Microwave Assisted Synthesis of Molybdenum Disulphide/Tungsten Trioxide/Reduced Graphene Oxide (MoS2/WO3/RGO) Nanocomposites for Organic Vapor Sensing

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Abstract. Hybrid nanostructures based on two-dimensional (2-D) materials such as transition metal dichalcogenides (2-D TMD’s), transition metal oxides (2-D TMO’s), and graphene are gaining significant attention for their potential application as semiconductor sensing devices owing to their excellent structural, electronic, and optical characteristics. The present work reported 2- D ternary nanocomposites (MoS2/WO3/RGO) as organic vapor sensing material, synthesized using microwave assisted method. Formation of ternary composite system proves to be an efficient strategy to develop novel high performance vapour sensors, providing multiple degrees of freedom and opportunity to exploit the synergistic properties of the resulting material to its full potential for a particular application. The synthesized MoS2/WO3/RGO nanocomposites has been characterized for morphological, and structural analysis through SEM, XRD and FTIR spectroscopic techniques. The electrical and sensing studies of synthesized material is evaluated through IV characteristics using Keithley electrometer. The sensing characteristics has revealed that the synthesized sensor has high sensitivity, good stability at room temperature and outperforms the result obtained from single or binary counterparts. The formation of the heterojunction and electronic modulations at the interface of MoS2, WO3 and RGO results in improved surface charge transfer mechanism and enhancement of sensing performance.

Keywords: 2-D materials, TMDs, TMOs, Graphene, Ternary Nanocomposite, organic vapor sensing

1. Introduction

Selective, fast, sensitive, and reliable alcohol monitoring is significantly needed in many industries including pulp and paper industries, food industries, pharmaceutical industries, etc., as long-term exposure of even low concentrated alcohol may result into acute illness related to eyes, nasal function, respiratory tract, nerve functioning etc.

In recent years, two-dimensional (2-D) materials emerges as the finest gas sensing materials owing to their substantial characteristics including room temperature operation, high surface to volume ratio, outstanding electron mobility, tunable band-gap and good electrical properties, as compared to conventional-metal-oxide vapor sensors. The conventional-metal-oxide vapor sensors require
high temperature operation (200 to 300 °C) to trigger the chemical absorption process of organic vapor to produce sensor response [1] so it is not feasible according to power consumption point of view. One decade ago, many researchers have reported graphene and their derivatives-based sensing materials for gas sensing application. In recent years, some other 2-D materials besides graphene derivative such as 2-D TMDs and 2-D TMO’s are gaining attention because of their extremely good properties such as tunable bandgap and excellent electrical properties [2-6]. As compared to individual 2-D materials, the hybrid nanostructures of 2-D materials improve the sensing response because of the formation of heterojunction between two different 2-D material which enhance the surface charge transfer mechanism [3,4]. Hence, the many researchers are trying to develop novel hybrid nanostructures to achieve the collaborative properties of 2-D materials and improve their sensing performance. Generally, binary hybrid nanostructures of graphene derivatives and 2-D TMDs (MoS2, WS2, MoSe2) or 2-D TMOs (WO3, MoO3) were reported for gas sensing applications [7-9]. As compared to binary hybrid nanostructure, ternary nanostructures develop multiple nanoheterojuctions that cause the modulation in interfacial electronics such as modulation in charge carriers, charge carrier densities, fermi-level and their charge carrier separation for the transportation of charges across the heterojunctions [10-12]. All these modulations are expected to enhance the sensing performance of the ternary nanocomposite.

In this work, attempts have been made to prepare microwave assisted ternary (MoS2/WO3/RGO) hybrid nanomaterial. The microwave synthesized MoS2 is hybridized with reduced graphene oxide and tungsten trioxide. RGO is prepared through Modified Hummers method. The synthesized nanostructure is evaluated for its application as organic vapor sensor.

2. Experimental details

2.1 Materials used:

The analytical grade reagents such as sulfuric acid, hydrogen peroxide, HCl (3.6 wt.%), Nitric acid (55%), hydrazine hydrate, sodium borohydride, Hydrogen peroxide Ammonium tetra thiomolybdate, Potassium permanganate (KMnO4), isopropanol and tungsten trioxide powder were procured from Sigma Aldrich for performing the experiment. Acidified graphite flakes (Analytical Grade 1721) were obtained through Asbury.

