

Defect Functionalization of MoS₂ nanostructures as toxic gas sensors: A review

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Abstract. Toxic gas sensing plays an important role in many parts of our life from environmental protection, human health, agriculture to biomedicine. The importance of detecting toxic gases in the environment cannot be minimised in today's highly polluted world and the reality of global warming. Carbon monoxide and NO gas are highly toxic air pollutants and can cause serious health problems. Therefore, materials able to detect these toxic gases are urgently needed. Doping and defect substitution is a versatile and new tool for changing the chemical and electronic properties of 2D layered materials and boosting the applications of these materials. Molybdenum disulphide (MoS₂) as a 2D layered material has unique properties and applications due its semiconducting nature, bandgap and layered structure. In the past decade, although, extensive research of Graphene as a gas sensor was conducted, the zero bandgap limited its potential and applicability. This is overcome in MoS₂ nanostructures (MSNs) and the current focus is defect engineering of MSNs. The large surface to volume ratio, bandgap and cheapness makes MSNs very attractive for gas sensor applications. The idea is fuelled by the recent finding of Ding et al [16] of successful doping strategies on monolayer MoS₂ for enhanced NO detection. Moreover, the work of Luo et al [17] shows that substitutional doping is the new way of boosting and engineering the properties of ML MoS₂. A short and focused report in this exciting field is presented in this review.

Key words: MSNs, Defect functionalization, bandgap, sensors

1. INTRODUCTION

Toxic gases like CO, NO, NO₂ and NH₃ in the environment is a serious problem and needs to be detected and redirected or made harmless by conversion to useful products. Oxygen delivery to the body organs, mainly heart and brain can be reduced by Carbon monoxide and it is a serious health threat. NO gas can cause serious respiratory and skin problems among people and it is important to monitor its levels especially in asthma patients. A robust, portable, low cost, highly sensitive and selective sensor is in urgent need. Inspired by the well known 2D material Graphene for gas sensing applications [1-5], extensive research has been conducted on other layered materials, especially MSNs. The reduced dimensionality of 2D layered materials leads to unique properties and bandgap dependent applications. Unlike Graphene which has zero bandgap, MoS₂ has a thickness dependent bandgap and has more potential in device applications. Recently, there have been several theoretical and experimental researches on MoS₂ as gas sensors [6-10]. The desirable direct band gap in monolayer (ML) MoS₂ and large surface area to volume ratio makes it highly suitable for such an application. This has been proved by various research results for example the first principles work of Yue et al [6] which shows the effect of electric field on the adsorption of various gas molecules H₂, O₂, H₂O, NH₃, NO, NO₂, and CO on ML MoS₂. The electrical response to NO₂ and other gases has been studied experimentally by Donarelli et al [7] for a few layers of MoS₂. Sensitivity of multilayer MoS₂ transistors to NO has been shown by Li et al [8]. The detection of NH₃ down to 1ppb and the single-molecule sensitivity for NO₂ detection was proposed by He et al [9]. Several experimental works have also been conducted to examine the effectiveness of ML and few layers of 2D MoS₂ for successful gas sensing applications. Multilayer MoS₂ films based on transistor sensors have been experimentally demonstrated to show stable sensitivity towards NO gas molecules by Late et al [10].



They have explored the performance of single and multilayer MoS₂ on NO₂ and NH₃ gas detection and also the effect of gate bias and light manipulations.

Chemical doping is an effective way to alter the binding configurations, modify electronic and transport properties and enhance the application of materials as a gas sensor. Chemisorption is found to be thermally more stable and enhanced by dopants. The recent years have seen some interesting theoretical investigations of doping of ML MoS₂ and absorption of various toxic gases NO, NH₃, CO. In their first principles calculation, Ma et al [11] show that the performance of NO and CO gas absorption is vastly improved by doping pristine ML MoS₂ with transition metal atoms like Au, Pt, Pd and Ni. The effect of non-metal doping of pure ML MoS₂ with Boron, Phosphorus and chlorine for NO shows strong chemisorptions, especially with B and P as reported by Ding et al [12]. Further, the adsorption of NO₂ and NH₃ by ML MoS₂ doped with Al, Si and P was studied by Luo et al [13] to determine the best gas sensor materials. This article presents a short review of the role of substitutional doping on MSNs from first principles calculations over the past five years. The paper summarizes the recent advances in this field with a focus on defect production, non-metal and metallic dopants on ML of MoS₂ and the gas sensing performance related to the dopant atoms.

