Synthesis of Transition Metal Dichalcogenides based hybrid nanostructures by thermal decomposition method

Melbin Baby\textsuperscript{1,2*} and K. Rajeev Kumar\textsuperscript{1,3}

\textsuperscript{1}Department of Instrumentation, Cochin University of Science and Technology, Cochin 682022.
\textsuperscript{2}Sophisticated Test and Instrumentation Centre, Cochin University of Science and Technology, Cochin 682022, Email: rajeev@cusat.ac.in.
\textsuperscript{3}Centre of Excellence in Advanced Materials, Cochin University of Science and Technology, Cochin, India.

*Author for correspondence: melbin_83@yahoo.co.in

Abstract. In this work, we report synthesis of hybrid nanostructures of Transition Metal Dichalcogenides via thermal decomposition method. Ammonium tetrathiomolybdate was used as not only growth templates but also as starting precursor for synthesis of hybrid nanostructures. The conditions for the synthesizing method were optimized using electron microscopy and x-ray diffraction. In this hybrid nanostructure synthesis, it was found that MoO$_3$ nanorods are interspersed on exfoliated MoS$_2$ nanosheets. The structural and optical properties of the hybrid nanostructure were investigated using transmission electron microscopy (TEM), Scanning electron microscopy (SEM), X-ray diffraction (XRD), Raman spectroscopy and Ultraviolet Visible spectrophotometry (UV-VIS). The hybrid nanostructure of MoO$_3$ on MoS$_2$ shows a band gap of 2.2 eV. It was also found that by tuning the preparation parameters viz temperature of heating and time of heating, the composition of the hybrid nanostructure can be varied.

1. Introduction

Different nanostructured materials possess different optical and electronic properties. When we combine them or combinations of these different nanostructured materials, the concept of hybrid nanostructure arises. Hybrid nanostructures consist of two or more individual components, with each component having at least one dimension on the nanometer range [1]. By tuning the parameters of nanomaterials like composition, structure, crystal phase, the distribution of each component and the interface between the components, it is possible not only to get enhanced material properties but also endows with new properties due to the synergistic effect of the materials, which makes them suitable for specific applications [1]. This hybrid nanostructure has been designed to either boost, improve or validate the desired property in the nanomaterials for choosing specific applications.

Recently, transition metal chalcogenides (TMDs) have emerged as fundamentally and technologically fascinating nanostructured materials with their unique structural, electronic and optical properties which makes wide spread applications in Nano devices and functional materials[2]. Among TMDs family, MoS$_2$ nanostructured material possess mechanical stability, photochemical reactivity and
tunable electric properties, which makes it a suitable candidate for potential applications such as Li-Ion batteries, catalysts, sensor and medicine field [3].

After the introduction of carbon fullerenes and nanotubes, synthesis of one-dimensional nanostructured materials has made a greater breakthrough in research and industrial fields due to their superior mechanical and unique electronic properties [4]. Over the last few years, remarkable effort has been made for the production of one-dimensional nanostructured materials like nanorods, nanowires, nanofibers because of its large surface to volume ratio and Debye length comparable to their small size. Owing to these properties, it is widely used to fabricate nanoscale electronic and optoelectronic devices [5]. One dimensional nanostructured materials are relatively stable when compared to two dimensional nanostructures [6].

While focusing on specific applications, one can see that hybrid nanostructures have acquired enhanced material performance rather than individual components do. This improvement is due to the synergistic effect of individual components. In spite of that the two dimensional nanostructured materials have high surface area, there is a tendency for restacking the surface [6]. The oriented electronic or ionic transport pathway of the one dimensional metal oxide nanostructures like nanorods, which are grown on exfoliated MoS₂ nanosheets, not only reduces the restacking tendency but also enhances the active edge sites and conductivity of MoS₂[7]. Till now, various synthesizing methods were used to prepare MoS₂-MoO₃ Hybrid nanostructures including hydrothermal process[8], CVD[9], heat assisted spray coating [10], laser ablation[11], microwave[12], low-temperature sulfurization [13] etc. Owing to their unique advantages, this nano platform has become one of the most promising candidates for wide range of applications like gas sensor [9], super capacitor [7], light emitting diodes [10], Hydrogen evolution reaction (HER) [14] etc.

1.1 Experimental techniques

1.1.1 Materials

Ammonium tetrathiomolybdate ((NH₄)₂MoS₄, molecular weight- 260.28) used for this experiment (purchased from Sigma Aldrich) and distilled water were used for this synthesis.

1.1.2 Synthesis of MoS₂-MoO₃ hybrid nanostructures

The synthesis of MoS₂ nanostructures which employs the thermal decomposition of Ammonium tetrathiomolybdate crystal (NH₄)₂MoS₄. In thermal decomposition synthesis, Ammonium tetrathiomolybdate (ATTM) crystal was used as the starting precursor. Firstly, Ammonium tetrathiomolybdate slurry was prepared by mixing of Ammonium tetrathiomolybdate and distilled water. This slurry is dried and used as the raw material for this experiment. This raw sample was placed in a ceramic pan and heated up to 700°C at a heating rate of 10°C under Nitrogen atmosphere. The raw samples were subjected to different thermal heating and used as for further characterization.

