

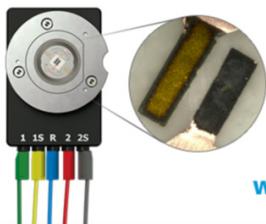
OPEN ACCESS

Enhancement in the Selectivity and Sensitivity of Ni and Pd Functionalized MoS₂ Toxic Gas Sensors

To cite this article: Levna Chacko *et al* 2020 *J. Electrochem. Soc.* **167** 106506

View the [article online](#) for updates and enhancements.

Visualize the processes inside your battery!
Discover the new ECC-Opto-10 and PAT-Cell-Opto-10 test cells!



- Battery test cells for optical characterization
- High cycling stability, advanced cell design for easy handling
- For light microscopy and Raman spectroscopy

www.el-cell.com +49 (0) 40 79012 734 sales@el-cell.com

EL-CELL[®]
electrochemical test equipment





Enhancement in the Selectivity and Sensitivity of Ni and Pd Functionalized MoS₂ Toxic Gas Sensors

Levna Chacko,¹ Ettore Massera,² and P. M. Aneesh^{1,*} 

¹Department of Physics, Central University of Kerala, Tejaswini Hills, Periyar, Kasaragod, Kerala 671316, India

²ENEA Research Centre, 80055 Portici, Italy

Atmospheric pollution is one of the major aspects of concern which led to the research of sensors for the detection of toxic gases. The supreme surface-to-volume ratio makes two-dimensional MoS₂ a promising material to be used as an electronic sensor. Here, we demonstrate the fabrication of a high-performance gas sensor based on atomic-layered MoS₂ nanoflakes synthesized by a facile hydrothermal process. Structural and morphological studies confirmed the formation of few-layered phase pure hexagonal MoS₂ nanoflakes. The results demonstrate that the Pd-MoS₂ layers exhibited a very high relative response to NO gas (700%) at 2 ppm concentration with a minimum NO detection limit of 0.1 ppm and Ni-MoS₂ demonstrated a relative response of 80% towards H₂S gas with a limit of detection of 0.3 ppm with good repeatability and selectivity, owing to the increased adsorption energy of NO on Pd-MoS₂ and H₂S on Ni-MoS₂ through the formation of PdNO_x and NiS₂ complexes respectively. The improved sensing performance of this MoS₂-based sensor also suggests the great potential and possibility of MoS₂ related 2D materials and its combinations for the development of futuristic highly sensitive nanosized gas sensors suitable for anti-pollution automotive system and as volatile biomarkers.

© 2020 The Author(s). Published on behalf of The Electrochemical Society by IOP Publishing Limited. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, <http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/1945-7111/ab992c]



Manuscript submitted March 23, 2020; revised manuscript received May 13, 2020. Published June 12, 2020. *This paper is part of the JES Focus Issue on 2D Layered Materials: From Fundamental Science to Applications.*

In the present scenario, detection and monitoring of toxic gases leading to tremendous deterioration of atmospheric environment as a result of industrial and automobile exhausts, increased population, combustion of fossil fuels, excessive use of chemicals in scientific, industrial and agricultural fields, explosives are of great demand for environmental and national security and for a sustainable biosphere. Researchers have studied on a variety of materials such as organic materials (polymers, porphyrins)^{1,2} metal-oxides,³ carbon nanotubes,⁴ graphene and based-oxides^{5,6} for the sensing of toxic gases such as NH₃, NO₂, NO, SO₂, CO, CO₂, organic vapors etc. NO, being one of the common and toxic air pollutants from automobile exhausts, combustion of fossil fuels, home heaters, furnace exhausts, arc welding, electroplating and power plants. On reaction with chemicals produced from sunlight, NO forms nitric acid which is a major constituent of acid rain and it also leads to the formation of ozone, smog etc. When inhaled by human beings, NO causes severe damage to human respiratory organs and nerves. Apart from this, NO is an abundant and signaling molecule produced in human body having many pathophysiological roles and is detected in the exhaled breaths of humans. The variations in the NO exhalation profile are a significant tool for understanding the normal and diseased functioning of lung and serves as a biomarker for lung diseases and pulmonary inflammations such as bronchial asthma.^{7,8} Similarly, H₂S is also identified as an endogenous mediator in human body. Morselli-Labate et al.⁹ demonstrated the presence of higher levels of H₂S and NO in the exhaled breaths of chronic pancreatitis.

Currently, owing to the unique physical, chemical, optical and electrical properties, two-dimensional (2D) layered nanomaterials show intriguing prospects for sensor application. Inspired by the enhanced performance of graphene and graphene-based nanomaterials for gas sensing applications because of their high sensitivity, large specific surface area, fast electron transport kinetics and strong surface activities led to increased research efforts on other graphene analogues for efficient and enhanced gas sensing. Also, the main drawbacks of metal oxide-based sensors such as the requirement of high operating temperatures, the easiness to get poisoned under sulfur atmosphere, long recovery periods, limited maximum sensitivity etc. stimulated an extensive research for highly sensitive and portable sensors that require low operating temperatures.

Two-dimensional (2D) layered material, MoS₂ have aroused great research interest as a promising gas sensing material due to their high surface-to-volume ratio, high surface activities and sensitivities, fast response time and good stability.¹⁰⁻¹³ Especially, the semiconducting nature of MoS₂ with suitable and tunable band gap energies has made it more desirable than graphene-based gas sensors.¹⁴⁻¹⁷

The direct band gap of MoS₂ is being considerably exploited and extensive theoretical and experimental research investigations are performed on the fabrication of MoS₂ nanodevices. Apart from these, the high surface-to-area ratio of 2D MoS₂ provides new avenues making MoS₂ and its various combinations as excellent sensing materials to various analytes such as NH₃, NO₂, H₂S, NO, humidity, SO₂, H₂ etc. and has been demonstrated by several research groups.¹⁸⁻²⁴ Yue et al. investigated the adsorption of a wide range of gas molecules such as H₂, O₂, H₂O, NH₃, NO, NO₂ and CO on monolayer MoS₂ using first-principles calculations. They also studied the effect of charge transfer mechanism between the adsorbed molecule and MoS₂ on the application of an external electric field.²⁵ In order to completely actualize the gas sensing capability of MoS₂, Zhao and co-workers demonstrated the adsorption of various gas molecules including CO, CO₂, NH₃, NO, NO₂, CH₄, H₂O, N₂, O₂ and SO₂ employing the first-principles calculations. It was found that the binding of NO, NO₂ and SO₂ with MoS₂ is the strongest among the other gas molecules.¹⁹ In another report Li et al. fabricated MoS₂ FET devices consisting of single and multilayer MoS₂ films to detect the adsorption of NO and it was found that the multilayer films exhibited high sensitivity to NO with a detection limit of 0.8 ppm.²⁶ Apart from these, several research works were also performed on MoS₂-based bio and DNA sensors,²⁷⁻²⁹ that find potential application as cancer biomarkers.^{30,31}

Being a widely studied material for gas sensing applications, ZnO possess large specific surface area, high carrier mobility, non-toxicity, good electrochemical stability etc.³¹ Also our earlier report on MoS₂-ZnO has already demonstrated its bio-activity presenting as an effective agent for anti-angiogenesis and anti-cancer theranostics.³² Moreover, several reports suggest the capability of Pd and Ni to adsorb certain molecules and form complexes leading to improved selectivity. Based on first principle calculations Wei et al.³³ have reported the interaction of H₂S and SO₂ molecule with Ni-MoS₂ surface by strong adsorption energy and has been proposed as a novel gas adsorbent to be used in SF₆-insulated equipment. Reports also suggests the ability of Pd to form complexes such as the

*E-mail: aneeshp@cuks.ac.in

hydrogen sensing performance of Pd functionalised MoS₂ by forming change in the work function of Pd upon transforming to PdH_x.³⁴ In this study, different MoS₂-based such as pure MoS₂, MoS₂-ZnO, MoS₂-Ni and MoS₂-Pd sensor devices were fabricated. The gas sensing characteristics and mechanisms of these sensors on exposure to NO, NO₂, NH₃ and H₂S gases were analyzed and their selectivity, sensitivity and repeatability were assessed. The enhanced response of Pd-MoS₂ and Ni-MoS₂ sensors towards NO and H₂S gases respectively can be exploited for application as both automobile pollution control system and as volatile biomarkers.