2. SENSING MECHANISMS

The realization of graphene field-effect transistors (FET) sensing devices and its limitations regarding selectivity has given way to the new generation MoS₂ sensors. The noticeable and specific changes in electronic properties like charge density and transport properties of the sensing material by gas molecules provide the necessary signals for detection of the gas. The gas sensing mechanisms could be resistance based, application of strain or electric field, or transistor based etc. As shown by Yue et al [6] the application of electric field on ML MoS₂ affects the adsorption of the gases NH₃, NO, NO₂, and CO by modulating the charge transfer process. The absorption energies and charge transfer for the stable configurations obtained from their first principles calculations show that all the gas species act as charge acceptors except NH₃, which acts as a donor. This is shown in Fig.1 by the charge density difference plot for the adsorption of the various gas molecules. Shown in the figure is the direction and value of the charge transfer. They also showed that the application of a perpendicular electric field can significantly modulate the charge transfer between the adsorbed molecules and the substrate.

Recently, single layer and multi-layers of MoS₂ sensors have been fabricated and investigated for performance. The relative change in resistance has been used as a sensing signal in several MoS₂ FET devices [8-14] for sensing NO, NO₂ and other gases. Li et al [8] have detected NO gas with a sensitivity of 0.8 ppm using mechanically exfoliated MoS₂ FET devices. Using mechanical exfoliation they deposited one-four layers of MoS₂ on Si/SiO₂ substrate to fabricate FET devices. Their work showed that although the ML MoS₂ has a fast response it was unstable and that the multilayers were more stable with better performance for NO detection. Transistors of varying thickness of large area MoS₂ sheets synthesized by micro-exfoliation were assembled on 300nm Si/SiO₂ substrates by Late et al [10] in the search for the ideal layer structure for enhanced gas absorption. Different conditions of gate bias, humidity and light irradiation were tested for the best performance of NO₂ and NH₃ absorption. Their results showed high sensitivity and recovery for few layers of MoS₂ as compared to ML MoS₂, which could be manipulated by gate bias and green light. Their DFT studies also confirmed this and the fact that resistance decreases due to charge transfer upon application of electric field.