2.2 Preparation of Reduced graphene Oxide (RGO)

Initially, GO was prepared by modified hummers method from Acidified carbon graphite flakes as described in our previous research publications [13]. RGO was synthesized by dissolving GO (100mg) in water. (100 ml). After that, 10 micro liter of hydrazine hydrate was added dropwise into this prepared GO solution and refluxed it for 1 hour at 80 oC. After that, 1 mg of NaBH4 (sodium borohydride) was added into this solution and again refluxed it for 36 hours at 100 oC and cool down to 25 oC. The synthesized material was filtered through Millipore filter paper and washed it with deionized water and dried it.

2.3 Synthesis of MoS2/WO3/RGO nanocomposites

The pure MoS2 is synthesized by direct microwave assisted reaction. Ammonium tetra thiomolybdate is taken for synthesis of MoS2. 10mg of Ammonium tetra thiomolybdate (NH4)2MOS4 crystals are mixed in 20ml hydrazine solution and 10 ml distilled water and mixed well. The solution is kept in microwave at 800W for 1 minute after that it is filtered off and washed three times with isopropanol. The as obtained pure MoS2 is kept in oven for air drying. 10 mg of each MoS2, WO3 and RGO is added into 20 ml of hydrazine and 10ml of distilled water solution. The solution is subjected to
microwave radiation treatment at 800W for 1 minute. The solution obtained is washed three times with isopropanol. The detailed synthesis procedure along with schematic representation is described in our previous publication [14]. The dilute solution of RGO/MoS2/WO3 (10 mg each) nanocomposite was prepared in dimethyl formamide (50 ml in vial) with and spin coated on glass slide. The same method is used to prepare RGO/MoS2 nanocomposite.

2.4. Characterizations

The surface morphology, structural behaviour and functional group of synthesized MoS2/WO3/RGO nanocomposite was analysed for scanning electron microscopy through SEM, ZEISS EVO, X-ray diffraction through XRD, Rigaku Smart lab using Cu Kα as source radiation (2θ range: 10° to 55°) and FTIR through Perkin Almer.

2.5 Gas sensing and device fabrication

Sensing device was fabricated by drop-casting the solution on a properly cleaned and dried glass substrate. The synthesized nanocomposite solution was spin coated on glass slide for IV characteristics. After drying the nanocomposite film, silver paste was deposited onto glass slide to make contacts using copper wires. A vapour delivery and measurement system assembled in the laboratory, was used for sensing evaluation in which electrical connection, exhaust flow of gas, inlet of gas is provided. The synthesized device was mounted inside the gas chamber and their silver contacts were connected to Keithley Source meter (6517 A/B)

3. Results and Discussion

3.1 Morphological structure of MoS2/ WO3/RGO

Figure 1 (a & b) represents the SEM image of microwave synthesized MoS2 and MoS2/WO3/RGO ternary nanocomposites respectively depicting their morphological characteristics. SEM image of nanocomposite film shows uniform distribution of MoS2 and WO3 on RGO sheets. The uniform distribution of MoS2, WO3 and RGO in nanocomposite has been confirmed through EDS mapping as shown in Figure 2.

Figure 1. SEM image of (a) Microwave synthesized MoS2 and (b) MoS2/WO3/RGO Ternary nanocomposites
3.2 Crystalline Structural and Functional Group Evaluation

The FTIR spectra for RGO/MoS2/WO3 film shown in Figure. 3 (a). The various absorption band of RGO were revealed by the distinctive peaks at 3437.51 cm$^{-1}$, 3046.36 cm$^{-1}$ and 1719.12 cm$^{-1}$ that were attributed to dissociation of hydroxide ions and C–H stretching vibrations as well as C=O, Carboxyl group, bond respectively. RGO peak at 1569.59 cm$^{-1}$ was allied with the C–H bending. The peak at 1402.02 cm$^{-1}$ represented Mo-S stretching mode in synthesized RGO/MoS2/WO3 nanocomposite film. Characteristic peak at 789.02 cm$^{-1}$ is ascribed to O=W=O stretching band of WO3 [15]. The XRD pattern of synthesized RGO/MoS2/WO3 film shown in Figure. 4(b). The peak of synthesized RGO at 26.65° was assigned to (002) plane. The diffraction characteristic 2θ peaks at 23.1°, 23.57°, 24.53°, 29.04°, 34.19°, 43.56° and 49.79° were indexed to WO3 basal planes 002, 020, 200, 112, 202,222 and 440 respectively [16-17]. The characteristic peaks at 2θ = 14.5 o, 32.4 o were assigned to 002, 100 planes of MoS2 [18].