Experimental

MoS₂ nanoflakes were synthesized by simple hydrothermal method as mentioned in our earlier report³⁵ using sodium molybdate dihydrate (Na₂MoO₄·2H₂O) and thiourea (CH₄N₂S) as precursor materials at a growth temperature of 200 °C for 12 h. Exfoliated flakes of MoS₂ for the device fabrication were obtained by sonicating a 2 mg ml⁻¹ solution of the as-synthesized MoS₂ powder in iso-propanol for 3 h. Stoichiometric amounts of nickel acetate dehydrate (Ni(CH₃COOH)₂·H₂O), dichlorobis(triphenylphosphine) palladium(II), and ZnO nanoparticles were added into MoS₂ to obtain MoS₂-Ni, MoS₂-Pd and MoS₂-ZnO nanostructures.

The architecture of the fabricated sensor is depicted in Fig. 1. Sensing devices were fabricated on a single side polished n-type, (1 0 0) orientation, (1–100) Ωcm resistivity silicon wafer. The wafer was cleaned by RCA (Radio Corporation of America) method to remove the organic contaminants, native oxides and metallic contaminants. 1 μm SiO₂ layer was grown on Si wafer using thermal oxidation method. This was coated with AZ5214E image reversal positive photoresist and the patterning was carried out using MJB4 optical lithography unit. Patterns were developed in MF26A solution. Sensing electrodes, 20 nm chromium and 100 nm gold, were deposited by sputtering technique. Finally, the wafer was subjected to lift-off in acetone, cleaning by IPA and drying under N₂ to get the patterned device structure. A few-layer MoS₂ flakes for the active channel were exfoliated using a conventional ultrasonication method and then transferred them onto a SiO₂/Si substrate by drop-casting. The gas response of different MoS₂-based sensors was measured using two-probe measurement system in synthetic air environment. The sensing performance of the sensors with and without exposure to various toxic gases such as NH₃, H₂S, NO and NO₂ were measured at room temperature with a bias voltage of 1 V.

X-ray diffraction (XRD) characterization with Cu Kα₁ radiation (λ = 1.5406 Å) using Rigaku MiniFlex 600 diffractometer was employed to analyze the crystalline structure and phase purity of nanostructured MoS₂ samples. Horiba JOBIN YVON LabRAM HR Raman Spectrometer equipped with 514.5 nm Ar-ion laser as the excitation source was used for Raman studies. Field emission scanning electron microscopy (FE-SEM ΣIGMA, ZIESS) was used in order to investigate the surface morphology of

nanostructured MoS₂. The current–voltage (I-V) characteristics of the device were measured using Agilent Technologies B1500A semiconductor device analyser. A two-electrode configuration was employed for the sensing measurements. The sensitivity of the sensor was monitored by applying a constant bias voltage of 1 V on the sensor and recording the variation in the current using Keithley 237 high voltage source measure unit. Prior to the measurements, the gas chamber was purged with synthetic gas. After a constant current was observed, the sensor was exposed to various analytes.

Results and Discussion

The crystalline structure, phase, purity and morphology of the MoS₂ nanostructure were investigated through X-ray diffraction (XRD), Raman analysis and field emission scanning electron microscopic (FESEM) images. The XRD pattern of MoS₂, MoS₂-Pd, MoS₂-Ni and MoS₂-ZnO nanostructures synthesized by hydrothermal method is shown in Fig. 2a. It is obvious that that all the diffraction peaks of MoS₂ and MoS₂-Ni can be indexed to hexagonal phase of crystalline MoS₂ without the presence of any secondary phases. The diffractograms of MoS₂-ZnO and MoS₂-Pd consists of planes corresponding to ZnO and Pd in addition to MoS₂ peaks. The distinct peak at (0 0 2) orientation of MoS₂ represents the well-ordered stacking of S-Mo-S layers.^{36,37} The calculated grain size and lattice parameters of the nanostructures are represented in Table I. The Raman shift between the two characteristic peaks, E_{2g}¹ and A_{1g}, representing in-plane and out-of-plane vibration modes respectively, indicates the presence of few-layer MoS₂ and is shown in Fig. 2b.^{38,39} The in-plane E_{2g}¹ mode originates from opposite vibration of two S atoms with respect to the Mo atom while the A_{1g} mode represents the out-of-plane vibration of only S atoms in opposite directions.⁴⁰ Also, in a report, Agrawal et al.⁴¹ have reported that the terrace sites favor the formation of E_{2g}¹ mode, whereas A_{1g} mode is preferred by the edges of MoS₂ and the increase in the intensity of A_{1g} mode represents the increased density of the edge-enriched MoS₂ flakes. The frequency difference between E_{2g}¹ and A_{1g} peaks can be attributed to the mixed signal from different layered structure of MoS₂ nanoflakes.⁴¹ Thus, the observed frequency shift in MoS₂-ZnO, MoS₂-Ni and MoS₂-Pd Raman peaks

Table I. Grain size and lattice parameters of MoS₂, MoS₂-ZnO, MoS₂-Ni and MoS₂-Pd nanostructures synthesized by hydrothermal method.

Sample	Grain Size (nm)	Lattice Parameters (Å)	
		a	c
MoS ₂	5	3.12	12.63
MoS ₂ -ZnO	6	3.12	12.74
MoS ₂ -Ni	6	3.12	12.84
MoS ₂ -Pd	6	3.12	12.70

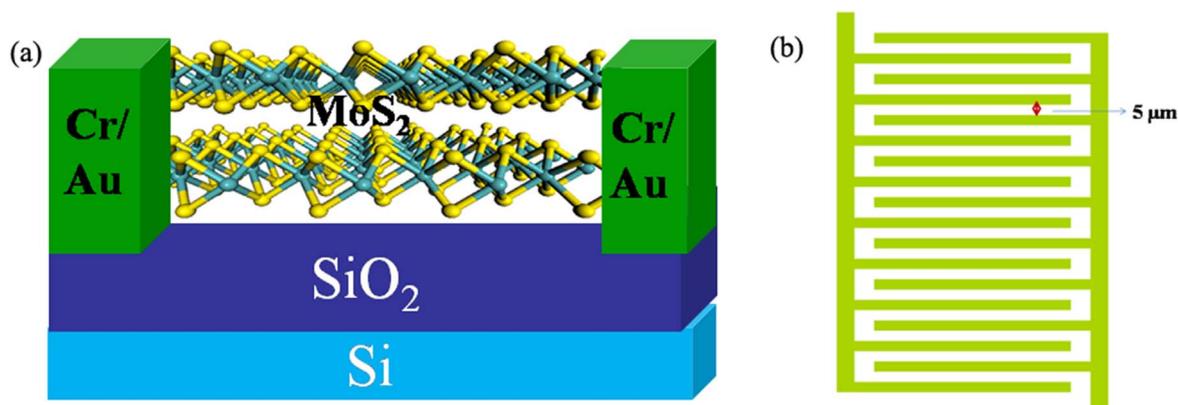


Figure 1. (a) Architecture of MoS₂-based sensing device, (b) Pattern of Cr/Au electrodes used in the sensor device.

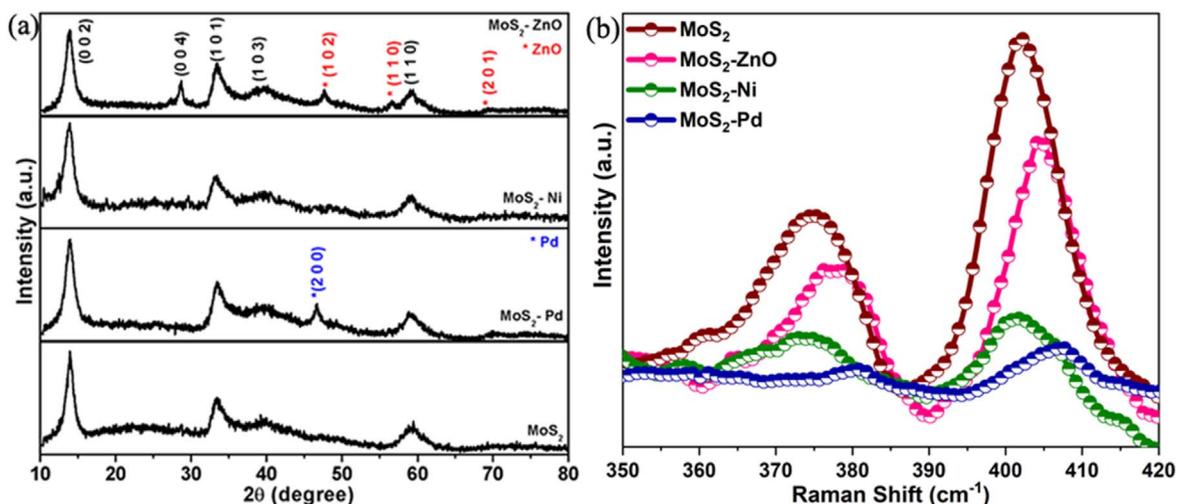


Figure 2. (a) XRD pattern and (b) Raman spectra of MoS₂, MoS₂-Pd, MoS₂-Ni and MoS₂-ZnO nanostructures.

can be ascribed to some structural changes and long-range Coulomb interaction in addition to the van der Waals interlayer coupling during functionalization.⁴²

The morphology of the as-prepared MoS₂, MoS₂-ZnO, MoS₂-Ni and MoS₂-Pd nanostructures were identified from FESEM (Fig. 3) showing uniform curly-like structure assembled into the nanoflakes, indicating that the samples have large specific surface areas. Presence of ZnO nanoparticles is also visible along with MoS₂ nanoflakes in the MoS₂-ZnO morphology (Fig. 3c), whereas, closely aggregated nanoflakes like structures are observed in the MoS₂-Pd morphology (Fig. 3d).

