Journal of Interfaces, Thin films, and Low dimensional systems 3 (1) Summer and Autumn (2019) 227-231

Optical MoS_2 nanosheets gas sensor: experimental study

Scientific research paper

Mohammad Sharif Shazileh[1], Saeid Shojaei[1,2*], Sohrab Ahmadi Kandjani[1,2]

[1]*Research Institute for Applied Physics & Astronomy (RIAPA), University of Tabriz, Tabriz, Iran*

[2]*Photonics & Plasma engineering Department, Faculty of Physics, University of Tabriz, Tabriz, Iran*

ARTICLE INFO

Article history:
Received 20 June 2020
Revised 7 October 2020
Accepted 11 October 2020
Available online 25 October 2020

Keywords:
2D materials
Gas sensors
Transitional metal
Di-chalcogenides (TMDCs)

ABSTRACT

We propose a full optical method for gas sensing by few-layer MoS_2 nanosheets obtained by liquid-phase epitaxy (LPE). Our samples are fully characterized by transmission electron microscopy (TEM), photoluminescent (PL) spectroscopy, and X-ray diffraction (XRD). Further characterization and evaluation of gas sensing application, had been done by implementing ultraviolet-visible spectroscopy (UV/Vis). For CO_2 gas which acts as a donor to our sample (based on the evaluation method that used in this work), we calculate the response in the visible region equal to 15% while in longer wavelengths (near-infrared) the response clearly decreased. Our experiments show that using 2D transitional metal dichalcogenide (TMDC) materials for Gas sensing applications may open a new horizon for using this kind of 2D material in various types of optical sensors.

1 Introduction

One of the most concerning issues in every society is the air pollution and release of dangerous gases like CO_2 and CH_4 which might cause some serious problems regarding life on Earth like global warming. In recent years, many efforts have been made in developing sensors based on optical absorption for gas sensing since some gases are highly explosive and usual electrical sensors may not prove suitable to be employed for sensing applications. For example, any electrical spark can cause huge disasters in such cases [1]. Recent methods have led to the development of systems with higher sensitivity, smaller size, wider cover range, and cost-effectiveness [2, 3, 4]. Among the two-dimensional materials, graphene is one of the materials that attracts the most attention [5]. Graphene-based gas sensors show better performance in comparison to most of the nanomaterials in terms of the high sensitivity and fast sensing of gas molecules because of their one-atom thickness, extremely high surface-to-volume ratio, huge gas-absorption capacity, and ultrafast carrier mobility [6,7]. However, the main problem feature of graphene is that this material has no band-gap which means that one can observe an absorption at all frequencies and there is no selectivity in desired frequency at which absorption occurs [8]. This has led researchers to look for a suitable two-dimensional alternative for graphene. Recently, other kinds of 2D materials have proved interesting to investigate. For instance, among materials, the transitional metal di-chalcogenide (TMDCs), has many significant advantages in comparison with other 2D materials. The TMDC's

*Corresponding author.
Email address: S_shojaei@tabrizu.ac.ir
DOI: 10.22051/jitl.2020.31874.1040

group has more than forty types of layered materials with the same stoichiometry MX_2. Where M (e.g. Molybdenum) refers to transitional metal and X refers to a chalcogenide (e.g. Sulfur).

TMDCs have a wide range of electronic, optical, mechanical, chemical, and thermal properties studied by researchers in recent decades [9, 10, 11]. Also, many new opportunities in various fields have become possible since new modern fabrication and characterization processes have been achieved. Similar to other layered material, every single layer in TMDC bulk crystal, bond to each other by Van der Waals force so they can easily exfoliate to a few layered forms which ensures us to easily use them for 2D optoelectronic applications [12]. Among these materials, MoS_2 has been extremely investigated theoretically and experimentally. Previous studies show TMDCs are highly layered-dependent so we can tune the band-gap for TMDCs such as MoS_2 with manipulating the thickness and number of the layers. Moreover, lately the studies have shown that the band-gap could change from 1.2 eV indirect for bulk material of MoS_2 to a direct gap semiconductor with 1.9 bandgaps for single-layer MoS_2 [9, 12, 13]. Consequently, MoS_2 has high surface-to-volume ratio and flexibility compared to graphene so we expect that this material can be a suitable candidate for chemical sensors particularly gas sensors. The paper continues as follows, in section 2 we introduce our experimental methods, then in section 3 we discuss our results, and finally, our work concludes in section 4.