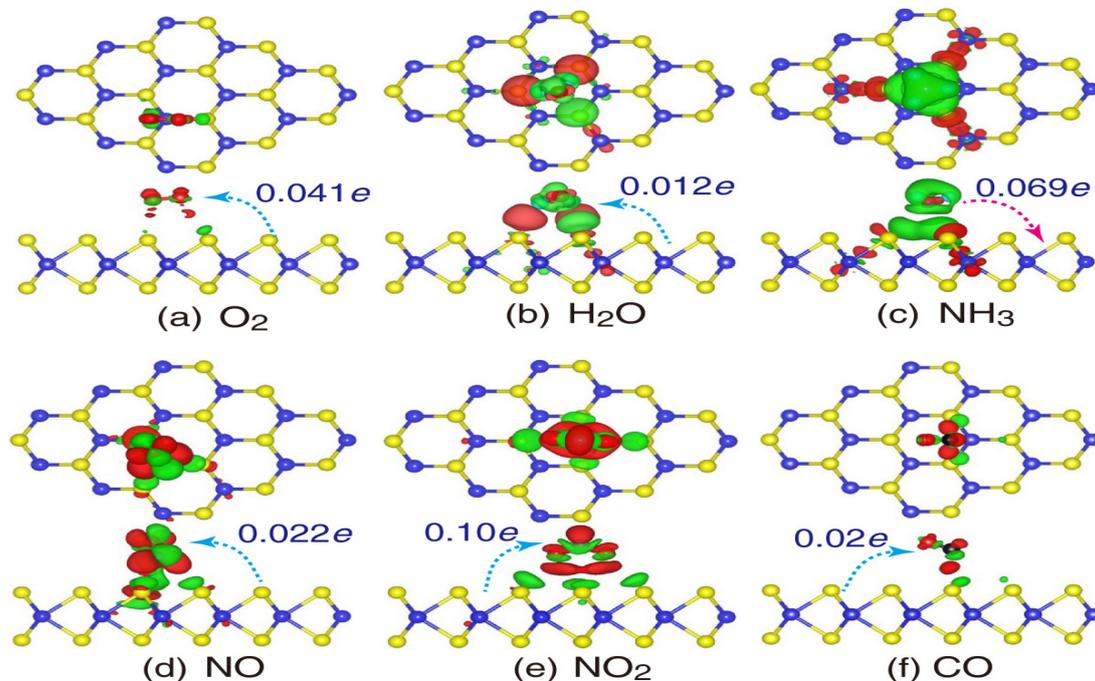


Fig. 1 Charge density difference plots for (a) O₂, (b) H₂O, (c) NH₃, (d) NO, (e) NO₂, and (f) CO interacting with ML MoS₂. The red (green) distribution corresponds to charge accumulation (depletion). The isosurface is taken as $5 \times 10^{-4} e/\text{\AA}^3$, ref [6].

Resistance type, liquid chemical exfoliated MoS₂ flake gas sensors were fabricated by Donarelli et al [7]. They investigated the response of MoS₂ flakes annealed in air at temperatures of 150°C and 250°C to NO₂ and other gases. Annealing at temperatures 250°C shows an n-type of gas sensor behavior with a detection limit of 20 ppb for NO₂. The presence of significant number of S vacancies from thermal annealing and the partial oxidation of the surface of MoS₂ flakes is the reason for this n-type as opposed to the p-type sensor annealed at 150°C, which has nitrogen substituted S vacancies. Fig. 2 shows the resistive response to 1 ppm of NO₂ in dry air for both devices.

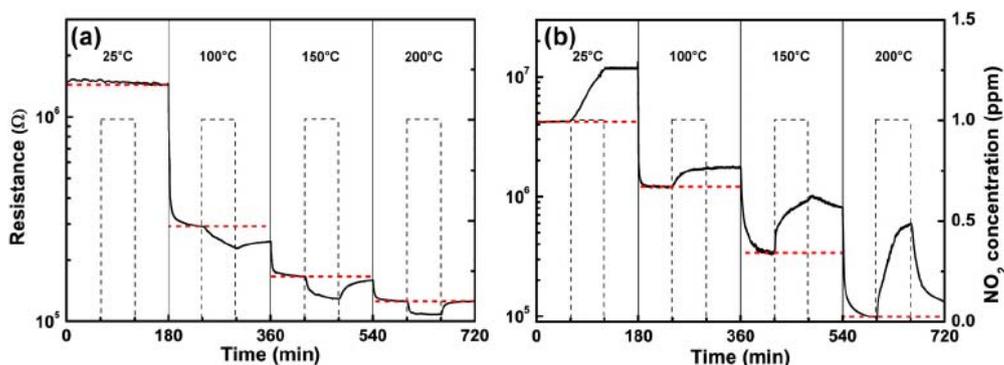


Fig. 2 Resistive responses as a function the operating temperature (a) of the “150°C annealed” device (p-type) and (b) of the “250°C annealed” device (n-type) [7]

From Fig. 2 we see that the response time for p-type is faster but the n-type has a resistance response that is much higher, almost 2.5(5) times the p-type at operating temperatures of 150°C (200°C). The ideal operating temperature is found to be 150°C considering the response intensities, time, and power consumption of the devices.