Energy dispersive X-ray (EDS) measurement of the samples was performed to identify the chemical composition and is shown in Fig. 4. Presence of Ni, Zn, O and Pd were observed supporting the formation of MoS₂-Ni, MoS₂-ZnO and MoS₂-Pd nanosystems.

In order to identify the suitability of MoS₂ and other nanostructures for the sensing applications, the I-V characteristic of the device without the presence of sensing gas was studied by two probe method and is shown in Fig. 5. The linear characteristics of the I-V curve confirm the ohmic nature of the contact with a resistance of the order of 176 Ω, 202 Ω, 210 Ω and 227 Ω for MoS₂, Ni- MoS₂, Pd-MoS₂ and MoS₂- ZnO nanostructures. Compared to other systems,

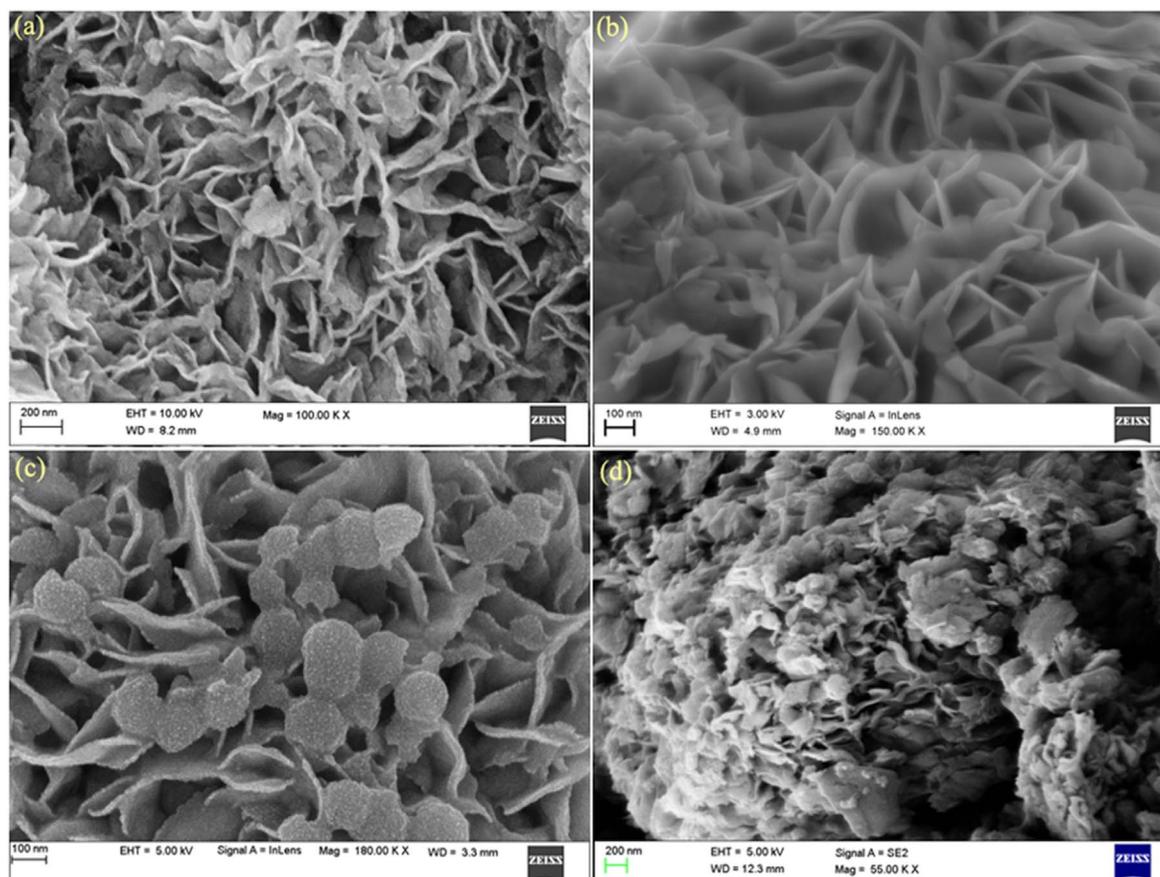


Figure 3. FESEM images of (a) MoS₂ (b) Ni-MoS₂ (c) MoS₂-ZnO and (d) Pd-MoS₂ nanostructures.

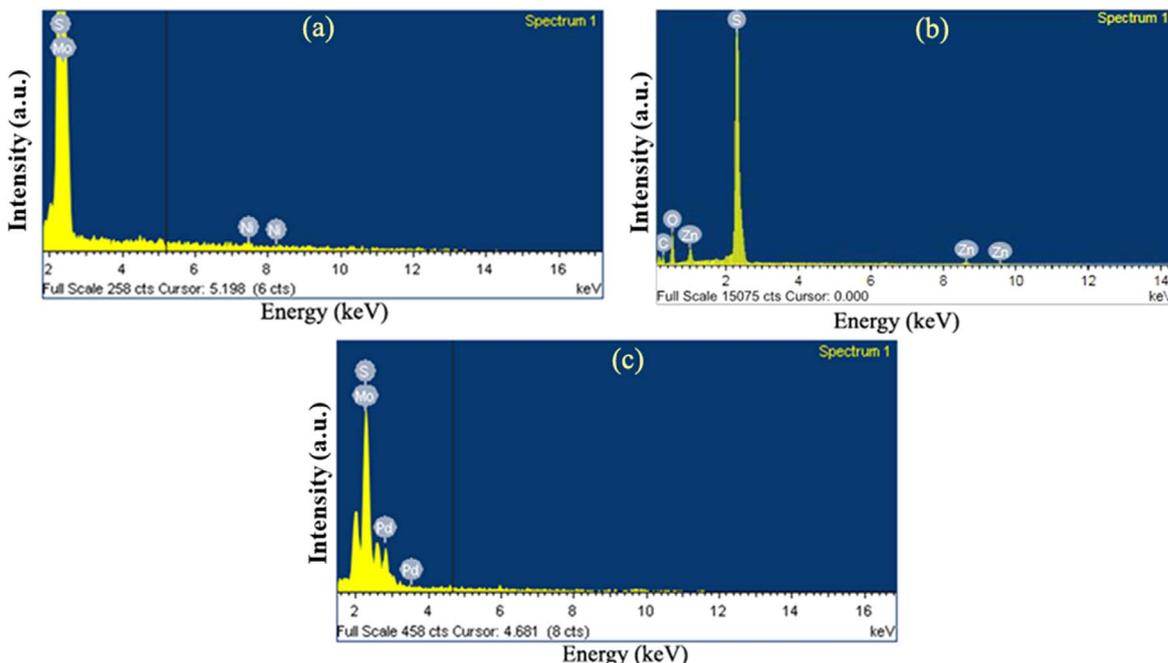


Figure 4. EDS spectra of (a) Ni-MoS₂ (b) MoS₂-ZnO and (c) Pd-MoS₂ nanostructures.

Pd-MoS₂ nanostructures are exhibiting a small forward current under light illumination (resistance of 198 Ω) representing the photoresponsive nature due to formation of more electron-hole pairs upon light illumination.

