Enhanced adsorption sites in monolayer MoS$_2$ pyramid structures for highly sensitive and fast hydrogen sensor

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HIGHLIGHTS

- Enhanced adsorption of H$_2$ gas on monolayer MoS$_2$ pyramids for H$_2$ sensing.
- Least response time, high sensitivity and fast recovery of bare MoS$_2$ for H$_2$ sensing.
- High sensitivity of 24% for 0.1% H$_2$ by monolayer MoS$_2$ pyramid structures.
- Verification of favourable H$_2$ adsorption sites by the DFT results reported.

ABSTRACT

Here, we present a highly sensitive and fast hydrogen (H$_2$) sensor for 1% H$_2$, well below the critical limit of explosion ignite in air, in a temperature range of 28–150 °C by using monolayer MoS$_2$ pyramid structures with enhanced adsorption sites. The monolayer MoS$_2$ pyramid structures is synthesized by modified chemical vapor deposition technique and characterized by field emission scanning electron microscopy, Raman, photoluminescence and atomic force microscopy. The highest sensitivity of 69.1% was achieved at a moderate temperature with a response time of 32.9 s for the monolayer MoS$_2$ pyramid structures. At room temperature (RT), the sensor showed a sensitivity of 6% with a faster response of 11.3 s and recovery time of 125.3 s. The availability of favourable H$_2$ adsorption sites on in-plane MoS$_2$ and edges of MoS$_2$ in monolayer MoS$_2$ structures provide enhanced adsorption sites for gas sensing and resulted in the high sensitivity and low response time compared to that of bare MoS$_2$ and other nanostructures-based H$_2$ sensor. The detailed gas sensing mechanism is proposed in the light of detail surface morphology and density function theory (DFT). This study reveals that tailoring the favourable adsorption sites in 2D materials is helpful to develop the highly sensitive and fast H$_2$ sensor for next generation safety devices for H$_2$ fueled vehicle and clean energy applications.

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Introduction

Recently, hydrogen (H₂) based energy sources emerged as a potential candidate for production of clean and renewable energy, which is considered as the next generation energy source [1]. H₂ energy has been significantly attractive to the worldwide community due to its very high heat combustion (142 kJ/g). Moreover, it also provide independence from limited fossils fuels, and produce clean combustion product compared to those produced by nonrenewable energy sources [2,3]. Nowadays, H₂ gas is broadly used in many areas like chemical, aero-scope, space transportation, oil refining industries and medicine. However, H₂ is extremely explosive and flammable gas if its concentration is greater than 4% over environment volume due to its low ignition energy (0.017 mJ). Hence, a small leakage of the H₂ in any system is very dangerous and detrimental to the safe operation of H₂. Thus, in order to find leakages before a hazardous situation occurs, a highly sensitive, selective, fast recovery and responsive H₂ gas sensor is required.

Over the past few years, semiconducting molybdenum disulfide (MoS₂), a promising member of the transition metal dichalcogenides family has been intensively become the focus of the research community. MoS₂ has exceptional electronic, sensing, optical, catalytic and biological properties [4–6]. MoS₂ consists of the stacked three atoms thick layers bounded by strong covalent bonds and a weak interlayer van der Waals bonds [7]. Bulk MoS₂ has the indirect bandgap of 1.2 eV, which converts to a direct bandgap of 1.8 eV when bulk MoS₂ is thinned down to one layer [7,8]. Due to the higher direct band gap (1.8 eV), faster charge transport, higher surface to volume ratio and higher electron concentration at the surface, MoS₂ has gained tremendous interest for the development of next generation memory devices, solar cells and photodetectors [9–12].

Moreover, MoS₂ has inherent electrical, physical and chemical properties for gas sensing applications [13]. MoS₂ has higher surface-to-volume ratio and an easy way to control adsorption sites in comparison to traditional sensors [14,15]. Recently, the research community has continuously developed H₂, NO₂, NH₃, and H₂S gas sensors based on MoS₂ [16–18]. There are some important parameters like sensitivity, response and recovery time to elucidate the performance of the any gas sensor. The sensitivity is defined as ratio of change in resistance after gas exposure to resistance in presence of air $R_{gas}/R_{air}$ × 100% where $R_{gas}$ and $R_{air}$ is the resistance in presence of H₂ and air, respectively. The response time is defined as time required for a sensor to change resistance from 10 to 90% and recovery time is the time required to decay resistance from 90 to 10% of overall change.