Fundamental insights of the influence of the adsorbed gas molecules on the electronic and transport properties of MSNs can be obtained by first principles calculations. These can then be used to design highly sensitive and selective gas sensors. Simulation studies help in understanding the interactions and optimizing sensor performance by indentifying the key response mechanism in the analyte-sensor interactions. Since, in reality the different methods of synthesis of MSNs produce defects, a systematic study of defects from first principles and experiment are essential and are discussed in the next section.

3. DEFECT PRODUCTION

Previous studies [4, 6] show that both pristine graphene and MoS₂ have only physisorption for gas adsorption. This can be altered by the introduction of defects that can change the electronic structure and chemical reactivity of the MoS₂ surface and increase the selectivity and adsorption performance by doping. It is expected that MoS₂ will show higher sensitivity, similar to defective and doped graphene that shows greater sensitivity for NO, NO₂, CO and other gases as reported by Ratinac et al [3], especially with the presence of edge states. Hence, information on defect formation plays an important role and both experimental and first principles works [19-24] have been carried out towards this end. Zhou et al [21] have made a systematic study of intrinsic point defects, dislocations, grain boundaries, edges etc in chemical vapor deposited (CVD) ML MoS₂. They have performed first principle calculations in addition to atomic imaging with consistent results. Their findings show the highest structural stability for S vacancies (V_S) which are very frequent compared to the antisite defects. Also, it is found that V_S is randomly distributed and V_{2S} is rarely observed as it requires twice the formation energy of V_S. This behavior is different from graphene where di-vacancies are preferred over mono-vacancy of C atoms. Fig.3 shows the image analysis of the various point defects.

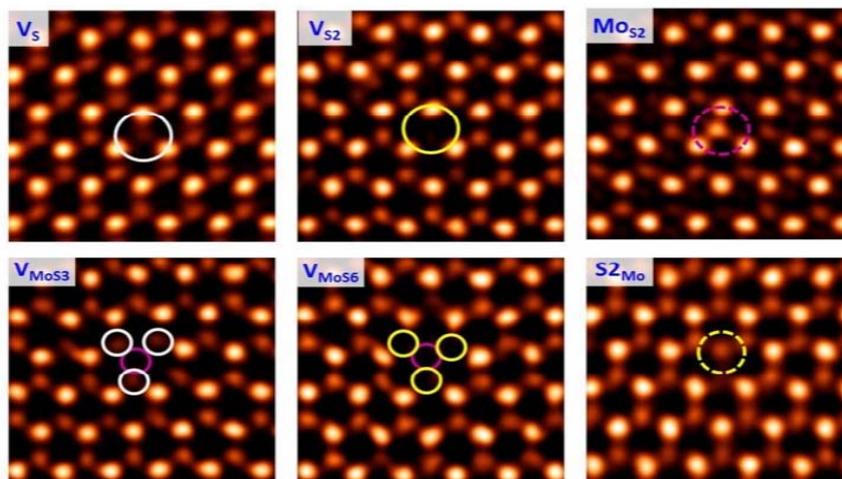


Fig.3 Image analysis for intrinsic point defects in ML MoS₂ [21]

In the filtered images the Mo atom has 2-2.5 times the intensity of S2 column and a single S atom (V_S) has half the intensity of S2 column. Najmaei et al [19, 20] have explored the sources of both intrinsic and extrinsic defects in CVD MoS₂ and ways to control production of the defects to suit the needs of a device application. Fig. 4 shows schematics of such a process.

