 Table 1 summarizes and compares the important features of SnS₂-based NO₂ gas sensors from literature. Kalantar-zadeh et al. heated their SnS₂ flake sensor to 120 °C to achieve a 30 ppb detection limit.24 Hao et al. heated a SnS₂ flower interspersed with SnO₂ to 100 °C to reach a 125 ppb detection limit.31 Ahn et al. built utilized vertical SnS₂ flake structures to detect NO₂ at 300 ppb, probably under its optimum conditions at 160 °C.32 Li et al. heated SnS₂ their flake devices to 120 °C to attain a 600 ppb detection limit.40 Wang et al. heated a SnS₂–SnO₂ composite flake device to 80 °C for

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**Fig. 2** Characterization of CVD produced single crystal SnS₂ nanosheet. (a) Height profiles of the dashed line shown in the inset AFM image. (b) Raman spectra of SnS₂ nanosheet. (c) High-resolution TEM image and corresponding (d) selected-area-electron-diffraction (SAED) pattern of a typical grown SnS₂ flake. (e) Low magnification bright field TEM image of a semi-hexagonal SnS₂ nanosheet. (f) EELS elemental mapping of the selected area in (e) with the result Sn : S = 1 : 1.86.
a 1000 ppb detection limit. While Xue et al. used SnS$_{1.5}$/Se$_{0.5}$ flake devices to detect 1000 ppb NO$_2$ at room temperature.

To better illustrate the photo-enhanced gas sensing properties, we summarized the signal/noise (S/N) ratios of the $R/R_0$ from response in Fig. 4(b and c) into Fig. 5(a). It is clear that there are 3 distinct regions. At high concentrations of NO$_2$ the S/N is almost constant (dark and 785 nm). This means the surface adsorption is almost saturated and has reached its upper limit. Increasing gas concentration does not increase the signal. In the medium concentration range (classic region), S/N increases linearly with gas concentration. In the low NO$_2$ concentration regime (<52 ppb) no effective signal is detected for dark conditions. But a signal is detected with illumination, which is especially prominent for the short wavelength light, indicating extra energy is required to desorb NO$_2$ from surface of SnS$_2$.

We fitted the desorption (adsorption) sections of the dynamic-sensing response curves under different laser illuminations with the expression $y = y_0 + Ae^{t/d}$ ($y = y_0 + Ae^{t/s}$), where $t_d$ ($t_a$) is the average desorption (adsorption) time. The average desorption times and average adsorption times under various laser illuminations are summarized in Fig. 5(b) and (c) respectively. It is clear illumination not only enables ultra-high sensitivity but also results in faster desorption and better S/N ratios. Interestingly, with the 405 nm laser illumination, the adsorption time first increases and then decreases with gas concentration when the concentration reaches ~78 ppb. While for dark and 785 nm laser illumination, both the desorption and adsorption times decrease with increasing gas concentration.
We replotted the dynamic-sensing response curves under 405 nm laser illumination based on the Langmuir model (Fig. 6). There are two classes of adsorption sites. Similar behavior has been observed under 785 nm and 650 nm laser illumination (Fig. S10†). For the adsorption process, NO₂ can adsorb on both sites but prefer sites with fast adsorption times. With increasing gas concentration, more NO₂ molecules will be adsorbed on sites with slower adsorption times which increases the average adsorption time. At yet higher gas concentrations all the fast adsorption time sites will be occupied. The NO₂

![Image](https://example.com/image)

**Fig. 4** (a) Optical microscope image of a SnS₂ device for gas sensor measurements. Dynamic sensing response of $\Delta R/R_0$ change versus time for the SnS₂-based sensor upon exposure to NO₂ gas with concentrations ranging from 6.5 ppb to 130 ppb under (b) dark environment and (c) 405 nm laser irradiation. (d) Comparison $I_{DS}$–$V_{DS}$ curves of the device under different light illuminations and NO₂ concentrations. (e) Multi-cycle responses of sensor when exposed to concentrations of 13, 39, and 78 ppb NO₂. (f) Sensitivity as a function of SnS₂ thickness.

