

Chemical Vapor Deposition Grown MoS₂ for Sensing Applications

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Conclusions, Challenges and Future Work

8.1 CONCLUSIONS

In this thesis work, the recent progress and remarkable development in gas sensing field (especially for NO₂ gas sensing) by using the 2D MoS₂ were presented. In gas sensing field on commercial sensing platform, this research work provides a valuable output in terms of a room temperature NO₂ gas sensor which does not require microheater for operation. In addition, to explore the application of CVD grown MoS₂ in optoelectronics, a vertical out-of-plane rGO/MoS₂ heterojunction was fabricated as a photodetector in visible light range wavelengths.

Some key issues and problems related to gas sensing and photodetector are addressed in this thesis work. All outcomes of this thesis work are summarized given below: -

We synthesized a wide range of different nanostructures and morphologies of the MoS₂ on the rigid substrate by using chemical vapor deposition (CVD) process. We also fabricated some different exciting nanocomposites, and hybrid of the MoS₂. Further, we described the all exciting gas sensing results of the MoS₂ gas sensor, and these results demonstrate that 2D MoS₂ could be the best candidate for developing a high-performance room temperature gas sensor. Although, the sensitivity of the MoS₂ sensor was enhanced by nanostructure/surface engineering because different structure and morphologies render the different number of reactive sites for gas molecules interaction. Horizontally and mixed 3D network of horizontally and vertically oriented MoS₂ flakes by using the conventional CVD method were fabricated. They demonstrated about two times higher sensitivity to NO₂ gas of 3D network than that of horizontally oriented MoS₂ flakes. Moreover, the sensor exhibited high selectivity towards NO₂ against various gases with full reversibility at its low operating temperature (100 °C). The high sensitivity and selectivity towards to NO₂ gas were attributed to high material density and chemisorption on edge sites through dangling bond because edge sites atoms are unsaturated with low co-ordination number. Besides the edge sites as reactive sites for more gas interaction, surface-area-per-unit-volume aspect is also important for enhancing the sensing response. So, we fabricated a highly exposed edge site containing MoS₂ nanowires network by using the CVD process through creating a turbulent flow regime for growth. The MoS₂ nanowires network exhibited high sensitivity with a low detection limit of 4.6 ppb NO₂ with fast response (16 s) and complete recovery (172 s) at its optimal operating temperature. The synergistic effect of modulation of the potential barrier at the interface of two nanowires under gas environment and abundant exposed edge sites helped to enhance the sensing performance of the MoS₂ nanowires network. As demonstrated above, the sensing performance of the MoS₂ could be improved through generating edge sites rather than terrace sites of the MoS₂ via changing morphology (from 2D to 3D and then 1D) because edge sites are more chemically reactive due to presence of dangling bonds and terrace sites on basal plane of the MoS₂ are chemical inert. As a result, the geometry/morphology of the MoS₂ played a crucial role in enhancing the sensitivity as well as reducing the operating temperature of the sensor. Geometry engineering was capable to enhance the sensitivity of the sensor but it was limited to achieve the complete recovery at room temperature.

Mostly MoS₂ gas sensing reported results demonstrated a high gas sensing performance through interface and defect engineering separately, but there was no availability of any report for a comprehensive joint effect of both. For this reason, we performed a gas sensing experiment for a complete study on the effects of sulfur vacancy and interfacing with rGO on

the gas sensing characteristic of the MoS₂. The sulfur vacancy was created in additionally rich edge active sites of vertically aligned MoS₂ (Sv-MoS₂) via a simple annealing process and an optimal value of the p-type rGO particles was decorated on the surface of n-type Sv-MoS₂. A strong chemical bonding between rGO and Sv-MoS₂ led to a large number of charge transfer between rGO and Sv-MoS₂, resulting in p-type rGO/Sv-MoS₂ hybrid sensing material. The Sv-MoS₂ sensor shown higher positive response than pristine MoS₂ because several charges transferred between sulfur vacancy and NO₂ molecules and however, it showed lesser recovery due to strong binding attraction on vacancy sites through chemisorption process. The rGO/MoS₂ sensor also showed a higher positive response to NO₂, because charge transfer in between rGO and pristine MoS₂ through van-der Waals was insufficient to change the semiconductor behavior of the rGO/MoS₂ hybrid. On the contrary, interestingly, the rGO/Sv-MoS₂ sensor exhibited approximately three times higher negative response to that of the pristine MoS₂. We believed that sensing performance of the sensor was improved by a combination of abundance active sites in Sv-MoS₂ and strong chemical or electronic sensitization by the rGO particles.