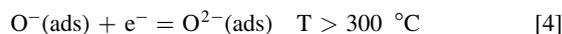
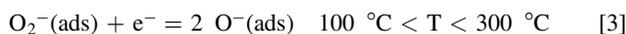
Gas sensing properties of pure MoS₂, Ni and Pd functionalized MoS₂ and MoS₂-ZnO nanocomposite sensor upon exposure to various gases were investigated using two-probe measurement system at room temperature with a bias voltage of 1 V. Fig. 6a illustrates the dynamic sensing response of MoS₂ sensor against various reducing (NO, H₂S, NH₃) and oxidizing (NO₂) gases at 2 ppm concentration. The relative response of the sensor was defined as

$$S = \frac{\Delta I}{I} = \frac{I_g - I_0}{I_0} \times 100 \quad [1]$$

where I_g is the current during the gas exposure, and I_0 is the current in the dry air. When the MoS₂ sensor is exposed to the gases, a charge transfer between the gaseous species and MoS₂ nanoflakes occurs resulting in a change in their carrier concentration/

conductance, which serves as an important principle for the working of sensing devices.

On exposure to synthetic air, oxygen molecules get adsorbed to the surface of MoS₂ nanoflakes and form surface acceptor states O₂⁻ (ads), O⁻ (ads), O²⁻ (ads) that captures free electrons from the conduction band of the MoS₂ and lead to formation of an electron depletion layer near the surface of n-type MoS₂. At low temperature, oxygen is adsorbed in its molecular state O₂⁻, whereas at high temperature it dissociates as atomic O⁻ and O²⁻.^{43,44}



Oxygen molecules are electron acceptors, which accept electrons from MoS₂ and result in the decrease of electrons concentration leading to decrease in the conductance of the sensor. On exposure to oxidizing gases, these gas molecules react with MoS₂ with an

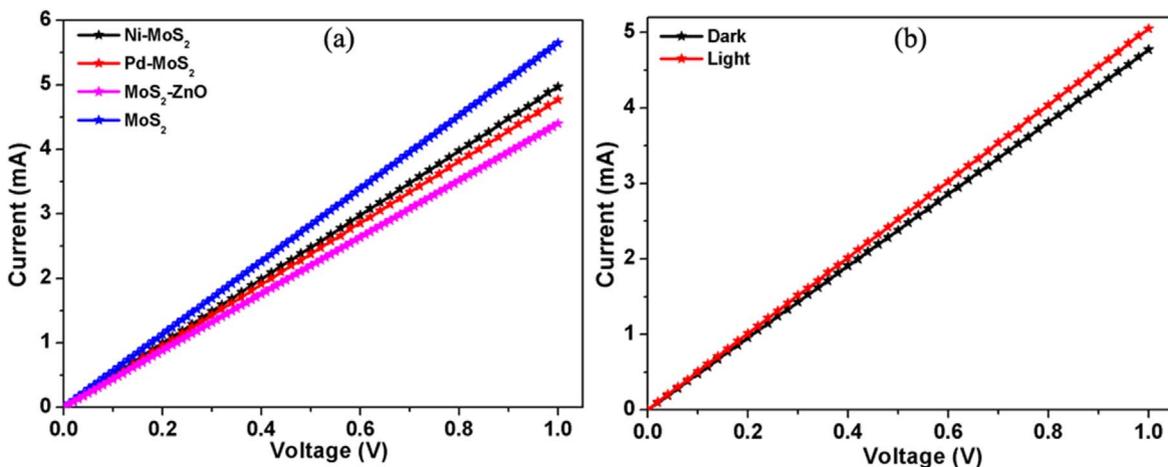


Figure 5. I-V characteristics of (a) MoS₂, Ni-MoS₂, Pd-MoS₂ and MoS₂-ZnO nanostructures under dark condition and (b) Pd-MoS₂ nanostructures under dark and light illumination condition.

increased quantity of oxygen ions due to further oxidation leading to a decrease in the sensor conductance. Whereas, on exposure to reducing gases, the gas molecules release the trapped electrons back to the conduction of MoS₂ leading to an increase in the electron concentration and conductance. That is the sensor conductance is found to decrease on exposure to oxidizing gases, whereas it increased for reducing gases indicating p-type and n-type conduction in nanocrystalline MoS₂ sensor respectively. For example, when the sensor is exposed to oxidizing gas NO₂, being an electron acceptor due to an unpaired electron from nitrogen atom, NO₂ results in p-type doping and hence they shift the Fermi-level of MoS₂ towards valence band edge. NO₂ gets adsorbed onto MoS₂ surface and the strong adsorption of NO₂ dominates over O₂⁻ and creates an extended depletion layer as NO₂ serves as electron acceptor which tends to the withdrawal of electrons from the conduction band of the sensing material MoS₂. As a result, the electron concentration in the conduction band of MoS₂ is found to decrease, thus increasing the resistance of MoS₂ sensor. This resulted in a decrease in sensor conductivity upon exposure to oxidizing gases.^{45,46} As observed in Fig. 6a it is evident that pure MoS₂ have a dynamic response towards various gases with a poor cross selectivity. But MoS₂ based sensors can be used for identifying ammonia leakage from ammonia refrigerants used in large industries. Automobile exhaust gases include toxic NO_x, SO₂, CO etc. and these MoS₂ sensors can be used to detect the average increase or decreased dosage of automobile exhaust.

In contrast to the general sensing mechanism, the sensor conductance of our MoS₂ sensor is found to decrease for reducing gases, which usually serves as electron donors in the charge transfer process. Usually, the reducing gases donate electrons to the

conduction band of MoS₂ thus increasing the carrier concentration in MoS₂ and hence shift the Fermi-level of MoS₂ towards conduction band edge.^{46,47} There are several factors that affect the electrical conductance of the sensor such as the chemisorbed oxygen, defects such as vacancies, interstitial sites, chemical potential etc.

Fan et al.⁴⁸ reported a reversal in the conductance during ZnO nanowire based NH₃ sensing. They observed that at room temperature the Fermi level of the material lies above the chemical potential of ammonia gas. As electrons transfer from the material with higher chemical potential to one with lower chemical potential until the system reaches equilibrium, ammonia withdraws electrons from ZnO nanowire leading to a decrease in the conductance. Whereas, at elevated temperature, they observed a downshift in the Fermi energy level of nanowire with a decrease in the chemical potential of NH₃. Similarly, the decrease conductance observed on exposure of reducing gases at room temperature can also be attributed to the higher chemical potential of MoS₂ compared to that of gases. In addition, the effect of oxygen molecules and the reaction of these reducing gases to form oxygen species also contribute to the enhanced electron withdrawing from MoS₂. As a consequence of which the reducing gases are expected to induce a p-doping effect on MoS₂.

The p-doping effect created by exposure of MoS₂ sensor to NO leading to a decrease in current has been demonstrated by Li and co-authors with a detection limit of 0.8 ppm.²⁶ Barazzouk et al.⁴⁹ reported the influence of chemisorbed oxygen species in the sensing mechanism with an increase in resistance of MoO₃ towards both NO and NO₂ gases. The observance of decreasing electrical conductance on exposure to both oxidizing and reducing gases in MoS₂ can be ascribed to these factors discussed above.