However, bare MoS₂ based H₂ gas sensors suffered from long response time, long recovery time and low sensitivity, which is quite impractical for fast detection of H₂ gas [3,19–21]. Moreover, these parameters are enhanced by forming MoS₂ heterostructures with metal nanoparticles, Carbon nanotubes, TiO₂, reduced graphene (rGO) and graphene [22–28]. These strategies improved sensing performance, but also lead to increase complexity in device manufacturing [28–31].

In a chemiresistive gas sensor, gas molecules interact/adsorb on the sensing materials and charge transfer takes place between them. This charge transfer induces the change in the electrical resistance of the sensing materials. It has been reported that the gas adsorption is strongly dependent on the particular favourable sites on MoS₂ flakes [22,23,23]. The researchers focused to enhance the favourable adsorption sites of bare MoS₂ by modified growth and orientation of MoS₂ [15,18,34]. However, these in-plane MoS₂ or edge-enriched MoS₂ based sensor either suffered from low sensitivity or higher response and recovery time.

Here, we developed H₂ gas sensor based on monolayer MoS₂ pyramid structures. The height of monolayer MoS₂ pyramids varied from 3 to 25 nm stacked in-plane layers and the top of the pyramids have edge-oriented flakes with a height between 3 and 6 nm. We studied the sensing behavior of sensor down to 1% H₂ gas in the temperature range of 28–150 °C. We observed the highest sensitivity of 69.1% at moderate temperature with a response and recovery time of 32.9 and 141.8 s, respectively. At moderate temperature, sensor also showed a good sensitivity of 24% down to 0.1% of H₂. At RT, the sensor showed significant sensitivity of 6% with fast response and recovery time of 11.3 and 125.3 s, respectively. We proposed that our response time is shorter for a bare MoS₂ based H₂ sensor due to availability of enhanced favourable adsorption sites on in-plane flakes as well as on edges of monolayer MoS₂ pyramid structures. This study revealed that increase in favourable adsorption sites could lead to a fast response and highly sensitive RT H₂ gas sensor.

Experimental section

Synthesis of monolayer MoS₂ pyramids structures

Monolayer MoS₂ pyramids with edge-oriented top flakes fabricated on SiO₂/Si substrate by using modified chemical vapor deposition (CVD) techniques. The sulphur (99.8%, Sigma Aldrich) and MoO₃ (99.8%, Sigma Aldrich) powder were used for the growth of MoS₂ layers. We used the modified three zone chemical vapor deposition technique to grow the monolayer MoS₂ pyramid with edge-oriented top flakes and a small quartz tube closed at one end of the small quartz tube. The small tube was placed inside the big quartz tube in such a way that the close end of the small tube faced in-gas flow. The sulphur powder was placed at the open end in zone 2 and MoO₃ powder was placed in zone 1 at the closed end. The schematic of the experimental setup is shown in Fig. 1(a) and the temperature profile is shown in Fig. 1(b). The growth temperature for the sulphur and MoO₃ powder was 350 °C and 800 °C. The growth time of the deposition was 5 min followed by the natural cooling of CVD. We kept the argon gas flow 175 sccm than slowly decrease up to 100 sccm.

Characterization

The synthesized monolayer MoS₂ pyramids were characterized by field emission scanning electron microscope (FE-SEM), photoluminescence (PL), Raman and atomic force microscopy (AFM). The PL and Raman spectroscopy were performed by
HORIBA iHR 320 spectrometer with a home built optical microscope setup with 532 nm laser at fixed power of ~1 mW and a spot size of 1 μm. The circular Au/Cr metal contacts of 250/5 nm thick and having diameter 100 μm with separation of 500 μm each was deposited by thermal evaporation. The H₂ gas was diluted with Ar gas to test at different concentration in home-build setup. 1% H₂ gas concentration mixed with 99% argon was mixed in a home-built gas setup. The sensing measurements were done by computer controlled 4200 Keithley setup. The biasing voltage was fixed at 4 V during all the sensing measurements by a computer controlled Keithley 4200.