The MoS₂ nanosheet is also used as a photoelectric gas sensor because it has a good photoelectric response to ultraviolet to near-infrared light. The photo-generated electron-hole pairs in MoS₂ significantly affect the absorption and deposition of gas. So, we fabricated a resistive gas sensor using MoS₂ nanosheet grown by CVD technique. The device was exposed to NO₂, NH₃, H₂, H₂S, CO₂, and CH₄ at room temperature under light illumination to address the selectivity of MoS₂ nanosheet. The results indicated that MoS₂ had the highest response to NO₂. Moreover, it was found that the decrement in response to NO₂ using thermo-activation and enhancement in response as well as ultrafast detection with complete recovery at room temperature of the MoS₂ gas sensor under optical energy. Thermal energy (temperature $\approx$ 100 °C) accelerated the desorption rate compared to the adsorption rate, which leads to a low response. On the other hand, under UV illumination, a photogenerated hole reacted with oxygen ion and formed O₂ (gas); thereby, the surface of MoS₂ was cleaned and had more reactive sites which were unoccupied by contamination and ambient oxygen. It was effectively regulated the sensing capabilities through light assistance, including detection sensitivity, selectivity and recovery rate.

However, nowadays, sensitivity is not the main issue in gas sensor technology, while selectivity, room temperature operation without a heater or UV-light energy source, and stability are the main challenges on the commercial platform. The individual MoS₂ based gas sensors show a substantial response to multiple gases with incomplete recovery at room temperature, which leads to poor selectivity of the gas sensors. Moreover, they also exhibited an unstable response with incomplete recovery in an air atmosphere at room temperature. To address these issue, we fabricated a NO₂ gas sensor operated at room temperature using MoS₂-MoO₃ hybrid micro flowers, and most importantly, we synthesized hybrid micro flowers using a simple one-step strategy of the conventional CVD process. The MoS₂-MoO₃ hybrid micro flowers consist of MoO₃ in core part and MoS₂ in the petal of the flowers as well as nanosheet on the substrate. In this work, n-type MoS₂ and n-type MoO₃ formed n-n type heterojunction, which leads to a potential barrier at the interface of MoS₂/MoO₃ due to different Fermi levels. The sensor showed a good response to a range of 10-100 ppm NO₂ with complete recovery at room temperature without any extra energy source such as optical or thermal energy. Moreover, a potential barrier modulation in the gas environment enhanced the sensitivity and stability of the MoS₂ and full recovery at room temperature was due to MoO₃ nanocrystals in the core of the micro flowers.

Table 8.1: Comparison between literature on MoS₂ material based NO₂ gas sensors and the present Works (MoS₂ Based Gas Sensor)