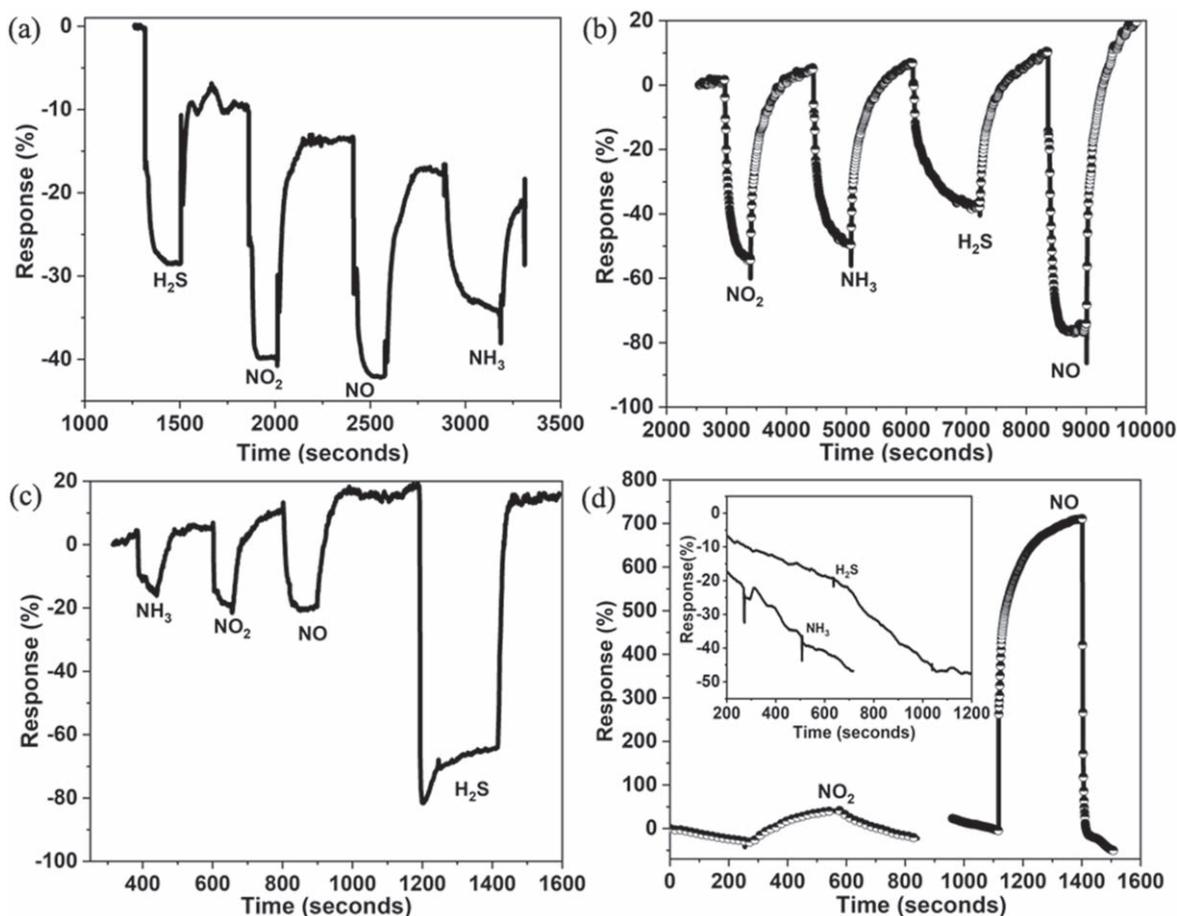


Figure 6. Current change of (a) MoS₂, (b) MoS₂-ZnO, (c) MoS₂-Ni and (d) MoS₂-Pd gas sensors upon exposure to 2 ppm concentration of NH₃, H₂S, NO₂ and NO gases.

In order to stabilize and enhance the cross sensitivity of MoS₂ based sensors, we functionalized MoS₂ using ZnO, Ni and Pd. The results shows that after the incorporation of ZnO, Ni and Pd, the cross-sensitivity has improved for MoS₂-ZnO, MoS₂-Ni and MoS₂-Pd and is shown in Figs. 6b–6d. MoS₂-ZnO displays a slightly increased sensitivity towards NO, whereas MoS₂-Ni sensor shows excellent selectivity towards H₂S gas and Pd functionalized MoS₂ exhibited a remarkable increase in the response towards NO gas. The MoS₂-Pd sensor does not exhibit any response towards H₂S and NH₃. These results can be attributed to the strongest interaction and charge transfer between the respective gases and active sensing material MoS₂, large adsorption and binding energies and also to the changes in the bond lengths. In case of Ni-MoS₂ sensor, a higher response is observed towards H₂S gas with sensitivity of around 80%. The incorporation of Ni into the MoS₂ matrix can lead to the formation of NiS₂ phases on exposure to H₂S gas. The increase in the adsorption energy of H₂S towards Ni-MoS₂ enhanced the charge transfer compared to other reactive gases showing low adsorption energies towards Ni-MoS₂.⁵⁰

Pd is a metal with high work function (5.1–5.6 eV) compared to MoS₂ (4.3–5.2 eV). As a result, electrons are transferred from MoS₂ to Pd creating a p-doping effect of Pd on MoS₂. On exposure to NO and NO₂, Pd forms PdNO_x complexes, with a work function lower than that of both Pd and MoS₂. Thus, the electron transferred from MoS₂ will be compensated by the transfer of electron from the PdNO_x complexes to MoS₂ and that results in the increase of the sensing current on the exposure of NO and NO₂. The theoretical study on the adsorptions of NO, NO₂, CO, SO₂ and NH₃ on MoS₂ nanotube represents the higher adsorption energy of NO ($E_{\text{ads}} = 129.3$ meV) on MoS₂ nanotube compared to that on monolayer MoS₂ ($E_{\text{ads}} = 77.4$ meV). An increased charge transfer was also observed between NO and MoS₂ nanotube (0.029 e) compared to monolayer MoS₂ (0.005 e).⁵¹ Hence, we can say that the increased

cross-sensitivity of Pd-MoS₂ towards NO is due to the higher adsorption energy of NO on MoS₂-Pd nanoflakes and associated charge transfer between Pd-MoS₂ and NO gas.

In a report, Niu et al. demonstrated the gas sensing behavior of N and Si co-doped graphene nanosheets with response value of about $26 \pm 1\%$ at 21 ppm of NO₂ concentration.⁵² Cho and co-authors obtained a sensitivity of about $\sim 26\%$ for NO₂ at concentration of 20 ppm and room temperature for CVD synthesized layered MoS₂.⁴⁶ In this study, we obtained a high relative response of about 80% for MoS₂-ZnO and 700% for MoS₂-Pd gas sensor at 2 ppm NO concentration and a relative response of 80% towards 2 ppm H₂S for MoS₂-Ni, which is significantly higher compared to other MoS₂ and graphene based sensors^{17,53–55} due to increased charge transfer between the analyte and MoS₂. The sensing mechanism in MoS₂ based sensors on exposure to air and other reactive gases are pictured in Fig. 7.

The responses of MoS₂-Ni and MoS₂-Pd based sensors to different concentrations of H₂S and NO respectively are shown in Figs. 8a and 8b respectively. As the concentration of gas molecules increases, more surface dipoles are formed, which results in more electron transfer between MoS₂ and analyte, thus increasing their interaction leading to higher response.⁵⁶ The response increases rapidly with increasing concentration of H₂S in the range of 0.3–2 ppm indicating good sensitivity of MoS₂-Ni sensor towards different H₂S concentrations. Similarly, response of MoS₂-Pd sensor upon exposure to NO with concentrations ranging from 0.1 to 2 ppm indicating the good sensitivity of MoS₂-Pd sensor towards NO gas. From the slope of sensor response vs target gas concentration plot (inset of Figs. 8a and 8b) we got the sensitivity of MoS₂-Ni and MoS₂-Pd sensors as 36 and 227%/ppm respectively. The repeatability of MoS₂-Ni towards H₂S over seven periodic sensing cycles and that of MoS₂-Pd sensor towards NO over six periodic sensing cycles are shown in Figs. 8c and 8d respectively. It was found that