2 Preparation and characterization

2.2 Preparation of MoS_2 nanosheets

There are many methods for the synthesis of few-layere MoS_2 such as chemical vapor deposition (CVD) [14], Pulsed Laser Deposition (PLD) [15], and solution processing techniques [16]. Among these methods, liquid phase epitaxy (LPE) has several superiorities such as low cost, mass production, and simple process. In this method, the few-layered MoS_2 are exfoliated by dispersing the bulk material in suitable solvents. In our work the preparation of MoS_2 Nanosheets using LPE involves the following three steps: First, we mixed the bulk MoS_2 with a suitable solvent N-methyl pyrrolidone (NMP) with an initial concentration of 10 mg/mL. In the next step, the mixture is ultra-sonicated for 1 hour in a probe sonicator equipment model of Q700 SONICATOR in order to break the weak Van der Walls forces between layers. Finally, the resultant solution is centrifuged at 1500 rpm for 60 minutes. For all material characterization and sensing applications, samples are prepared by the drop-casting method [17]. In this work, we used silica as a substrate and pipet as a drop-casting instrument.

2.2 Material characterization

2.2.1. Transmission electron microscopy (TEM)

TEM is the standard tool to find the length and the width of nanosheets. For few-layered samples, high-resolution TEM is utilized to confirm the single layer formation and also to find the number of layers. Usually, a drop of a given dispersion is placed on a holey carbon grid and dried in ambient condition. In this work, TEM images were taken by Zeiss LEO 906 instrument. As shown clearly in Fig. 1, large areas of transparent two-dimensional objects were observed with the average size of 180-200 nanometer which completely agrees with previous studies about MoS_2 nanosheets [18]. In the case of self-folding or multilayer nanosheets, we see that some parts of these sheets become dimer.

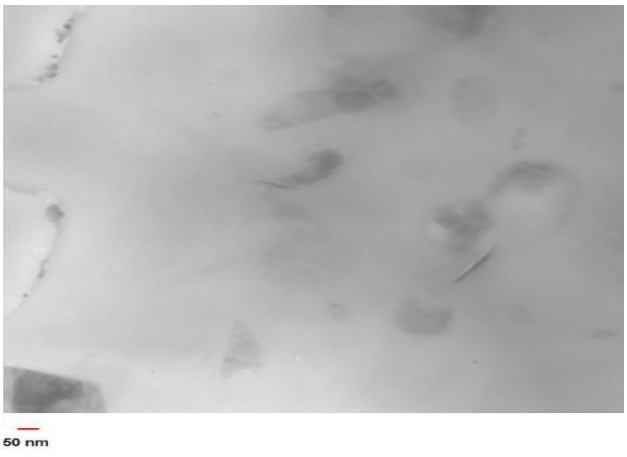

Figure 1. TEM image of the exfoliated MoS_2.

2.2.2. Ultraviolet-visible and photoluminescent spectroscopy

We used Ultraviolet-visible spectroscopy (UV/Vis) and photoluminescent (PL) spectroscopy to evaluate the quality of our sample. In our work, we used UV-2450 SHIMADZU UV VISIBLE SPECTROPHOTOMETER. As clearly shown in Fig. 2a, four peaks at 395 (A), 455 (B), 615 (C), and 675 nm (D) are observed that are in agreement with previously reported works [18, 19, 20]. The A and B peaks are due to transitions between higher density state regions of the MoS_2 band structure whereas C and D peaks result from interband excitonic transitions. Also, the photoluminescent (PL) spectroscopy is performed with JASCO FP-6200 spectrofluorometer.