Material	Operating temperature	Gas NO ₂	Sensing response	Response time	Recovery time	LDL	Ref.
Horizontal MoS ₂ flakes	RT	100 ppm	27.92 %	249 s	Not recovered	0.5 ppm	Kumar et al., 2017
Horizontal MoS ₂ flakes	RT @ UV	100 ppm	35.16 %	29 s	350 s	100 ppb	Kumar et al., 2017
Horizontal MoS ₂ flakes	100 °C	50 ppm	11.86 %	62 s	220 s	0.6 ppm	Kumar et al., 2018
Vertical MoS ₂ flakes	100 °C	50 ppm	24.26 %	34 s	232 s	84 ppb	Kumar et al., 2018
MoS ₂ nanowires	60 °C	5 ppm	18.1 %	16 s	172 s	4.6 ppb	Kumar et al., 2018
rGO/Sv-MoS ₂	50 °C	50 ppm	72 %	56 s	328 s	50 ppb	Kumar et al., 2019
MoS ₂ -MoO ₃	RT	10 ppm	33.6 %	19 s	< 3 min	25 ppb	Kumar et al., 2018
MoS ₂ flakes	RT	1000 ppm	1372 %	3 min	Not recovered	-	Late et al., 2013
MoS ₂	RT @ UV	10 ppm	25.3 %	-	44 s	-	Kang et al., 2019
MoS ₂ hollow sphere	150 °C	100 ppm	40.3 %	79 s	225 s	500 ppb	Li et al., 2019
MoS ₂ Aerogel	200 °C	0.5 ppm	11 %	33 s	107 s	50 ppb	Long et al., 2017
MoS ₂ vertical	RT	100 ppm	10 %	-	-	-	Cho et al., 2015
Mixed MoS ₂ flakes	125 °C	10 ppm	7.79 %	4.4 s	19.6 s	-	Agrawal et al., 2018
MoS ₂	RT	20 ppb	>20 %	5-9 min	25 hours	-	Liu et al., 2014
P-type MoS ₂	200 °C	1 ppm	1.15 %	11 min	12 min	-	Donarelli et al., 2015

N-type MoS ₂	200 °C	1 ppm	5.58 %	41 min	39 min	20 ppb	Donarelli et al., 2015
MoS ₂	RT	25 ppm	97 %	3 min	8 min	-	Cho et al., 2015
MoS ₂	RT	400 ppb	671 %	16 s	65 s	20 ppb	Guo et al., 2019
MoS ₂	90 °C	5 ppm	25 %	-	-	0.15 ppm	Jung et al., 2018
MoS ₂ -Pt NPs	RT	0.5 ppm	6 %	-	>30 min	2 ppb	He et al., 2012
Pt-MoS ₂	RT	1.2 ppm	16 %	30 min	>30 min	-	Qiyuan et al., 2012
MoS ₂ /Graphene	200 °C	0.5 ppm	10 %	<1 min	<1 min	50 ppb	Hu et al., 2016
MoS ₂ /SnO ₂	RT	10 ppm	28 %	6.8 min	2.7 min	0.5 ppm	Cui et al., 2015
MoS ₂ /PbS	RT	100 ppm	23 %	30 s	235 s	-	Xin et al., 2019
MoS ₂ on SiO ₂ NRs	RT	50 ppm	390 %	-	Not recovered	2.3 ppb	Shim et al., 2018
Graphene/MoS ₂	150 °C	5 ppm	6.83 %	>1 min	> 15 min	-	Cho et al., 2015
rGO/MoS ₂	60 °C	2 ppm	59.8 %	>1 min	Not recovered	-	Zhoua et al., 2017
MoS ₂ -SWCNT	RT	40 ppm	54 %	-	-	1.5 ppm	Kim et al., 2018
MoS ₂ -Au	RT @ UV	2.5 ppm	30 %	4 min	14 min	-	Zhou et al., 2018
MoS ₂ -ZnO	RT @ UV	50 ppb	20 %	<1 min	<1 min	50 ppq	Zhou et al., 2018
Sv-MoS ₂ -ZnO	RT @ IR	0.2 ppm	226 %	75 s	111 s	0.1 ppb	Xia et al., 2020