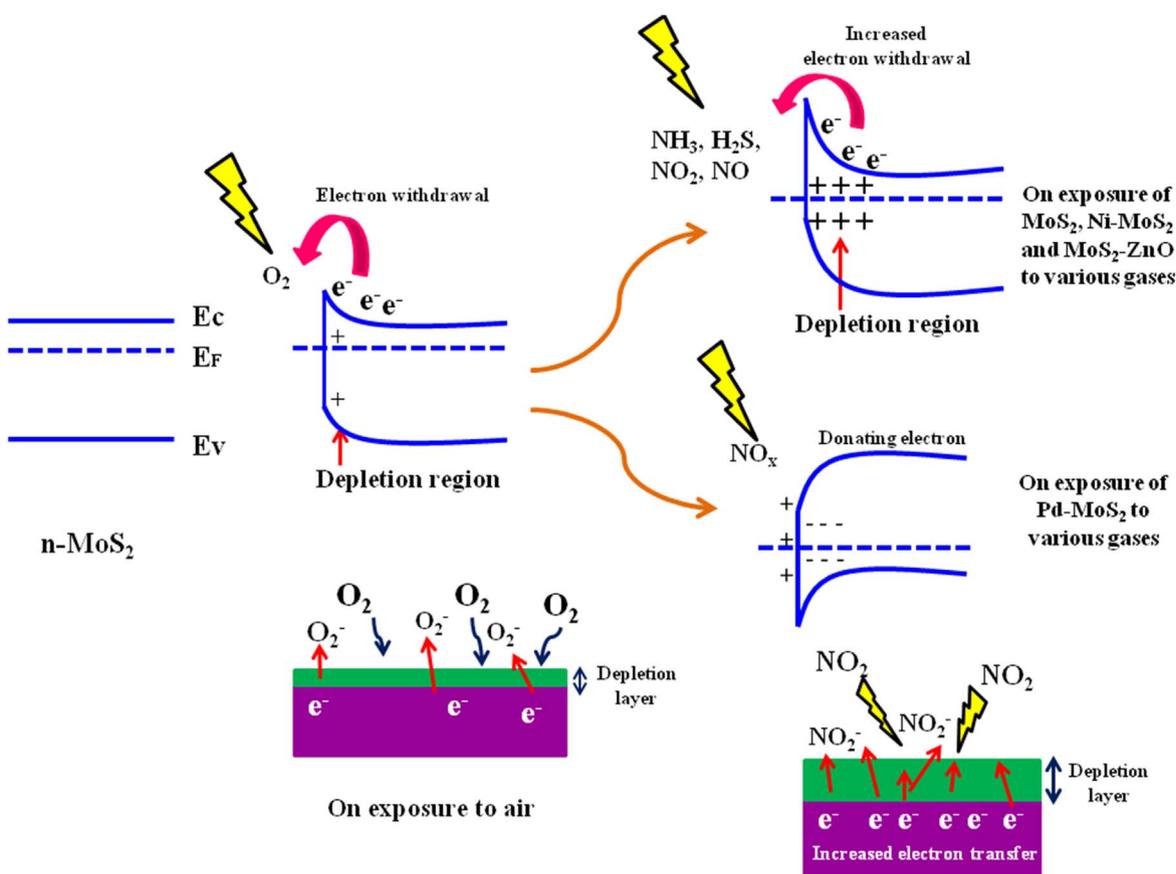


Figure 7. Schematic illustration of proposed band edge alignment across MoS₂ and Ni, ZnO, Pd functionalized MoS₂ on exposure towards various gases.

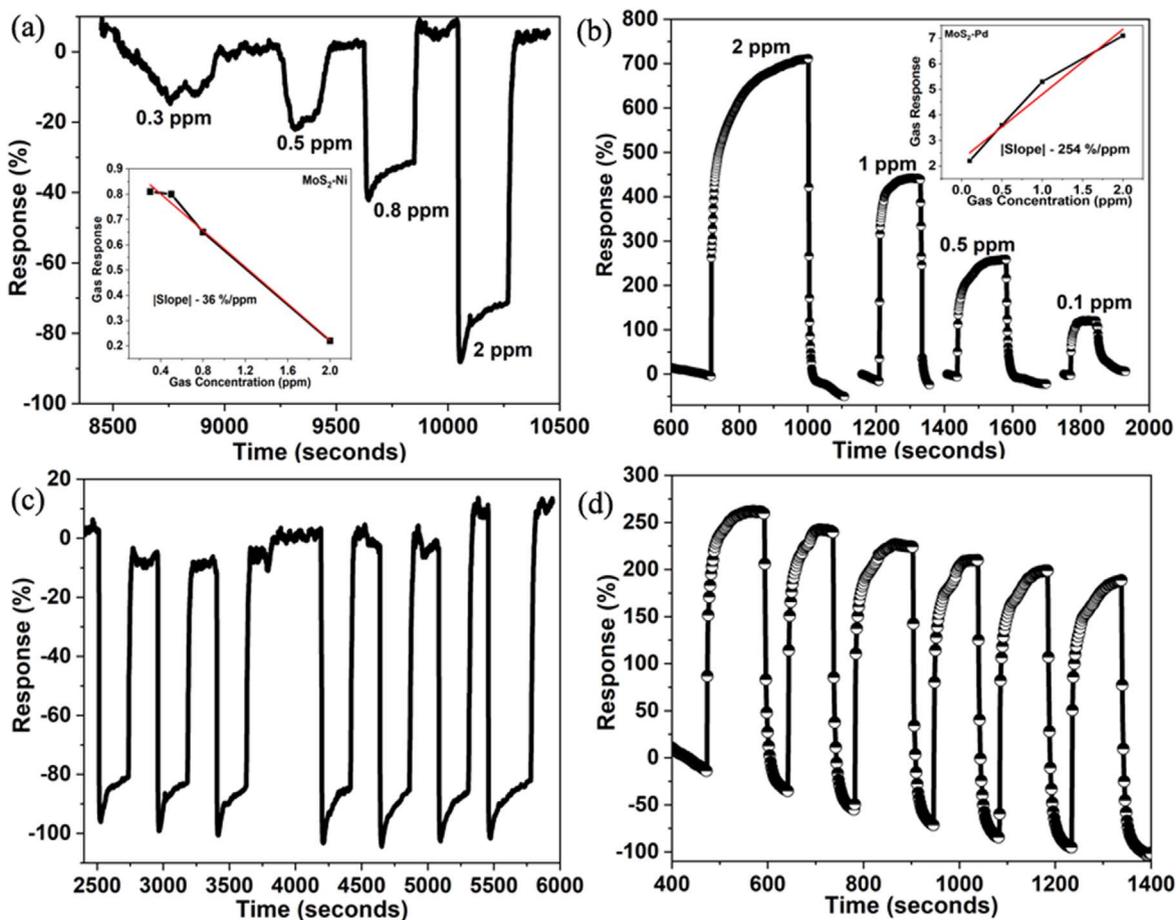


Figure 8. Response variation of (a) MoS₂-Ni based sensor as a function of H₂S concentrations with inset showing the slope of sensor response vs target gas concentration of MoS₂-Ni sensor (b) MoS₂-Pd based sensor as a function of NO concentrations with inset showing the slope of sensor response vs target gas concentration of MoS₂-Pd sensor, Repeatability of (c) MoS₂-Ni gas sensor upon exposure to successive pulses of 2 ppm H₂S gas and (d) MoS₂-Pd gas sensor upon exposure to successive pulses of 0.5 ppm NO gas.

sensors exhibit almost stable response upon repeated exposure to H₂S and NO confirming the excellent repeatability of the sensor material suitable for automotive antipollution system. The results also suggest that MoS₂-Pd sensor having high response towards NO is a promising biomarker for pulmonary inflammations and a combination of both MoS₂-Pd and MoS₂-Ni sensors can serve as a biomarker for chronic pancreatitis. It can be stated that the presence of high surface area makes MoS₂ nanoflakes highly sensitive to the adsorption of gaseous molecules on the surface causing high sensitivities.

The humidity effect on MoS₂ and its related systems is well recognized (Fig. 9) and it is a concern for the MoS₂ based sensor. It is observed that, on changing humidity from 5% to 55%, a current variation of 0.006 μ A is noticed on MoS₂-Ni device while on MoS₂-Pd device the current variation is 1.5 μ A. This humidity variations can be considered to be negligible compared to H₂S and NO gas responses on the device. It is also observed that MoS₂-Ni sensor is showing high response towards H₂S gas with a current variation of around 14 μ A (response of 80%) at a concentration of 2 ppm. Whereas, the same MoS₂-Ni sensor shows small current variation of around 2–4 μ A (response of 15%–20%) towards other gases (NO, NO₂, NH₃) at a concentration of 2 ppm. Similarly, in the case of MoS₂-Pd sensor, the sensor exhibits remarkable response towards NO gas at a concentration of 2 ppm with a very large current variation around 34 μ A (response of 700%). On the other hand, it is evident that MoS₂-Pd sensor is showing very small current variation of around 4 μ A (response of 44%) on passing NO₂ gas at a

concentration of 2 ppm. From these current variations, we confirmed the selectivity of MoS₂-Ni towards H₂S and MoS₂-Pd towards NO gas and the negligible variation in humidity compared to gas sensing.

The highly selective, sensitive and stable gas-sensing performance achieved in 2D-MoS₂ based nanostructures promises a new avenue of metal dichalcogenides toward the development of electronic sensors. However, the humidity effect should also be tested directly by measuring the gas sensing behavior while changing the humidity level and the selectivity should be discussed with the sensing results based on mixed gases, not a single gas for the complete study on the sensing characteristics of a sensor.