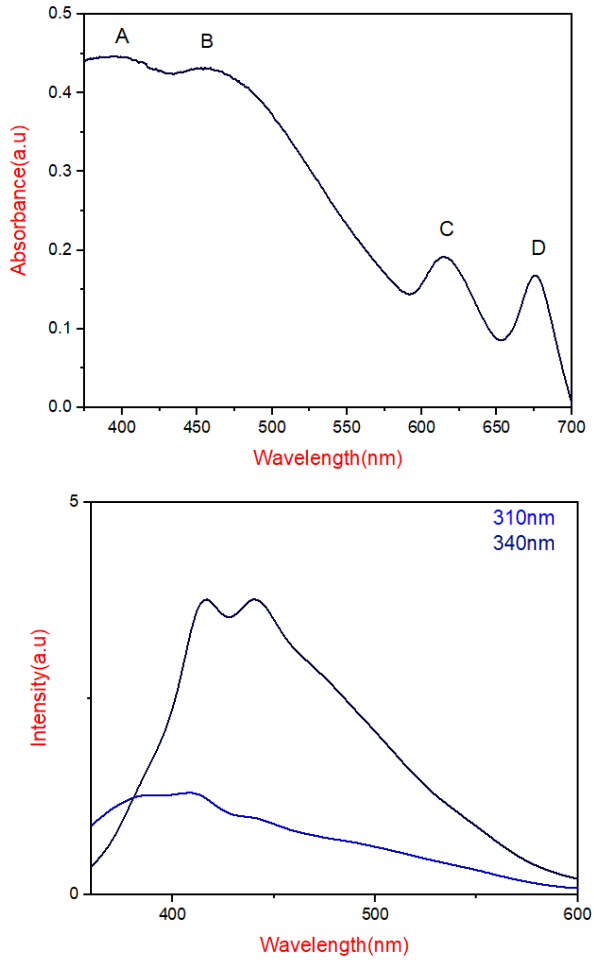

Figure 2. a) Optical absorption spectroscopy of few-layer MoS_2 sample. b) Photoluminescence spectroscopy of few-layer MoS_2 sample.

Figure 2b depicts that at the 310 and 340 excitation wavelengths we have the same results which have good consistency with valid references, these results can ensure that our sample contains nanosheets [20].

2.2.3 X-Ray Diffractometer

Finally, to complete our characterizations, we use the X-ray diffraction (XRD) characterization method to confirm the crystalline nature of MoS_2 nanosheets with the Simens D500 equipment and the result is illustrated in Fig.3. The [002] peak observed in 14.4 degrees can absolutely confirm that we successfully exfoliated bulk MoS_2 into layered MoS_2. We also illustrate the XRD diagram of a substrate (Silica: SiO_2) alone (right diagram) to highlight the formation of few layer MoS_2 compared to the left diagram. [20, 21].

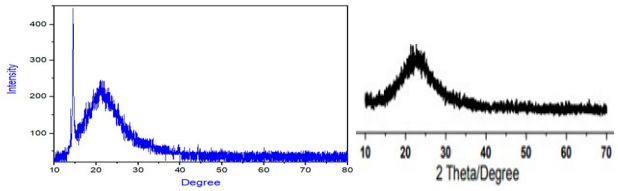

Figure 3. a) XRD analysis of few-layer MoS2 with silica substrate and b) XRD analysis of silica substrate solely.

3 Gas sensing result and discussion

For gas sensing test we prepare our sample in the same way that we prepare it for characterization and we used SHIMADZU UV VISIBLE spectrophotometer for evaluating our sample. Fig. 4 shows our experimental setup with both a photograph and a schematic diagram. A CO_2 capsule is used for injecting gas into the quartz tube, also we can use an air pump for relaxing our sample from being exposed to CO_2 continuously. As mentioned before many researchers took advantage of the possible application for MoS_2 or other TMDCs [22-25].