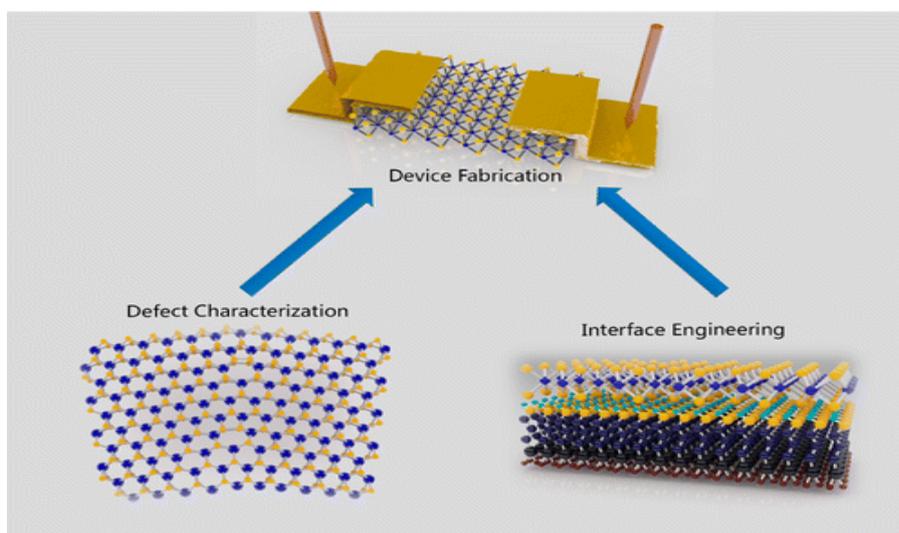


Fig.4 Defect engineering for device application [19]

The vast range of possibilities with the creation of defects and simultaneous doping with atom of another species has been realized by Komsa et al [23, 24], who studied the effect of electron irradiation on vacancy production. Using transmission electron microscopy (TEM) and DFT calculations they have shown that various structural defects can be induced in a controlled manner and the vacancies created by electron irradiation can be doped with other atomic species for tuning the electronic properties.

4. DEFECT SUBSTITUTION

The process of defect engineering and property modulation for suitable gas sensing applications with metal and non-metal atoms doping has been studied in graphene [25-31] over the last decade. In all cases it was found that the introduction of defects and dopants altered the sensitivity and selectivity of the gas sensors. Taking a cue from the encouraging results for graphene, doping MSNs is the state of art tool for the next generation of gas sensors. Several experimental studies [7, 10, 32-34] have proved the high potential of MSNs as gas sensors for NO_x and NH_3 adsorption. The recent years have also seen some interesting theoretical investigations of doping of ML MoS_2 for enhanced absorption of various toxic gases NO , NO_2 , NH_3 , and CO . The next section discusses this issue for non-metal and metallic dopants from first principles case studies in the last 2-3 years.

The effect of non-metal doping of pure ML MoS_2 with Boron, Phosphorus and chlorine for NO adsorption was demonstrated by Ding et al [16]. All dopants show good adsorption and the interactions of NO with MoS_2 is described by charge density changes, which is responsible for changes in the conductivity. Strong chemisorptions, especially with B and P were reported and the fact that pure MoS_2 shows only weak physisorption was also ascertained by them. Weak interactions between gas molecules and the sensing material cannot provide accurate readings and sensitivity. Doping provides the necessary sensitivity through chemical interactions and strong adsorptions. The adsorption is so strong with B with large energies that desorption time is very large and practically impossible. The best sensors are the ones that have adsorption energies in the intermediate range and the best candidate in the present scenario is the P doped MoS_2 , which makes both a sensitive and reversible sensor.

In their first principles calculation, Ma et al [15] show that doping pristine ML MoS_2 with transition metal (TM) atoms like Au, Pt, Pd and Ni leads to vast improvement in the performance of NO and CO gas absorption. Using the Vienna Ab-initio Simulation Package (VASP) they have simulated the TM doped at the S vacancies of ML MoS_2 and calculated the most stable adsorption configurations. The adsorption energies, distance of gas molecules to sensor surface, the DOS, charge densities etc have all been evaluated. Fig.5 shows the side view of the atomic structure and spin

density iso-surfaces for the adsorption of CO and NO gas on TM doped MoS₂. The bond length of the gas molecule and also distance between Gas molecule and TM are shown in the figure.