Figure 2. EDS Mapping Image of RGO/MoS2/WO3 ternary Nanocomposite

Figure 3. (a) FTIR spectrum of synthesized RGO/ MoS2 and RGO/MoS2/WO3 nanocomposite film.
3.3 Characteristics

The I-V characteristics of synthesized device was performed on Keithley 6517 A/B. The constant voltage of 1V was applied in the range from -1V to 1V and the sensing current was measured from -1V to 1 V which was shown in Figure 5. The current flow of synthesized nanocomposite film of MoS2/WO3/RGO in the range of -0.02 to 0.16 µA was plotted from −1 V to 1 V. The nanocomposite film of MoS2/WO3/RGO shows maximum conductivity of $0.16 \times 10^{-6}$ S cm$^{-1}$.

![Image of I-V characteristics](image)

**Figure 4.** The I-V characteristics of synthesized RGO/MoS$_2$ and RGO/MoS$_2$/WO$_3$ nanocomposite films.

3.4 Organic vapour sensing Studies

The RGO, RGO/MoS$_2$ and RGO/MoS$_2$/WO$_3$ nanocomposite films are evaluated for sensor response recovery characteristics towards various reducing organic vapours such as ethanol, methanol, acetone, propanol and oxidizing vapours such as nitrobenzene, formaldehyde, and benzaldehyde vapours. RGO and RGO/MoS$_2$ does not respond to any applied organic vapours while Figure 6, which depicts the typical sensor response-recovery characteristics of RGO/MoS$_2$/WO$_3$ ternary nanocomposites, clearly indicates that the sensor is highly responsive to alcohols and only slightly to acetones, but not to other vapours. The sensor response (%) of 3.15%, 2.36%, 1.36% and 0.43% towards ethanol, methanol, propanol and acetone respectively are depicted in Figure 6.

While developing organic vapour sensor devices, especially hand-held devices for different applications, response time and recovery time being two significant parameters to characterize a sensor. The RGO/MoS$_2$/WO$_3$ nanocomposite film shows fast response and recovery time of ~1 sec and ~10 sec respectively at room temperature for ethanol. The mechanism responsible for sensing can be illustrated based upon the surface adsorption of vapour and the resulting charge transfer in the nanocomposite structure. The alcohol (ethanol, methanol and propanol) vapours are reducing in nature, so it is assumed that RGO/MoS$_2$/WO$_3$ exhibits p-type semiconducting nature, whereas WO$_3$ are responsible for providing active sites where alcohol replace adsorbed oxygen and release free electrons that results in the subsequent decrement of charge carrier concentration, and hence decrease in electrical conductivity of nanocomposite sensor film [19].

The nanosheets of RGO provides faster conducting network and its mechanical strength enhances the durability of the sensor material. The interfacial electronic modulation at number of heterojunctions developed in RGO/MoS$_2$/WO$_3$ hybrid nanostructure decides the overall electronic structures that results in fast recovery and response time to the organic vapours.
Figure 5. Resistance changes in RGO/MoS$_2$/WO$_3$ nanocomposite film on exposure towards various organic vapour at room temperature.

Figure 6. Sensor Response of RGO/MoS$_2$/WO$_3$ sensor towards ethanol, methanol and acetone

4. Conclusion

In the present work, RGO/MoS$_2$/WO$_3$ ternary nanocomposites are developed through microwave assisted method as potential candidate for chemiresistive alcohol vapour sensing. The vapour sensing response has been evaluated towards a series of reducing and oxidizing organic vapours. The ternary nanocomposite film shows selective response towards alcohol vapours with very fast response (1 sec for ethanol) and recovery time (10sec for ethanol) at room temperature. The selective sensing response of RGO/MoS$_2$/WO$_3$ nanostructures film towards alcohol with quick response time probably attributed to the synergistic exploitation of the advantages offered by all three components, RGO, MOS$_2$ and WO$_3$. The resultant electronic structure of the nanocomposite due to electronic modulations at multiple number of heterojunctions formed at interface is responsible for the specific sensing response shown by RGO/MOS$_2$/WO$_3$ ternary nanocomposites.
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