According to our best knowledge in this work for the first time, we investigate the optical properties of MoS_2 nanosheets for CO_2 sensing. As shown in Fig. 5, the absorbance diagram increases, as the Gas exposure time continues. This dedicates the electron charge transfer between absorbed CO_2 molecules to our substrate containing MoS_2 sheets. This shift of the

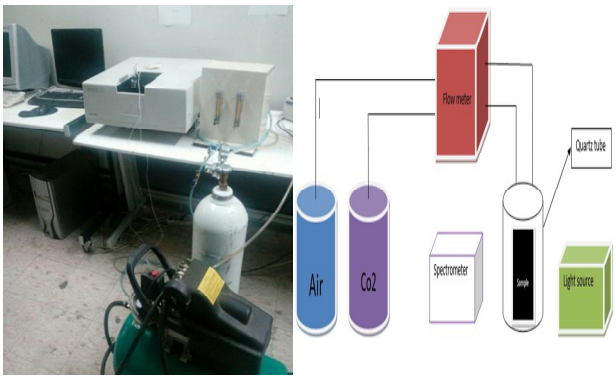

Figure 4. Our experimental setup for gas sensing and the schematic diagram.

absorption to higher energies due to the doping of the impurities is called Burstein- Moss shift [26]. The gas sensor response, S, is defined using the following equation [27]

$$S\ (\%) = \frac{Igas - Iair}{Iair} \times 100, \qquad (1)$$

where Iair and Igas are the optical absorption intensity of GQDs in air and CO_2 gas exposure, respectively. From Fig. 5 and taking Eq. (1) into consideration, we can calculate the sample sensitivity in the wavelength of 395 to 455 around 15%. Also for both 615 and 675 peaks at the wavelength of near-infrared, the response is 6% which is much less than of UV-Visible region, and as the wavelength reaches the infrared region, response completely converges to the basic response (0 Min). These results are completely in agreement with our predictions since the Burstein-Moss shift affected the direct transitions rather than excitonic transitions. Also, the absorption spectrum is largely altered if the doping level is increased by contaminating our sample with exposure to gases such as CO_2, this shift in the absorbance diagram gradually tends to the point of degeneracy after 10 minutes.

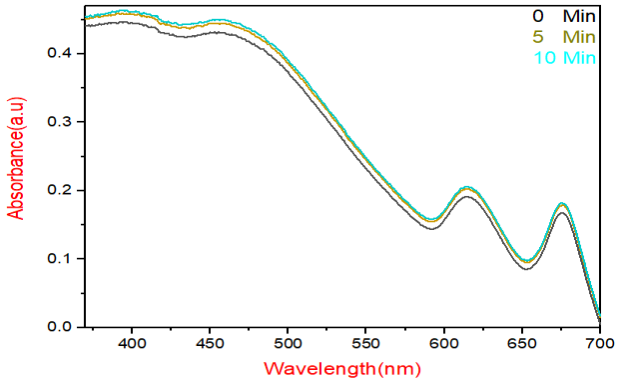

Figure 5. Difference between absorbance diagram of MoS_2 nanosheet sample before and after exposing to CO_2.

4 Conclusion

In this work, we produced a few-layer MoS_2 with a cost-effective and also applicable method. Our characterization results prove the precision of our method. After that, we show the capability of few-layered MoS_2 as sensing material with our cost-effective gas sensing set up. Our works introduces one of the less seen features of transitional metal dichalcogenides applications. Our sensor has a good response in the UV-Visible region due to the band-gap properties of the MoS_2 nanosheets. We hope that this work cause enthusiasm for using TMD's family for many chemical and gas sensors in the future.

References

[1] I. Matias, S. Ikezawa, J. Corres, Fiber Optic Sensors: current status and future possibilities, Springer, 2016.

[2] K. Wetchakun et al., "Semiconducting metal oxides as sensors for environmentally hazardous gases." Sensors and Actuators B: Chemical, **160** (2011) 580.

[3] J. Ren et al., "Few-layer MoS_2 dendrites as a highly active humidity sensor." Physica E: Low-dimensional Systems and Nanostructures, **116** (2020) 113782.

[4] C. Neto et al., "The electronic properties of graphene." Reviews of modern physics, **81** (2009) 109.