In the view of the MoS₂ photodetector, the photoresponsivity of the MoS₂ based photodetector depends on the number of layers. The monolayer MoS₂ phototransistor exhibits less photoresponsivities as compared to multilayer MoS₂ based phototransistor. A strong variation in photoconductivity, photogain and response time of MoS₂ photodetector were observed with varying the geometries and operating condition of photodetector. Moreover, ambient conditions also affect the optical and electrical properties of 2D materials because of high surface to volume ratio and less activation energy for adsorbates. So far, to exploit the potential of 2D materials in optoelectronics, many phototransistors were fabricated with p-n junction through van der Waals heterostructures of different 2D materials. However, the transistor has extra gate bias which leads to a high value of leakage current and high dark current forms self-heating effect in channel. In this context, we demonstrated a vertical out-of-plane rGO/MoS₂ heterojunction based photodetector in order to examine the interaction of the MoS₂ with light in the visible wavelengths. The photodetector exhibited excellent photo-sensing behaviour without applying any gate voltage in air ambient. Integration of the MoS₂ with rGO nanoparticles developed depletion regions at nano junctions due to different work functions of the MoS₂ and rGO nanoparticles, thereby, a passivation layer on the surface of the MoS₂ is created after forming continuous film through combining all depletion regions with each other. It increased the stability of the MoS₂ in air atmosphere and also increased the lifetime of the photodiode. Meantime, the formation of a heterogeneous structure through molybdenum sulphide and rGO, especially the vertical out-of-plane p-n junction, change the bandgap structure of the device, which caused a better separation of electrons and holes by the developed electric field at the heterojunction. The rGO also tuned carrier concentration of the MoS₂ via photogating effect. Moreover, rGO helped to enhance the light absorption capability of the MoS₂. As a result, as-designed new vertical out-of-plane heterostructure materials after incorporating rGO material into the MoS₂ improves the photo-sensing performance of the photodetector through a synergistic effect of photogating and enhanced light absorption. Thus, surface decoration of 2D material with another material has been proved a simple design to form vertical PN heterojunction for optoelectronic device applications.

8.2 CHALLENGES AND FUTURE WORK

Overall, despite to all encouraging ongoing efforts and exciting sensing results of the MoS₂ gas sensor, it still needs to optimize the morphologies, structure, and hybrid of the MoS₂ for practical implementation on a sensing platform. Gas sensing mechanism needs to be further explained in great details by considering various factors such as surface states, edge sites, defects, crystallinity, electronic or chemical properties, strain, and chemical composition. All the above explanations are still qualitative. To be more precise, quantitative calculations are often required. The adsorption energy between material and gas, as well as the number of adsorption sites, have a profound impact on the gas-sensitive properties. Therefore, the studies of adsorption energy and adsorption sites are of great significance to further explain the mechanism. The gas sensor based on van der Waals heterostructure of the MoS₂ is still in a nascent stage, which provides more excitement and opportunities to a researcher to explore this field and to bring it on a commercial platform. However, in physical/chemical vapor deposition techniques, precise control and alignment of the material position restrict the formation of the MoS₂ heterostructure with other 2D materials for mass production of sensor devices. Thus, there is still a challenge for developing a robust, reliable and advanced fabrication approach for developing a sensor device on the industrial platform by using the nanocomposite/hybrid or van der Waals heterostructure of the MoS₂.

Over the last decade, Internet-of-Things (IoT) has registered its exponentially increasing presence with energy-efficient chip-scale devices due to the true realization of powerful computing and analytic capabilities for a variety of applications[Hart et al., 2015; Kelly et al., 2013; and Pang et al., 2015].. Nowadays, smartwatches, smartphones, smart tablets, and smart glasses on flexible substrates with wireless connectivity are fascinating [Camposeo et al.,

2009; Han et al., 2017; and Yan et al., 2014]. Moreover, chemical sensing applications of IoT have also received significant attention for the real-time detection of environmental pollutants and which is crucial not only in the medical diagnosis of several diseases but also to take preventive measures [Khan et al., 2016; Haghi et al., 2017; Yang et al., 2019; Dias et al., 2018; and Mukhopadhyay et al., 2015]. Despite the enormous potential of flexible and stretchable sensors in wearable technology [Han et al., 2017; and Singh et al., 2018], this field still remains less explored, particularly in chemical sensing applications. Conventional semiconductors can also be used in developing flexible electronic sensors. For instance, Si can be used for making flexible devices by thinning it down below a particular value [Shahrjerdi et al., 2013]. However, Si poses a severe threat to the reliability of the devices due to its brittle nature [Wang et al., 2016]. Other approaches including use of organic semiconductors for making flexible devices were also investigated [Forrest et al., 2004]. However, these technologies also suffer setbacks due to a low value of mobility of charge carriers and high operation voltages [Gao et al., 2017]. The lowered value of mobility reduces the driving capacity of the device, and the large voltage requirement makes the circuitry complex. Interestingly, polycrystalline Si offers a high value of mobility but deteriorates the performance of the device due to the considerable value of leakage current and high cost of flexible electronic devices [Pecora et al., 2008]. Thus, traditional approaches face several impediments restricting their use by the flexible industry.