Results & discussion

Structure and morphological study

Fig. 2(a) shows the surface morphology of as-synthesized monolayer MoS₂ pyramid structures. The black region in FE-SEM image shows in-plane monolayer MoS₂ pyramids while white region on top of black pyramid shows edge-oriented MoS₂ flakes [16,18,34]. We further performed close view of completely developed MoS₂ pyramids shown in Fig. 2(b).

Fig. 2(c) shows an individual MoS₂ pyramid where growth of vertically aligned MoS₂ flakes just started. A small hump can be seen clearly in Fig. 2(c) which converts in complete vertically aligned MoS₂ structures with time. Some more FESEM images are added in supplementary information as Fig. S2 for better clarity. Two characteristic Raman peaks are observed at 387.4 and 412.3 cm⁻¹ respectively corresponding to in-plane (E₁₂g) and out of plane (A₁g) lattice vibrations of MoS₂ as shown in Fig. 2(d) [29, 30]. The E₁₂g peak arises due to in-plane vibration of S and Mo atoms in opposite direction, while A₁g peak arises due to out of plane vibration of only S atoms, keeping Mo atom at rest. Thus, the peak intensity ratio A₁g/E₁₂g can be used to identify the orientation of MoS₂ flakes. The intensity ratio between A₁g/E₁₂g is 0.6 and ascertained that most of Raman intensity signals are corresponding to in-plane MoS₂ flakes [34–36]. Fig. 2(e) depicts the photoluminescence spectra of MoS₂ film and showed two prominent peaks at wavelength of 632.71 nm and 678.00 nm. These two peaks arise due to direct excitonic transfer between conduction band minimum to two split valence bands maximum. The valence band is split due to spin orbit coupling [37]. The crystal structure and phase identification has been done by the XRD. We observed the four sharp XRD peaks (002), (004), (101) and (006) at the 14.09°, 29.10°, 32.5°

Fig. 2 — (a–c) FE-SEM image of monolayer MoS₂ pyramids with edge-oriented top flakes. (d) The Raman spectra of MoS₂ film with two well-known peaks corresponding to E₁₂g and A₁g vibrations. (e) PL spectra of MoS₂ film having B and A exciton peaks at 632.71 nm and 678.00 nm. (f) XRD spectra obtained from the film confirming the purity of the grown MoS₂ flakes.
and 44.05°. These peaks are well reported in vertical MoS₂ growth and can be indexed to hexagon phase of MoS₂ [38,39]. The XRD peaks for the MoS₂ further confirmed with JCPDS Card No. 37–1492. The synthesis of the MoS₂ flakes is a two-step process. (i) Reduction of MoO₃ in reduced MoO₂ (ii) Sulphurization of reduced MoO₃ to MoS₂ flakes. The possible chemical reactions are as follows:[34]

\[ \text{2MoO}_3 + S \rightarrow \text{2MoO}_2 + \text{SO}_2 \]  
\[ \text{MoO}_2 + 3S \rightarrow \text{MoS}_2 + \text{SO}_2 \]  

If there is any presence of reduced MoO₃, it should reflect in XRD. However, we did not observe any peak of reduced MoO₃. Thus, XRD spectra confirming the pure crystal structure of grown monolayer pyramid MoS₂ flakes.

The schematic of sensor device is shown in Fig. 3(a). When H₂ molecules were exposed to MoS₂ structures, they changed the resistance of the MoS₂ structures. We have studied the IV profile at RT and 150 °C with and without the H₂ exposure, shown in Fig. 3(b–c). We found that I–V curves are linear with and without H₂ exposure. The increase in current due to H₂ exposure is discussed in 3.3. The gas sensing measurements were performed with variable concentration of H₂ at different temperature range of 28 - 150 °C.