In conclusion, we successfully fabricated MoS₂, MoS₂-ZnO, MoS₂-Ni and MoS₂-Pd nanostructures-based sensors. The gas-sensing performance of the as-prepared MoS₂ nanostructures-based sensor was investigated towards various hazardous gases. The MoS₂-based sensors showed excellent sensing performances with high sensitivity at room temperature, which can serve as an excellent alternative to the common semiconductor metal oxide gas sensors that require high optimal working temperatures for good response. It was identified that Ni-MoS₂ sensors have high sensitivity towards detection of H₂S gas. The Pd-MoS₂ sensor exhibited excellent sensitivity, stability and high selectivity for NO detection making it an attractive candidate for automobile exhaust gas sensing applications and a promising biomarker for pulmonary inflammations. The enhanced gas sensing properties were probably attributed to the synergetic effect of MoS₂ nanoflakes with good specific

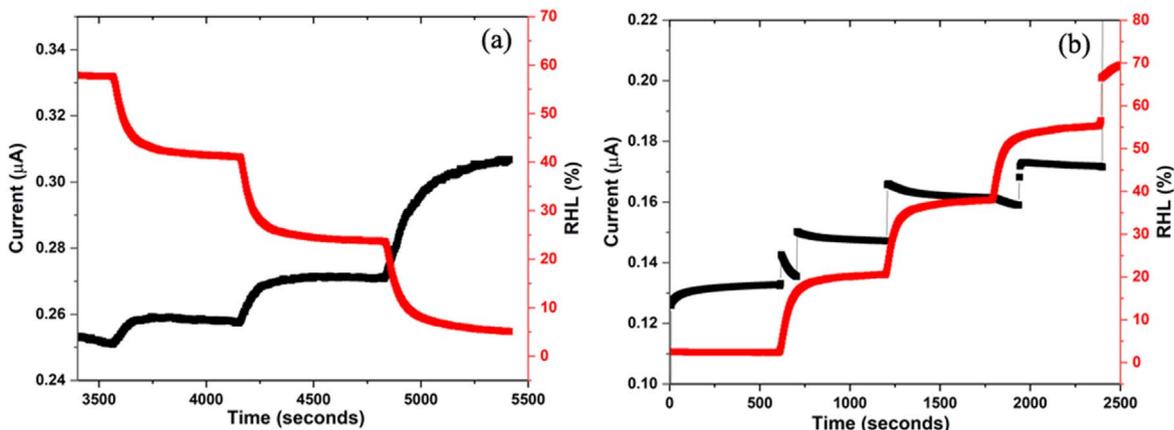


Figure 9. Humidity sensing response of (a) MoS₂-Ni and (b) MoS₂-Pd based sensor.

surface area. The results demonstrate that the MoS₂-based sensors can open up new horizons in the development of futuristic multi-functional chemical and bio-sensors.

Acknowledgments

Levna Chacko acknowledge Department of Science and Technology (DST), New Delhi, India for INSPIRE fellowship. The authors acknowledge Prof. M. K. Jayaraj, CUSAT, Kerala, India for Raman facilities under Nanoscience and Technology Initiative, DST, Government of India. The authors gratefully acknowledge Centre for Nanoscience and Engineering (CeNSE), Indian Institute of Science, Bangalore through the Indian Nano User Programme (INUP), funded by the Department of Electronics and Information Technology (DeitY), Govt. of India for device fabrication facilities.

ORCID

P. M. Aneesh  <https://orcid.org/0000-0002-0225-1714>

References

- Z. Jin, Y. Su, and Y. Duan, "Development of a polyaniline-based optical ammonia sensor." *Sensors Actuators, B Chem.*, **72**, 75 (2001).
- M. Evyapan and A. D. F. Dunbar, "Applied surface science controlling surface adsorption to enhance the selectivity of porphyrin based gas sensors." *Appl. Surf. Sci.*, **362**, 191 (2016).
- G. F. Fine, L. M. Cavanagh, A. Afonja, and R. Binions, "Metal oxide semi-conductor gas sensors in environmental monitoring." *Sensors*, **10**, 5469 (2010).
- T. Zhang, S. Mubeen, N. V. Myung, and A. D. Marc, "Recent progress in carbon nanotube-based gas sensors." *Nanotechnology*, **19**, 332001 (2008).
- S. S. Varghese, S. Lonkar, K. K. Singh, S. Swaminathan, and A. Abdala, "Recent advances in graphene based gas sensors." *Sensors Actuators, B Chem.*, **218**, 160 (2015).
- S. Prezioso, F. Perrozzi, L. Giancaterini, C. Cantalini, E. Treossi, V. Palermo, M. Nardone, S. Santucci, and L. Ottaviano, "Graphene oxide as a practical solution to high sensitivity gas sensing." *J. Phys. Chem. C*, **117**, 10683 (2013).
- P. J. Barnes and S. A. Kharitonov, "Exhaled nitric oxide: a new lung function test." *Thorax*, **51**, 233 (1996).
- N. M. Tsoukias, Z. Tannous, A. F. Wilson, and S. C. George, "Single-exhalation profiles of NO and CO₂ in humans: effect of dynamically changing flow rate." *J. Appl. Physiol.*, **85**, 642 (1998).
- A. M. Morselli-labate, L. Fantini, and R. Pezzilli, "Hydrogen sulfide, nitric oxide and a molecular mass 66 u substance in the exhaled breath of chronic pancreatitis patients." *Pancreatology*, **7**, 497 (2007).
- S. Varghese, S. Varghese, S. Swaminathan, K. Singh, and V. Mittal, "Two-dimensional materials for sensing: graphene and beyond." *Electronics*, **4**, 651 (2015).
- B. Cho et al., "Charge-transfer-based gas sensing using atomic-layer MoS₂." *Sci. Rep.*, **5**, 8052 (2015).
- M. Donarelli, S. Prezioso, F. Perrozzi, F. Bisti, M. Nardone, L. Giancaterini, C. Cantalini, and L. Ottaviano, "Response to NO₂ and other gases of resistive chemically exfoliated MoS₂-based gas sensors." *Sensors Actuators B Chem.*, **207**, 602 (2015).
- A. Shokri and N. Salami, "Gas sensor based on MoS₂ monolayer." *Sensors Actuators B Chem.*, **236**, 378 (2016).
- Y. Han et al., "Design of hetero-nanostructures on MoS₂ nanosheets to boost NO₂ room-temperature sensing." *ACS Appl. Mater. Interfaces*, **10**, 22640 (2018).
- K. Kalantar-Zadeh and J. Z. Ou, "Biosensors based on two-dimensional MoS₂." *ACS Sens.*, **1**, 5 (2016).
- S. Yang, C. Jiang, and S. Wei, "Gas sensing in 2D materials." *Appl. Phys. Rev.*, **4**, 021304 (2017).
- H. Long, A. Harley-Trochimczyk, T. Pham, Z. Tang, T. Shi, A. Zettl, C. Carraro, M. A. Worsley, and R. Maboudian, "High surface area MoS₂/graphene hybrid aerogel for ultrasensitive NO₂ detection." *Adv. Funct. Mater.*, **26**, 5158 (2016).
- D. Ma, W. Ju, T. Li, X. Zhang, C. He, B. Ma, Z. Lu, and Z. Yang, "The adsorption of CO and NO on the MoS₂ monolayer doped with Au, Pt, Pd, or Ni: a first-principles study." *Appl. Surf. Sci.*, **383**, 98 (2016).
- S. Zhao, J. Xue, and W. Kang, "Gas adsorption on MoS₂ monolayer from first-principles calculations." *Chem. Phys. Lett.*, **595-596**, 35 (2014).
- L. Yu, F. Guo, S. Liu, J. Qi, M. Yin, B. Yang, Z. Liu, and X. H. Fan, "Hierarchical 3D flower-like MoS₂ spheres: post-thermal treatment in vacuum and their NO₂ sensing properties." *Mater. Lett.*, **183**, 122 (2016).
- A. V. Agrawal, R. Kumar, S. Venkatesan, A. Zakhidov, G. Yang, J. Bao, M. Kumar, and M. Kumar, "Photo-activated mixed in-plane and edge-enriched p-type MoS₂ flakes based NO₂ sensor working at Room temperature." *ACS Sens.*, **3**, 998 (2018).
- D. Zhang, J. Wu, P. Li, and Y. Cao, "Room-temperature SO₂ gas sensing properties based on metal-doped MoS₂ nanoflower: an experimental and density functional theory investigation." *J. Mater. Chem. A*, **5**, 20666 (2017).
- S. Y. Park et al., "Highly selective and sensitive chemoresistive humidity sensors based on rGO/MoS₂ van der Waals composites." *J. Mater. Chem. A*, **6**, 5016 (2018).
- A. V. Agrawal, R. Kumar, G. Yang, J. Bao, M. Kumar, and M. Kumar, "Enhanced adsorption sites in monolayer MoS₂ pyramid structures for highly sensitive and fast hydrogen sensor." *Int. J. Hydrogen Energy*, **45**, 9268 (2020).
- Qu Yue, Zhengzheng Shao, Shengli Chang, and Jingbo Li, "Adsorption of gas molecules on monolayer MoS₂ and effect of applied electric field." *Nanoscale Research Letters*, **8**, 425 (2013).
- H. Li, Z. Yin, Q. He, H. Li, X. Huang, G. Lu, D. W. H. Fam, A. I. Y. Tok, Q. Zhang, and H. Zhang, "Fabrication of single- and multilayer MoS₂ film-based field-effect transistors for sensing NO at room temperature." *Small*, **8**, 63 (2012).
- T. Wang, H. Zhu, J. Zhuo, Z. Zhu, G. V. Lubarsky, J. Lin, and M. Li, "A biosensor based on ultrasmall MoS₂ nanoparticles for electrochemical detection of H₂O₂ released by cells at nM level." *Anal. Chem.*, **85**, 10289 (2013).
- X. Wang, F. Nan, J. Zhao, T. Yang, T. Ge, and K. Jiao, "A label-free ultrasensitive electrochemical DNA sensor based on thin-layer MoS₂ nanosheets with high electrochemical activity." *Biosens. Bioelectron.*, **64**, 386 (2015).
- X. Wang, W. Deng, L. Shen, M. Yan, S. Geb, and J. Yu, "A sensitive quenched electrochemiluminescent DNA sensor based on the catalytic activity of gold nanoparticles functionalized MoS₂." *New J. Chem.*, **39**, 8100 (2015).
- H. Nam, B.-R. Oh, P. Chen, M. Chen, S. Wi, W. Wan, K. Kurabayashi, and X. Liang, "Multiple MoS₂ transistors for sensing molecule interaction kinetics." *Sci. Rep.*, **5**, 10546 (2015).
- Y. Zhou, C. Gao, and Y. Guo, "UV assisted ultrasensitive trace NO₂ gas sensing based on few-layer MoS₂ nanosheet-ZnO nanowire heterojunctions at room temperature." *J. Mater. Chem. A*, **6**, 10286 (2018).
- L. Chacko, A. Poyyakkara, V. B. S. Kumar, and P. M. Aneesh, "MoS₂-ZnO nanocomposites as highly functional agents for anti-angiogenic and anti-cancer theranostics." *J. Mater. Chem. B*, **6**, 3048 (2018).
- H. Wei, Y. Gui, J. Kang, W. Wang, and C. Tang, "A DFT study on the adsorption of H₂S and SO₂ on Ni Doped MoS₂ monolayer." *Nanomaterials*, **8**, 646 (2018).
- D. Baek and J. Kim, "Few-layered MoS₂ gas sensor functionalized by Pd for the detection of hydrogen." *Sensors Actuators B Chem.*, **250**, 686 (2017).