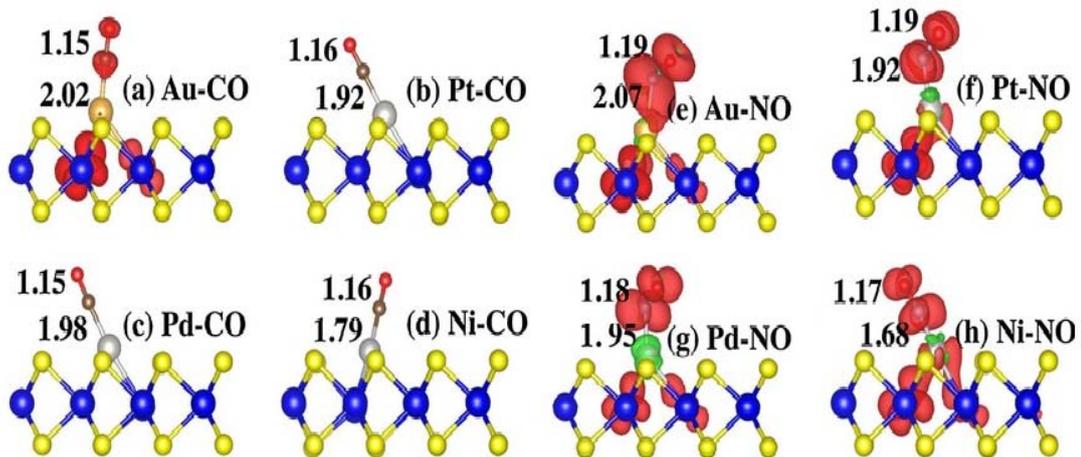


Fig. 5 Side view of the atomic structures and spin-density iso-surfaces of the CO and NO systems. The red and green regions represent positive and negative values (in $0.002 e/\text{bohr}^3$), respectively [15]

Again, in an attempt to determine the best gas sensor materials for the adsorption of NO₂ and NH₃, Luo et al [17] studied ML MoS₂ doped with Al, Si and P. The density of states (DOS) and the charge transfer between the gas molecule NO₂ and substrate taking place is shown for Si substitution as an example in Fig. 6 from their work.

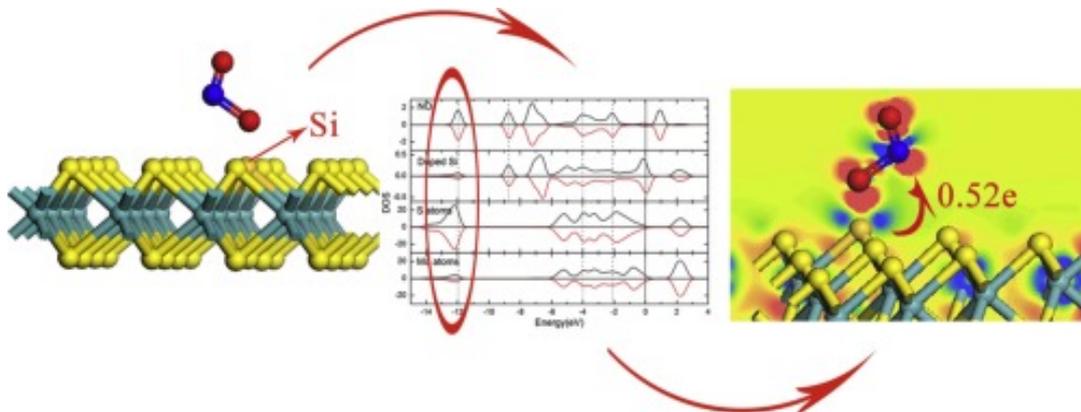


Fig. 6 Side view of the atomic structures, DOS and charge transfer

The dopants increase the stability of the adsorbing molecules by improving the orbital hybridization with the MoS₂ substrate and causing charge transfer.

The effect of Cu impurities embedded in ML MoS₂ on the adsorption of gases NO, NO₂, NH₃ and O₂ were investigated by Zhao et al [18]. The Cu atom is strongly attached to the S vacancy and shows high adsorption energy for NH₃ that acts as an electron donor, whereas, all the others act as electron acceptors. This can be seen from Fig.7 which shows side view of the stable atomic structures and charge difference densities for the adsorption of the different gas molecules. The yellow and cyan regions in the charge density plots represent the positive (electron accumulation) and negative (electron depletion) values respectively, and we see for NH₃ that the cyan color is predominant indicating it to be an electron donor.