**Hydrogen gas sensing study**

Fig. 4(a) shows sensitivity vs time profile for all temperatures. The sensitivity is higher for higher temperature which implies increased interaction of H₂ gas molecules with monolayer MoS₂ pyramids at higher temperature. It is observed that the resistance decreases with increased H₂ exposure. Fig. 4(b) and (c) shows the response and recovery time of sensor. It can also be seen that lowest response time at RT is 11.3 s. The response time for other temperature ranges from 11.0 to 33.0 s. The calculation for response and recovery time is shown in Fig. 5(a–f) for the RT and at moderate temperature 150 °C. The current vs time graph for the RT and 150 °C is shown in Fig. 5 (a) and (d). It has been observed that the response time is increased with increase in the temperature from 28 to 150 °C. When H₂ gas molecules exposed to sensor, it adsorbed to favourable adsorption sites on the monolayer MoS₂ pyramids with edge oriented top flakes. At RT, the H₂ gas molecules easily adsorbed on the MoS₂ flakes and give response quickly. However, when the temperature of the device increases, the adsorption of H₂ gas is not so easy due to generated thermal energy. Atoms vibration in MoS₂ increases with increase in the temperature. At elevated temperature, now H₂ gas molecules need time to adsorb on the MoS₂ flakes in comparison to RT. Thus, the response time is also increased.

The nearly constant recovery time of 125–142 s implies that desorption of H₂ molecule is constant throughout all the temperatures. Fig. 4(d) depicts sensitivity profile of sensor. At RT, sensitivity of monolayer MoS₂ pyramids with edge-oriented top flakes is 6%. The sensitivity increased constantly and reached up to maximum sensitivity of 69.1% at 150 °C for 1% H₂. Higher temperature leads to increased diffusivity of H₂ molecule which increases sensitivity correspondingly In the present study, we studied the H₂ sensing performance from 28 to 150 °C. Kumar et al.; studied the H₂ sensing response from reverse biased MoS₂/GaN heterojunction in the temperature range from 25 to 180 °C [40]. The authors achieved the highest sensitivity at 150 °C. Beyond 150 °C, the H₂ sensing performance was decreased. The decreased sensitivity was attributed to dominate desorption rate of H₂ gas over the diffusion process. Moreover, in present study, the sensitivity increases from 28 °C to 125 °C rapidly from 6% to 66%. However, at higher temperature from 125 °C to 150 °C, the sensitivity is increase from 66% to 69%. At higher temperature beyond 100 °C, the device showed nearly constant increase in sensitivity. Hence, we study the device sensing behaviour from 28 to 150 °C. Also, our priority was to develop the H₂ sensor at lower temperature and ideally to work at RT. Hence, we study the device sensing behaviour from 28 to 150 °C. We have compared our results with other traditional metal oxides, bare MoS₂, MoS₂ hybrid and metal particle decorated sensor in Table 1. The combination of high sensitivity and low response time for our H₂ sensor at RT and moderate temperature is better than metal oxide nanostructures and any other bare MoS₂ H₂ sensor reported in literatures [41]. Our fabricated device also showed a very low response time in all temperature ranges even at RT compared to other bare MoS₂ based sensors [16,24,30,42,43].

The sensitivity for vertical MoS₂–Si heterostructure was reported to be ~685%; however, the reported sensor was nearly 10 time slower than our H₂ sensor [43]. The observed response time for monolayer MoS₂ pyramids is even better than our previous H₂ sensor on edge-enriched MoS₂ flakes with enhanced sensitivity at RT and at moderate temperature.
Hydrogen gas sensing mechanism