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<table>
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<th>Reference</th>
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<td>UV illumination</td>
<td>This work</td>
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<td>SnS₂/Se₃</td>
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molecules will be adsorbed on the sites with slow adsorption times, which can be treated as one site adsorption. According to the Langmuir model considering one adsorption site, 

\[ \tau_D = \frac{1}{aN_c} \]

where \( N_c \) is proportional to the gas concentration. This is why the average adsorption time first increases and then decreases with gas concentration. On the other hand, for the desorption process at low concentrations it is the sites with slow desorption times that are the limiting factor. With increasing gas concentration, more molecules will be desorbed from the sites with faster desorption times, thus decreasing the average desorption time. Moreover, NO\(_2\) molecules absorb on sites with faster adsorption times will significantly decrease the overall conductance compared with NO\(_2\) molecules bound to sites with slow adsorption.

To investigate whether S vacancies could give such an effect, we calculated the adsorption energy, charge density distribution, and conductance of NO\(_2\) molecules on a SnS\(_2\) monolayer with and without S vacancies. Details of the calculations can be found in the Methods section. Fig. 7(a) and (b) show the optimized atomic structures of a NO\(_2\) molecule adsorbed on pristine SnS\(_2\) and SnS\(_2\) with a surface S vacancy respectively. For a NO\(_2\) molecule adsorbed on pristine SnS\(_2\), the perpendicular distance between the O atom of a NO\(_2\) molecule and the nearest S atom of the SnS\(_2\) (\( R \)) is about 2.95 Å and it is decreased significantly to 0.5 Å for a NO\(_2\) molecule on SnS\(_2\) with a S vacancy, indicating the S vacancy induces strong adsorption between SnS\(_2\) and NO\(_2\). To understand the adsorption mechanism, the adsorption energy as a function of distance \( R \) is plotted in Fig. 7(c). The adsorption energy is 1.011 eV when a NO\(_2\) molecule adsorbed on SnS\(_2\) with a S vacancy. While for a NO\(_2\) molecule adsorbed on pristine SnS\(_2\), the corresponding adsorption energy is only 116 meV. Thus, NO\(_2\) molecules adsorbed on the SnS\(_2\) monolayer with S vacancies have a larger adsorption energy compared with a pristine SnS\(_2\) monolayer, indicating that extra energy is required to desorb NO\(_2\) molecule from the S vacancy site (Fig. 7(d)). The adsorption energy for chemisorption is usually an energy of 1–10 eV, but for physisorption the energy is smaller than this. Therefore, the adsorption mechanism may change from physisorption to chemisorption when a NO\(_2\) molecule adsorbed on SnS\(_2\) with a S vacancy. Moreover, there is a large partial charge transfer between S and the O atoms of a NO\(_2\) molecule adsorbed on SnS\(_2\) with S vacancy in Fig. 7(e) and (f).

The electrical conductivity of an NO\(_2\) molecule adsorbed on pristine SnS\(_2\) and on SnS\(_2\) with a single S vacancy at 300 K are shown in Fig. 8. We found that monolayer SnS\(_2\) contains a narrow electrical conductivity tail near \( \mu = 0 \) resulting from electrons crossing the Fermi level from thermal agitation at \( T = 300 \) K, shown in Fig. 8(a). When this pristine SnS\(_2\) adsorbs an NO\(_2\) molecule there is an additional conductivity peak region near \( \mu = 0 \) with small values of \( 1.1 \times 10^3 \) and \( 3.0 \times 10^5 \) (1/Ω m\(^{-1}\)) for \( \sigma_{xx} \) and \( \sigma_{yy} \), respectively, as shown in Fig. 8(b). However for SnS\(_2\) with a S vacancy adsorbing a NO\(_2\) molecule, there is a broad additional conductivity region around \( \mu = 0 \) with values about \( 1.5 \times 10^4 \) and \( 1.9 \times 10^4 \) (1/Ω m\(^{-1}\)) for \( \sigma_{xx} \) and \( \sigma_{yy} \), respectively, shown in Fig. 8(c). These results from transport and DFT analysis are consistent with the experimental conclusions on the resistance changes, and also indicate charge transfer between NO\(_2\) and SnS\(_2\) is critical. It also suggests that the sites with fast adsorption times are S vacancies and the sites with slow adsorption times are the areas of pristine SnS\(_2\). To
The $\frac{dI}{dt} - I$ relationship of Fig. 4(c). (a) The $\frac{dI}{dt} - I$ curve of 17.5 ppb NO$_2$ test. (b) The $\frac{dI}{dt} - I$ curve of 54 ppb NO$_2$ test. In both of two picture, the fitting lines are shown, with blue line depicting the fast desorption process, violet line depicting slow desorption process, red line depicting fast adsorption process and green line depicting slow adsorption process.