35. L. Chacko, A. K. Swetha, R. Anjana, M. K. Jayaraj, and P. M. Aneesh, "Wasp-waisted magnetism in hydrothermally grown MoS₂ nanoflakes." *Mater. Res. Express*, **3**, 116102 (2016).
36. Z. Wan, J. Shao, J. Yun, H. Zheng, T. Gao, M. Shen, N. Qu, and H. Zheng, "core-shell structure of hierarchical quasi-hollow MoS₂ microspheres encapsulated porous carbon as stable anode for Li-ion batteries." *Small*, **10**, 4975 (2014).
37. Y.-H. Tan, K. Yu, J.-Z. Li, H. Fu, and Z.-Q. Zhu, "MoS₂@ZnO nano-heterojunctions with enhanced photocatalysis and field emission properties." *J. Appl. Phys.*, **116**, 064305 (2014).
38. H. Li, H. Wu, S. Yuan, and H. Qian, "Synthesis and characterization of vertically standing MoS₂ nanosheets." *Sci. Rep.*, **6**, 21171 (2016).
39. A. V. Agrawal, R. Kumar, S. Venkatesan, A. Zakhidov, Z. Zhu, J. Bao, K. Mahesh, and M. Mukesh, "Fast detection and low power hydrogen sensor using edge-oriented vertically aligned 3-D network of MoS₂ flakes at room temperature." *Appl. Phys. Lett.*, **111**, 093102 (2017).
40. L. Chacko, M. K. Jayaraj, and P. M. Aneesh, "Excitation-wavelength dependent upconverting surfactant free MoS₂ nanoflakes grown by hydrothermal method." *J. Lumin.*, **192**, 6 (2017).
41. A. V. Agrawal, N. Kumar, S. Venkatesan, A. Zakhidov, C. Manspecker, Z. Zhu, F. R. H. Carlos, J. Bao, and M. Kumar, "Controlled growth of MoS₂ flakes from in-plane to edge-enriched 3-D network and their surface energy studies." *ACS Appl. Nano Mater.*, **1**, 2356 (2018).
42. A. Molina-Sanchez and L. Wirtz, "Phonons in single-layer and few-layer MoS₂ and." *Phys. Rev. B*, **84**, WS2 155413 (2011).
43. S. Chang, T. Hsueh, I. Chen, and B.-R. Huang, "Highly sensitive ZnO nanowire CO sensors with the adsorption of Au nanoparticles." *Nanotechnology*, **19**, 175502 (2008).
44. Z. Li, Y. Huang, S. Zhang, W. Chen, Z. Kuang, D. Ao, W. Liu, and Y. Fu, "A fast response and recovery H₂S gas sensor based on α -Fe₂O₃ nanoparticles with ppb level detection limit." *J. Hazard. Mater.*, **300**, 167 (2015).
45. B. Liu, L. Chen, G. Liu, A. N. Abbas, M. Fathi, and C. Zhou, "High-performance chemical sensing using schottky-contacted chemical vapor deposition grown monolayer MoS₂ transistors." *ACS Nano*, **8**, 5304 (2014).
46. Byungjin Cho et al., "Charge-transfer-based Gas Sensing Using Atomic-layer MoS₂." *Scientific Reports*, **5**, 8052 (2015).
47. D. J. Late et al., "Sensing behavior of atomically thin-layered MoS₂ transistors." *ACS Nano*, **7**, 4879 (2013).
48. Z. Fan and J. G. Lu, "Chemical sensing with ZnO nanowire field-effect transistor." *IEEE Trans. Nanotechnol.*, **5**, 393 (2006).
49. S. Barazzouk, R. P. Tandon, and S. Hotchandani, "MoO₃ - based sensor for NO, NO₂ and CH₄ detection." *Sensors Actuators B*, **119**, 691 (2006).
50. G. A. Asres et al., "Ultrasensitive H₂S gas sensors based on p-type WS₂ hybrid materials." *Nano Res.*, **11**, 4215 (2018).
51. R. Cao, B. Zhou, C. Jia, X. Zhang, and Z. Jiang, "Theoretical study of the NO, NO₂, CO, SO₂, and NH₃ adsorptions on multi-diameter single-wall MoS₂ nanotube." *J. Phys. D: Appl. Phys.*, **49**, 045106 (2016).
52. F. Niu, J. Liu, L. Tao, W. Wang, and W. Song, "Nitrogen and Silica co-doped graphene nanosheets for NO₂ gas sensing." *J. Mater. Chem. A*, **1**, 6130 (2013).
53. G. Lu, L. E. Ocola, and J. Chen, "Reduced graphene oxide for room-temperature gas sensors." *Nanotechnology*, **20**, 445502(1-9) (2009).
54. W. K. Nomani, R. Shishir, M. Qazi, D. Diwan, V. B. Shields, M. G. Spencer, G. S. Tompa, N. M. Sbrockey, and G. Koley, "Chemical highly sensitive and selective detection of NO₂ using epitaxial graphene on 6H-SiC." *Sensors Actuators B*, **150**, 301 (2010).
55. S. Y. Jeong, S. H. Choi, J.-W. Yoon, J. M. Won, Y. C. Kang, J.-S. Park, and J.-H. Lee, "Selective NO₂ sensors using MoS₂-MoO₂ composite yolk-shell spheres." *J. Sens. Sci. Technol.*, **24**, 151 (2015).
56. J. Z. Ou et al., "Physisorption based charge transfer in two-dimensional SnS₂ for selective and reversible NO₂ gas sensing." *ACS Nano*, **9**, 10313 (2015).