To understand the high sensitivity and low response time of our monolayer MoS2 pyramidal structures, we investigated the detail surface morphology of monolayer MoS2 pyramids. We did AFM measurements to study surface topography of grown structures. The AFM analysis is shown in Fig. 6(a). Surface topography of MoS2 film clearly shows layer by layer growth of monolayer MoS2. To gain more insight into the growth, we studied the line profile of grown pyramid MoS2 flakes and the result is shown in Fig. 6(b). A step like growth pattern is obtained from the line profile. Moreover, we also observed a sudden increase in the line profile at the top of these stacked layer. The number of stacked in-plane layers is 8–30 monolayer with the height of 5–20 nm. Fig. 6(c) shows zoomed area of the line profile. The height of single layer pyramid is around 0.7 nm which implies each stack is monolayer MoS2 flakes. At the top, growth of edge-oriented MoS2 takes place which confirmed from sudden increase in height of line profile. The height of edge-oriented flakes is varied from 3 to 7 nm. The surface morphology and step like line profile shown in Fig. 6(a–c) revealed pyramid like growth of MoS2 structure. The line profile shows that size of individual island varied from 1 to 2 μm and the uncovered in-plane region on each monolayer pyramid varied from 20 to 30 nm, as shown in Fig. 6(c). Thus, this modified growth method

Fig. 4 – (a) Sensitivity vs time profile at different temperatures. (b) Response time profile (c) Recovery time profile (d) Sensitivity of monolayer MoS2 pyramids with edge-oriented top flakes in the temperature range 28–150 °C.

Fig. 5 – Calculation of response time and recovery time at (a–c) RT (d–f) at 150 °C for the 1% concentration of H2 gas.
provides more favourable adsorption sites as well as a higher surface area in monolayer MoS₂ pyramid structures for H₂ molecule interaction. A 3D schematic of monolayer MoS₂ pyramids with edge-oriented top flakes is shown in Fig. 6(d).

The deposition rate, growth rate and sulphur rich environment are the important parameter to grow these special structures. Here, we first create sulphur rich environment in the small tube which plays vital role to synthesize MoS₂ flakes [58]. It is reported that closed end of the tube has very small gas velocity at closed end in comparison to open end of the tube [59]. Thus, MoS₂ vapor formed by the vaporization of the S and MoO₃ powder deposited slowly on the substrate.

Initially, we heat the sulphur powder first to create sulphur rich environment. For the growth of monolayer MoS₂ pyramids, Sulphur and MoO₃ react with each other and form MoS₂ vapors. Vaporized MoS₂ condensed on substrate and form in-plane monolayer MoS₂. With increase in growth time, more incoming MoS₂ vapors start condensing on the substrate and form isolated islands. Incoming atoms/molecules nucleate and formed first, second, third stacked on islands stacked.

Therefore, after a certain critical thickness of in-plane MoS₂ flakes, other factors like strain and screw dislocation may take place in the MoS₂ film. These factors restrict the growth direction in the in-plane. Thus, the growth direction of MoS₂ film changes from in-plane to vertical aligned direction [58]. The islands developed on whole substrate and formed monolayer MoS₂ pyramids with edge-oriented top flakes following the Stranski Krasanov growth model [34,60]. The growth of monolayer pyramids reveals the stacked monolayer and large number of exposed atomic edges [61]. Hence, with these monolayer pyramids not only the exposed area is increased but also large number of favourable adsorption sites are increased which enhanced H₂ gas adsorption. Therefore, in our case we controlled the surface reaction rate and mass transfer rate by controlling the gas flow [34]. Thus, tube in tube arrangement provide the slow and controlled sulphurization of the MoS₂ flakes on the substrate and plays an important role to achieve monolayer MoS₂ pyramid structures [58,62].

We proposed H₂ sensing mechanism based on the preferential and enhanced adsorption sites for H₂ of monolayer MoS₂ pyramids. The gas molecules adsorption on MoS₂ is highly position dependent [33]. The gas molecule interaction is examined by adsorption energy and charge transfer between MoS₂ and gas molecules at different sites. It has been well reported theoretically and experimentally that gas molecules adsorption on MoS₂ can be happen on four adsorption sites top of hexagon (H), top of Mo atoms (TM), top of S atoms (TS) and top of Mo–S bonds (B) as shown in Fig. 6(d) [63,64]. The adsorption energy calculated by

\[ E_a = E_{\text{MoS}_2 + \text{molecule}} - (E_{\text{MoS}_2} + E_{\text{molecule}}). \]