[5] B. Shivananju et al., "The Roadmap of Graphene-Based Optical Biochemical Sensors." Advanced Functional Materials, **27** (2017) 1603918.

[6] D. Raeyani, S. Shojaei, S. AhmadiKandjani, "Optical graphene quantum dots gas sensors: experimental study." Materials Research Express, **7** (2020) 015608.

[7] M. Polini et al., "Artificial honeycomb lattices for electrons, atoms and photons." Nature Nanotechnology, **8** (2013) 625.

[8] S. Manzeli et al., "2D transition metal dichalcogenides." Nature Reviews Materials, **2** (2017) 17033.

[9] L. Xiong, et al., "Research progress on the preparations, characterizations and applications of large scale 2D transition metal dichalcogenides films." FlatChem **21** (2020) 100161.

[10] Y. Jiandong, G. Yang, "2D group 6 transition metal dichalcogenides toward wearable electronics and optoelectronics." Journal of Applied Physics, **127** (2020) 030902.

[11] W. Qing Hua et al., "Electronics and optoelectronics of two-dimensional transition metal dichalcogenides." Nature nanotechnology, **7** (2012) 699.

[12] L. Xiao, H. Zhu, "Two-dimensional MoS_2: Properties, preparation, and applications." Journal of Materiomics, **1** (2015) 33.

[13] A. Wilson, A. D. Yoffe, "The transition metal dichalcogenides discussion and interpretation of the observed optical, electrical and structural properties." Advances in Physics, **18** (1969) 193.

[14] C. Chunxiao et al., "Synthesis and Optical Properties of Large-Area Single-Crystalline 2D Semiconductor WS_2 Monolayer from Chemical Vapor Deposition." Advanced Optical Materials, **2** (2014) 131.

[15] V. Fominski et al., "Ion-assisted deposition of MoS_x films from laser generated plume under pulsed electric field." Journal of Applied Physics, **89** (2001) 1449.

[16] V. Nicolosi et al., "Liquid exfoliation of layered materials." Science, **340** (2013) 1226419.

[17] J. Shanshan et al., "Exfoliated MoS_2 nanosheets as efficient catalysts for electrochemical hydrogen evolution." Electrochimica Acta, **109** (2013) 269.

[18] J. Coleman et al., "Two-dimensional nanosheets produced by liquid exfoliation of layered materials." Science, **331** (2011) 568.

[19] A. Harith et al., "S-band Q-switched fiber laser using molybdenum disulfide (MoS_2) saturable absorber." Laser Physics Letters, **13** (2016) 035103.

[20] G. Deepesh et al., "MoS_2 quantum dot-interspersed exfoliated MoS_2 nanosheets." ACS nano, **8** (2014) 5297.

[21] Z. Qiaohong et al., "Facile preparation of highly-dispersed cobalt-silicon mixed oxide nanosphere and its catalytic application in cyclohexane selective oxidation." Nanoscale research letters, **6** (2011) 1.

[22] L. Hongxing et al., "Markedly different adsorption behaviors of gas molecules on defective monolayer MoS_2: a first-principles study." Physical Chemistry Chemical Physics, **18** (2016) 15110.

[23] S. Mohapatra et al., "Modulation of gas adsorption and magnetic properties of monolayer-MoS2 by antisite defect and strain." The Journal of Physical Chemistry C, **120** (2016) 14113.

[24] S. Byung, J. YongáSong. "Sensor based on chemical vapour deposition-grown molybdenum disulphide for gas sensing application." RSC advances, **6** (2016) 75839.

[25] A. Shokri, N. Salami. "Gas sensor based on MoS2 monolayer." Sensors and Actuators B: Chemical, **236** (2016) 378.

[26] Pallab Bhattacharya, Semiconductor optoelectronic devices. Prentice-Hall, Inc., 1994.

[27] R. C. Bailey et al., "Chemical and biological sensors and analytical methods II." The Electrochemical Society Proceedings, Pennington, NJ 511 (2001).