The last few years have witnessed the exploration of several properties of atomically thin layered 2D materials particularly for flexible and stretchable devices [Akinwande et al., 2014; Kim et al., 2015; Han et al., 2018]. Their low-power consumption, high mobility of charge carriers, lightweight, high stretchability, reliable mechanical robustness, excellent optical transparency, and good environmental stability make them excellent candidates for flexible devices. Recently, several 2D materials, including graphene, TMDCs, and MXenes, have shown their potential for fabricating stretchable and flexible devices that can be used in foldable displays, memory devices, photodetectors, supercapacitors, and lithium-ion batteries [Jang et al., 2016; Shao et al., 2015; Singh et al., 2017; Singh et al., 2019; Wang et al., 2018; Zhang et al., 2017; Dong et al., 2018; and Yang et al., 2018]. The large surface-to-volume ratio establishes 2D materials as the torch-bearer in chemical sensing applications. The 2D MoS₂ could be directly used in a flexible and wearable gas sensor because of its good transparency and mechanical properties such as large strain limit and high elastic modulus. Detection of gases at room temperature by the MoS₂ eliminates micro heater from the sensor and makes it a perfect choice for flexible gas sensor. The utilization of the MoS₂ in the emerging flexible and wearable sensing field is still a new area. Thus, it is expected that more unprecedented sensing results and new concepts would be investigated and developed in the coming years. This developing field is continuing to provide fascinating new opportunities for researcher and industries via uptake the MoS₂ into flexible and wearable sensors.

On the other hand, the replacement of rigid metal electrodes by depositing flexible 2D metallic materials as electrodes in sensor device would enhance the sensing performance, transmittance as well as flexibility, and pave the way for e-skin-oriented and e-textiles nano-gas sensor by improving conformal contact with the human body and ease integration with textile or single fiber, respectively. So, the 2D MoS₂ material is also suitable for e-skin-oriented and e-textiles nano-gas sensor through the flexible nanotechnology as they offer atomic-scale thickness with a high value of flexibility and transparency. On the other hand, detection of gases at room temperature by the flexible MoS₂ material based gas sensors also reduce the cost of the sensor through reducing the cost of the heater as well as removing complex fabrication technology' steps. The fabrication of the sensor using MoS₂ material on a common cellulose paper via facile wet-chemical process make it cheaper and disposable. Moreover, low power consumption helps to reduce the thermal effects on the human body as well as increases long-term operation.

In the field of opto-electronics, 2D MoS₂ material has been gained enormous attention of the research communities and academicians for developing advanced photodetector devices for

outstanding performance because of its remarkable optical, electrical and physical properties. However, each materials has its own advantages and limitations. The device's performance uniformity and stability in an atmosphere ambient are main issues and moreover, highly crystalline MoS₂ on large-scale as well as mass production are still challenges for developing practical devices on commercial and industrial platform. There are many reports on photo-detection in UV and visible range, however, photo-detection in infrared range is rare which limits its exploitation in useful infrared light communication. Moreover, spectral response of the photodetector should be analysed for finding suitable wavelengths regions as well as exploring silent features and underlying physics. Metal electrodes physics as well as lowering contact resistance value are most important factors for modulating performance of the opto-electronics devices. Despite having issues for photo detection, some have been addressed and further also need to be made in future for improving main aspects such as sensitivity, speed, wavelength range and dynamic range of photodetector. The surface decoration of the 2D materials with 0D quantum dots is a good hybrid approach for improving the performance of photodetector. The emerging van der Waals heterostructures and photogating transistors enhance photo-gain and improve ultrahigh responsivity. In order to further enhance light-matter interaction, integration of optical waveguides and microcavities, and incorporation of plasmonic nanostructures are very helpfull techniques. Overall, simple and reliable cost-effective fabrication technique, mixed dimensional heterostructures and a novel device design should be optimized or developed for better device performance. Integration of the MoS₂ material with current Si photonics could be a possible approach for commercial acceptance. The collaborative efforts of academia and industry can built a bridge over a gap between lab research and commercial product.

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