Here, \( E_{\text{MoS}_2 + \text{molecule}} \) is total adsorption energy of jointly formed MoS₂ and H₂ gas molecule bonded on it. \( E_{\text{MoS}_2} \) and \( E_{\text{molecule}} \) are total energy of individual MoS₂ and H₂ gas molecule, respectively [63]. For favourable adsorption of gas molecule, the adsorption energy should be negative and the reaction is exothermic in nature. The highest negative adsorption energy of a sensing material for a particular gas implies more selective and sensitive nature of the material for that gas. Another important parameter is the electron transfer between gas molecules and MoS₂ flakes. If the electron transfers from gas molecule to MoS₂ then gas called as electron donor while if electron transfer from MoS₂ to gas molecule then gas called as electron acceptor. [62]. Yue and his co-workers reported that possible adsorption sites on MoS₂ for H₂ gas molecules adsorption are \( T_M \) and \( T_S \) sites with theoretically calculated adsorption energies of \(-82\) meV, \(-70\) meV and \(-49\) meV, respectively [63]. The \( T_H \) sites are highly probable at in-plane MoS₂ flakes while \( T_M \) and \( T_S \) sites are probable at edge-enriched MoS₂ flakes and on in-plane MoS₂ flakes. In another report by Ganji et al.; H₂ gas adsorption studied on MoS₂ and WS₂ flakes [64]. The adsorption energy for H₂...
adsorption on MoS$_2$ is $-131.61$ meV at the top of Mo atoms. Moreover, authors found positive 0.004e charge transfer from MoS$_2$ to H$_2$ molecules. In our monolayer MoS$_2$ pyramid structures, we not only enhanced H site on stacked in-plane MoS$_2$ pyramids but also enhanced T$_M$ and T$_S$ sites on exposed edges simultaneously.

Also, it is clear that combination of these three sites on in-plane MoS$_2$ and edge-enriched MoS$_2$ in such a large extent is not possible. The stacked in-plane monolayer MoS$_2$ pyramids increases H sites and exposed edges of in-plane and edge-oriented flakes at top increases T$_M$ and T$_S$ sites [63]. The H$_2$ gas molecule interaction with MoS$_2$ pyramids having edge-oriented top flakes is shown in Fig. 6(e). Fig. 6(e) revealed that each stacked in-plane layer not only provides large surface area for H$_2$ gas interaction but also favourable in-plane and edge sites. The combination of T$_M$, H and T$_S$ sites available in monolayer MoS$_2$ pyramids is mainly responsible for high sensitivity, fast response and comparatively low recovery time. Moreover, the net positive electron transfer from MoS$_2$ to H$_2$ molecules is 0.004e for both H sites and T$_M$ sites and 0.008e at the T$_S$ site; this also verified that H$_2$ has an electron acceptor nature for the MoS$_2$ [63]. The chemical reactions between the MoS$_2$ and H$_2$ gas molecules is shown in Fig. 6(f). Exposed H$_2$ molecules are interacting with all layers from base to top in monolayer MoS$_2$ pyramids. The monolayer MoS$_2$ flakes provided all possible three combinations (H sites, T$_S$ sites and T$_M$ sites) of the favourable adsorption sites required for H$_2$ gas molecule adsorption. Thus, exposed H$_2$ gas molecules strongly adsorbed on the MoS$_2$ flakes. Hence, when H$_2$ gas turned off, H$_2$ gas molecules need time to desorbed from the monolayer MoS$_2$ pyramids. Which leads to high recovery time.

The electron acceptor nature of H$_2$ gas on MoS$_2$ flakes is also observed in our previous reports. We fabricated the highly dense vertical aligned MoS$_2$ flakes [16]. The vertical aligned MoS$_2$ flakes have the T$_M$ and T$_S$ sites only which is favourable adsorption sites for H$_2$ adsorption. The vertical aligned MoS$_2$ flakes showed n-type behaviour and when H$_2$
exposed to vertical aligned MoS$_2$ flakes, the resistance of the film is increased which also implies that H$_2$ gas takes electrons from vertical aligned MoS$_2$ flakes. The possible H$_2$ adsorption reactions between MoS$_2$ and H$_2$ gas molecules are as follows:

$$\text{MoS}_2 + \text{H}_2 \rightarrow (\text{MoS}_2)^+ + (\text{H}_2)^- \quad (3)$$