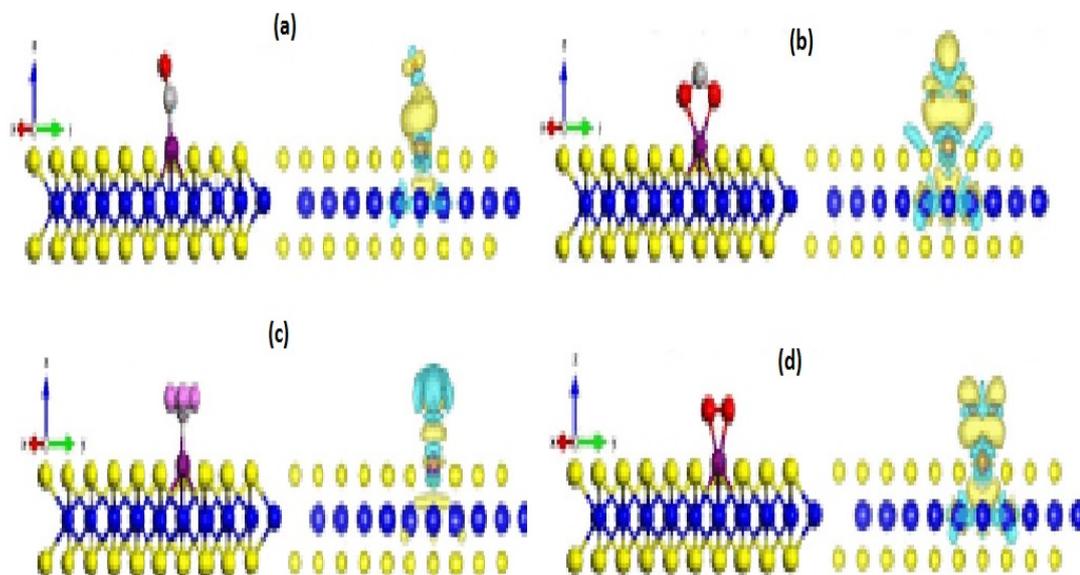


Fig. 7 Side views of the geometric structures and the charge density difference of a) NO b) NO₂ c) NH₃ and d) O₂ adsorption on MoS₂-Cu system, the pink, gray, violet, red, blue, and yellow spheres represent the H, N, Cu, O₂, Mo and S atom, respectively [18]

The hybridization of orbital between the TM Cu atom and the gas molecules gives rise to a change in the charge densities as observed. The environment around the dopants and nearby Mo atoms is changed by relaxations and chemical interactions to form an effective way of changing the transport properties of MoS₂ and increasing their performance as sensors. This exciting field of investigation of MSNs sensors through defect doping requires more first principles modeling for technological and feasibility assessments.

5. CONCLUSIONS AND OUTLOOK

Toxic gas sensing plays an important role in many walks of our life from environmental protection, human health to agriculture. Doping and defect substitution is a versatile and new tool for changing the chemical and electronic properties of 2D layered materials and boosting the applications of these materials. In the past decade, although, extensive research on Graphene as a gas sensor was conducted, the zero bandgap limited its potential and applicability. This is overcome in MoS₂ which is a direct bandgap semiconductor, with a large surface to volume ratio similar to graphene and can exhibit excellent sensing performance. MoS₂ as a 2D layered material has unique properties and the current focus is on defect engineering of MSNs for high sensitivity and selectivity. The large surface to volume ratio, bandgap and cheapness makes MSNs very attractive for gas sensor applications. Chemical doping is an effective way to alter the binding configurations and improve and enhance the application as a gas sensor. This promising method requires further investigations and research for industrial scale mass productions and for fabricating robust, low cost, highly sensitive and selective sensors that can be tested for best performance, reliability and repeatability to become a reality. It is hoped that this focused account of important first principles work on this new and promising research field will guide and encourage scientists and experimentalists to explore further.

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