(a) and (b) Side view and top view of the atomic structure of NO$_2$ molecule adsorbed on Sn$_9$S$_{18}$ and Sn$_9$S$_{17}$ surfaces, respectively. The large dark spheres represents Sn atoms, while the yellow, blue and red spheres represent the S, N and O atoms, respectively. (c) Adsorption energy as a function of distance $R$ (defined as the perpendicular distance between the O atom of NO$_2$ molecule and the nearest S atom of the Sn$_9$S$_2$) for NO$_2$ molecule adsorbed on Sn$_9$S$_{18}$ and Sn$_9$S$_{17}$ surfaces. (d) Schematic of adsorption energies for an NO$_2$ molecule adsorbed on pristine SnS$_2$ and on SnS$_2$ with a S vacancy. (e) and (f) Charge density difference distribution for NO$_2$ molecule adsorbed on Sn$_9$S$_{18}$ and Sn$_9$S$_{17}$ surfaces, respectively. The charge density difference in yellow indicate increases in charge density, while blue indicates a decrease in charge density (isosurface $= 0.0015$ eV Å$^{-3}$).
further highlight the importance of S vacancies for the gas sensor performance, we measured the gas performance of gas sensors based on same thick SnS$_2$ but with different S vacancy density, where the density of S vacancies was determined by mapping the whole sensor using the EDS equipped in the SEM chamber. A relatively low detection limit or high gas performance was achieved for the sample with higher S vacancy density. For example, for gas sensors based on 106 nm thick SnS$_2$, the detection limit for sensor with an atomic ratio of Sn : S = 1 : 1.72 is 6.5 ppb and that for sensor with an atomic ratio of Sn : S = 1 : 1.84 is 13 ppb. We would like to stress that the nanoscale defects are naturally occurring defects forming during chemical vapor deposition. Therefore, they are quite stable when interacting with NO$_2$ molecules.

It is reported that Schottky junction$^{59,60}$ and photo-excited electron–hole pairs can contribute the gas sensing performance. Since our gas sensing performance depends crucially on the wavelength of the photons and same bias voltage is used, here we focus our discussion on effect due to photo-excited electron–hole pairs. We measured the gas sensing performance of another sensor under 365, 405, and 650 nm laser illuminations (Fig. S11†). Only 365 and 405 nm lasers can excite electron–hole pairs, because the band gap of SnS$_2$ is around 2.2 eV. The 365 and 405 nm laser illuminations have similar detection limit, better than 650 nm. More importantly, the average adsorption time first increases and then decreases with NO$_2$ concentration under the 365 and 405 nm laser illuminations, indicating the importance of photo-excited electron–hole pairs for the charge transfer process upon NO$_2$ adsorption. Therefore, the observed distinct behavior of the adsorption time may be due to the photo-excited electron–hole pairs. We would like to stress that the average adsorption time is faster under the 405 nm photo illumination than the 365 nm, indicating that the 405 nm laser illumination is more efficient since the adsorption spectrum of NO$_2$ peaks at ~400 nm at 293 K.$^{41}$

In summary, NO$_2$ gas sensors were fabricated based on CVD grown SnS$_2$. An ultra-high sensitivity of 2.5 ppb at room temperature was achieved by utilizing inherent defects under photon illumination. Our results further show S vacancies in SnS$_2$ work as additional adsorption sites and the detection limit, signal to noise (S/N) value, and desorption time can be significantly improved by photo illumination, thus providing a plausible way to design high performance gas sensors based on 2D materials with nanoscale defects.

Method

The detailed experiments and characterizations are shown in the ESL†

Author contributions

H. C. W. conceived the study. D. Y. C., and Y. L. L. grew the sample. W. J. Y., H. J. X. and Z. W. fabricated the sample. J. C., M. C., and B. S. C. carried out the TEM measurements. W. J. Y. and C. C. performed the gas sensing measurements. H. R. F. and C. R. C. conducted the DFT simulation. Z. T. J. and H. J. L. gave scientific advice. H. C. W., W. J. Y., D. Y. C., and C. C. wrote the manuscript. All authors discussed the results and commented on the manuscript.

Conflicts of interest

There no conflicts to declare.

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