In another report, we studied the NO$_2$ sensing by utilizing the p type mixed MoS$_2$ flakes [18]. Mixed MoS$_2$ flakes have the combination of in-plane MoS$_2$ flakes and vertical aligned MoS$_2$ flakes. The favourable NO$_2$ adsorption sites in the mixed MoS$_2$ flakes are H sites, Ts site and B site. In this case of mixed MoS$_2$ flakes, we also studied the H$_2$ sensing performance on the mixed MoS$_2$ flakes. We again observed similar behaviour with H$_2$ gas. H$_2$ and NO$_2$ both behaves as the electron acceptor and the resistance of the film decreased. However, this time H$_2$ sensing performance has been decreased due to less availability of favourable adsorption sites in mixed MoS$_2$ flakes. It is clear now that H$_2$ takes electron from MoS$_2$ film. However, resistance is decreased with H$_2$ exposure which implies that grown MoS$_2$ is of p-type in nature. This p-type behaviour can also be seen from IV curve taken at RT and 150°C shown in Fig. 3(b–c). The monolayer MoS$_2$ flakes with edge oriented top flakes having the p type nature, which implies MoS$_2$ flakes have the holes as the majority charge carrier while electrons as the minority charge carriers. When H$_2$ gas exposed to device, H$_2$ gas molecules withdraw the electron from p type MoS$_2$ flakes due to its electron acceptor nature. Hence majority of holes carriers increases in p type MoS$_2$ flakes which decreases the resistance of the films. Thus, the current is increased with H$_2$ exposure, as can be seen from Fig. 3(b–c).

The p type behaviour of monolayer MoS$_2$ pyramid structures may be attributed to the various defects and oxygen adsorption on the surface of MoS$_2$. In a report by Neal et al. the author predicted that a controlled adsorption of oxygen or interaction with MoS$_2$ may induce a p type doping. Furthermore, some other factors like defects generated during the synthesis of pyramid MoS$_2$ by chemical vapor deposition, charge interaction-transfer from the substrate, effect of metal semiconductor contact, annealing results in the controlled p type behaviour of MoS$_2$ flakes [18,65,66].

Finally, we did the cyclability and dynamic concentrations measurement to check the stability of the H$_2$ gas sensor. Cyclability is an important parameter to understand the stability of the chemiresistive gas sensor. The current vs time profile for the 16 cycles at 150°C is shown in Fig. 7(a–b). We have tested the stability over the span of two months at all temperatures. We have observed that sensitivity is nearly constant for this sensor. The dynamic plot for the different concentrations is shown in Fig. 7(c). The H$_2$ concentration is varied from the 0.1, 0.3, 0.5, 0.7 and 1%. For the 0.1% H$_2$ concentration the sensitivity is 24%, which is quite high for such a low concentration of H$_2$ and shows the high sensitivity of sensor for even very low concentration of H$_2$.

**Conclusion**

In conclusion, we synthesized monolayer MoS$_2$ pyramid structures by modified CVD. Each pyramid consists 3–25 layers of in-plane monolayer MoS$_2$ flakes while capstone of each pyramid has edge-oriented MoS$_2$ flakes with a height from 3 to 7 nm. The uncovered region in each stacked layer is around 24–28 nm with size of each pyramid in the range of 1–2 μm. The sensitivity of these pyramid MoS$_2$ flakes is 6% for 1% H$_2$ with a fast response time of 1.13 s at RT. Furthermore, the gas sensing mechanism based on DFT also confirmed that our proposed modified growth method is responsible for highly sensitive and fast detection of H$_2$ gas molecules on monolayer MoS$_2$ pyramids with edge-oriented top flakes. Monolayer MoS$_2$ pyramids with edge-oriented flakes at top provided highly favourable adsorption sites at top of hexagon (H), top of Mo atoms (T$_{Mo}$) and top of S atoms (T$_S$). We believe that proposed research work clearly provides more insight to understanding role of favourable adsorption sites to design a highly sensitive and fast H$_2$ sensor for safe operation of next generation H$_2$ based fuel systems.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ijhydene.2020.01.119.

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