MoS$_2$/CeO$_2$ Based Composite for Ammonia Sensing

Nitesh Dogra$^1$, Kajal Dadwal$^1$, Arun Kumar$^2$ and Sandeep Sharma$^1$

$^1$Department of Physics, Guru Nanak Dev University Amritsar, Punjab-143005, India
$^2$Swami Premanand Mahavidyalaya, Mukerian, Punjab-144211, India

E-mail: Sandeep.phy@gndu.ac.in

Abstract. Here, we report synthesis of MoS$_2$/CeO$_2$ composite using a two-step hydrothermal techniques. A two-terminal sensor device made from the composite was further used for ammonia detection at room-temperature. The device has shown selective behavior toward ammonia gas molecules as compared to acetone, ethanol and N-methyle pyroliddone (NMP). Further, the sensor display delayed recovery and a relative-response of eleven percent for ammonia (30 ppm). The decrease in resistance after interaction with ammonia gas molecules indicate n-type conduction of the composite. Conduction type was further confirmed using Mott-Schottky measurements which gives a positive slope with composite as working electrode. These initial studies indicated that transition-metal dichalcogenides based composite with metal oxide semiconductor could be optimized for selective detection of various volatile organic compounds.

Keywords: ammonia sensor, transition metal dichalogenides (TMDCs), 2D materials, selectivity and CeO$_2$

1. Introduction

Development of gas sensor that can operate at room-temperature has remained a challenging task. Various factors influence the gas sensing performance of the sensors made from different materials. Past few decades have seen extensive growth in investigating metal oxide semiconductor (MOS) for gas sensing applications[1]. Though, they offer a large sensing response but their operation at elevated temperature and accompanied inferior selectivity limit their use. In addition to MOS, recently, 2D transition metal di-chalcogenides (TMDCs) with a formula MX$_2$, have emerged as an alternative for gas sensing applications[2]. Here, X (S or Se etc) represents a chalcogen atom whereas M (Mo or W) represents a transition metal atom. These 2D materials possess layer dependent physical properties which make them attractive for various applications ranging from nanoelectronics, optoelectronics and gas sensing also. Their, 2D structure and hence large surface to volume ratio accompany with semiconducting nature facilitate their potential use for gas sensing applications. Though, gas sensing using MoS$_2$, WS$_2$ and their composites has been demonstrated [3, 4] but in a few cases, delayed recovery arising due to thick layered structure has been reported [5, 6]. Therefore, to overcome some of these problems various other methodologies, for instance, grain size control, doping and making composite with other materials have been used. Among these methods, composite formation has proven to be successful as it provides enhanced device performance and better selectivity over the individual host
material. For instance, MoS\textsubscript{2}/SnO\textsubscript{2} n-n heterojunctions [4, 7], MoS\textsubscript{2}/multiwalled carbon nanotubes hybrids [8], MoS\textsubscript{2}/WO\textsubscript{3} composite[3] and MoS\textsubscript{2}/Co\textsubscript{3}O\textsubscript{4} composite[9] were found to have enhanced ammonia sensing performance. Therefore, a composite based approach may offer solution to the problems faced by sensor made from either MOS and TMDCs alone. Here, we report the synthesis of MoS\textsubscript{2}/CeO\textsubscript{2} composite via two-step hydrothermal technique. Two-terminal sensing device made from composite has shown n-type conduction with preferential ammonia detection at room-temperature. The large response/recovery times limits device performance and future work is further required to improve the performance of such type of composite based sensor devices.

2. Experimental Section

Synthesis of MoS\textsubscript{2}/CeO\textsubscript{2} composite was performed using simple hydrothermal method. Various synthesis steps are shown in Fig.1.

All precursors namely, sodium hydroxide (NaOH), cerium nitrate hexahydrate (Ce(NO\textsubscript{3})\textsubscript{3}.6H\textsubscript{2}O) and ammonium tetra-thio-molybdate ((NH\textsubscript{4})\textsubscript{2}MoS\textsubscript{4}) were acquired from Sigma Aldrich, India and used as received. Hydrazine was obtained from Loba Chemie India and also used as received. In the first step CeO\textsubscript{2} was synthesized at 130°C. In particular, 0.7 g of Ce(NO\textsubscript{3})\textsubscript{3}.6H\textsubscript{2}O was added to 40 ml of de-ionized (DI) water and obtained solution was stirred for fifteen minutes. To this solution 20 ml of NaOH was added and obtained mixture was stirred for another two hours until solution changed to pink colour. Obtained mixture was put in an autoclave and kept in a furnace at 130°C for 18 hours. The autoclave was then allowed to cool under ambient conditions and obtained precipitates were washed and filtered. These precipitates were subsequently dried in a vacuum oven and light yellow colored CeO\textsubscript{2} was obtained. In the next step, 0.3 g of CeO\textsubscript{2} was mixed with DI-water and bath-sonicated for 15 minutes. Thereafter 0.5 g (NH\textsubscript{4})\textsubscript{2}MoS\textsubscript{4} and 13 ml of hydrazine were added to the suspension obtained in previous step. Obtained mixture was sonicated for another 15 minutes. This mixture was transferred into an autoclave which was kept at 200°C in a furnace for 12 hours. Autoclave was allowed to cool under ambient conditions and obtained black colored precipitates of MoS\textsubscript{2}/CeO\textsubscript{2} composite were washed and dried. A paste made from composite was applied on already deposited electrical contacts (with a separation of 2 mm) on an alumina substrate. A home built 40 L test chamber having a controlled oven and a circulatory fan was used for performing gas sensing measurements. Desired gas environment was achieved by inserting appropriate volume of analyte into the test chamber containing a furnace. The gas concentration is calculated using equation [10]:

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C = \frac{22.4p\rho}{T V_s M} \times 100
\]

where, \(p\) refers to liquid density (g/mL), \(T\), \(V_s\) and \(M\) refer to working temperature in K, evaporated liquid volume in \(\mu\)L and molecular weight of liquid in g/mol, respectively. \(V\) and \(C\) represent the test chamber volume (L) and concentration of different gases in ppm, respectively [3]. Further, Mott-Schottky (MS) plots were acquired with an electrochemical workstation (M204 Autolab, The Netherlands). Three electrode configuration was employed to perform MS measurements in 0.5 M H\textsubscript{2}SO\textsubscript{4} solution. The measurement geometry consists of a platinum wire as a counter electrode, Ag/AgCl reference electrode and MoS\textsubscript{2}/CeO\textsubscript{2} composite as a working electrode[3].
3. Result and Discussion

3.1 Ammonia sensing using two-terminal device

Fig. 2 displays the response-recovery transients for a sensor made from composite. In Fig. (a), as the ammonia gas enters into the measurement chamber, sensor resistance reduces to a certain minimum value and again displays an increase in resistance when measurement chamber is opened to remove the gas molecules. Here, we also define three parameters for a sensor device. The response time ‘t\text{response}’ is the time taken by the device to attain 90% change w.r.t base resistance (R\text{b} in air). On the other hand, once sensor has reached minimum resistance value in presence of gas, the time taken to recover to a resistance value lying 10% above the base resistance, is termed as recovery time ‘t\text{recovery}’. If ΔR is the maximum resistance change, then ΔR/R\text{b} defines the relative response for the sensor. As can be seen, the response time in present case is close to 180 s whereas the recovery is quite slow. Various factors may result in delayed recovery of the device. One possible reason could be large adsorption energy for the composite. Larger recovery time may limit the device operation and in a few cases external device heating or ultraviolet light exposure have shown improved results. Fig. (b) displays, sensor response to three different ammonia concentrations given in ppm. The response increases with increase in ammonia concentration. In Fig. (c), the sensor response for successive three cycles with same ammonia concentration is shown. Device displays less than 5% change in the relative response. As our environment consists of various gases, selectivity of sensor device towards a particular gas becomes an important concern. The sensor response was checked for acetone, ethanol and NMP in addition to ammonia and results are shown in Fig (d). The composite based device has shown selective ammonia detection compared with other analytes.
Figure 2. (a) Response-recovery transient when sensor exposed to NH$_3$. Figure also define response, recovery time and relative response of a device. (b) Response-recovery transient for three different concentrations of NH$_3$ (c) repeatability and (d) selectivity test of the device. All measurements were performed at room-temperature.

3.2 Mott-Schottky measurements
Further, Mott-Schottky measurements in three electrode configuration were performed to assess the conductivity type of the device. Sensor when exposed to ammonia gas molecules, exhibited a decrease in resistance, implying n-type conduction in the composite. The MS plot shown in Fig.3, displays a positive slope confirming the dominant n-type conduction in sample.
Figure 3. Mott-Schottky plot with positive slope indicating n-type character of the working electrode made from MoS$_2$/CeO$_2$ composite.

3.3 Sensing Mechanism
Hydrothermally synthesized MoS$_2$ behaves like an n-type material [8]. In present study a composite of MoS$_2$/CeO$_2$ also displays n-type conduction. A widely acceptable sensing mechanism for MOS assume ambient oxygen adsorbed on MOS surface. However, in case of composite, the mechanism may differ in a sense that both MoS$_2$ and CeO$_2$ behave like an n-type material. CeO$_2$ possesses a band gap of 3.2 eV and work function of 4.69 eV[11]. On the other, the work function for air exposed MoS$_2$ is 4.47 eV [12]. Lower work function of MoS$_2$ causes electron transfer from MoS$_2$ to CeO$_2$ and give rise to a depletion layer. Depletion layer modulation takes place whenever a charge transfer between composite surface and adsorbed gas molecule occurs. This conductivity modulation is reflected as change in measured resistance of the device. Adsorbed oxygen after interaction (electron capture) with MOS turns in to oxygen ion (O$^{2-}$). Such a surface when exposed to reducing gas such as ammonia, electron transferred from ammonia to MOS causes a reduction in depletion layer width. Net result will be a reduction in the resistance of the device.

4. Conclusion
Here, we presented a systematic study involving interaction of ammonia gas molecules with MoS$_2$/CeO$_2$ composite surface. We also demonstrated that composite based sensor has a linear response with ammonia concentration. Sensor exhibited a decrease in resistance when exposed to ammonia. This implies an n-type conduction process which was cross checked using Mott-Schottky measurements. The sensor possesses a relative response of 3-3.5% and response time of 180 s accompanied with delayed
recovery. Sensor exhibited preferential room-temperature ammonia detection as compared to ethanol, acetone and NMP. Though, the obtained response and recovery times are a bit large and further work is required to address these issues.

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