1.1.3 Characterization

Crystallographic information of the MoS₂-MoO₃ hybrid nanostructures was characterized using Bruker D8 Advance Twin- Twin diffractometer (Cu-Kα radiation 1.5406Å) in the range 10⁰ to 80⁰ with a step size of 0.02°. Elemental composition of this nanostructures was obtained by Oxford XMX N. The surface morphology was analyzed with scanning electron microscope (SEM, JEOL, JSM-6390LA) and transmission electron microscope (TEM, JEOL, JSM-2100 operating at 200 kV with LaB6 Electron gun). The optical properties like absorption spectra was carried out using a UV-Vis spectrophotometer (JASCO). Thermal properties of the samples were carried out using a thermogravimetric-differential thermal instrument (TG-DTA) in the range of room temperature to 700°C with a flow rate of 200.0 mL/min and a heating rate of 10°C min⁻¹.
2. Results and Discussion

2.1 Optimization of hybrid nanostructure preparation

2.1.1 Effect of heating

Firstly, the raw sample is subjected to thermal treatment from room temperature (RT) to 700°C with heating rate of 10°C/min under nitrogen (N₂) atmosphere with constant flow rate of 200mL/minute. Approximately equal weight of raw material was taken for the synthesis. TGA, XRD and electron microscopy were used for optimization of the hybrid nanostructure growth. The TGA curve of the starting precursor is shown in Fig. 1.

From TGA graph, it is evident that initial weight loss of approximately 3% occurred at 175°C, which corresponds to the removal of water content from the sample. In this temperature range, we can observe three decomposition stages at 185°C-230°C, 230-350°C and 350-455°C respectively. First change which occurred between 185°C-230°C with weight loss of approximately 26% is associated with the release of vapours of one H₂S molecule and two ammonia molecules which leads to the formation of molybdenum trisulphide (MoS₃). Second weight loss occurred between the range of 230°C-350°C, which is endothermic reaction and is due to the conversion of MoS₃ to MoS₂. Up to 350°C, MoS₂ is found to be stable. After 350°C, oxidation process starts gradually and at 455°C, the sample is completely converted to MoO₃. This conversion process is an exothermic reaction. The temperature stages of this decomposition mechanism are in well agreement with previous reports [15].

During the thermal heating, the structural and morphological nature of the samples at different intervals of temperature points viz 360°C and 700°C were analyzed and is shown in figure 2, figure 3 and figure 4. The surface morphology of the raw sample treated at different intervals of temperature is examined by TEM analysis and is shown in fig 2. From the TEM result, the average size of the nanorod growth on nanosheet is found to be 10.8nm. SEM analysis was also used for confirming the TEM results and is shown in fig 3. After thermally heating the raw sample from room temperature to 700°C, we randomly selected different temperature points for the optimization studies. The surface morphology of the sample at different temperature points were analyzed by electron microscopy.
From the microscopy results, the raw sample (fig. 2a) is found to have an agglomerated morphology without having a definite shape. The electron micrographs (fig. 2b) shows that sample at 230°C has agglomerated sheet like morphology. From the SEM and TEM images we can notice the gradual change of the agglomerated raw material to a hybrid material of sheets and rods. The sample at temp 230°C is also agglomerated but, is having a sheet like morphology. As we move on to the sample heated at 300°C, the sheets are found to be exfoliated and is shown in (fig 2c). Sheet like structure is visible up to 350°C. The formation of a hybrid nanostructure consisting of sheets and rods is clearly visible in the fig 2d, for the sample heated at 360°C.

During the preparation of raw material, the starting precursor (ammonium tetrathiomolybdate) is partially dissolved in water that produces ammonium molybdate also in the raw material. The dried raw sample contains both ammonium tetrathiomolybdate and ammonium molybdate, that are the source of MoS$_2$ and MoO$_3$. The raw sample is subjected to heat treatment up to 360°C in nitrogen atmosphere. Both materials are thermally decomposed at a particular temperature [15,16]. In case of MoO$_3$, the decomposed material is converted to metastable h-MoO$_3$ (hexagonal MoO$_3$) and further oxidized to form stable o-MoO$_3$ (Orthorhombic MoO$_3$) at 455°C, which is confirmed by XRD spectra. The formation of this hybrid nanostructure is due to synergetic effect of both ammonium tetrathiomolybdate and ammonium molybdenum oxide which exist in the raw sample. A further rise in temperature, the morphological studies reveal the transformation of hybrid structure into nanocrystals.
The crystalline nature and phase type of the samples were examined by XRD. The XRD pattern of the raw sample exhibits the presence of ammonium tetrathiomolybdate (PDF number 01-071-1788) and ammonium molybdenum oxide hydrate (01-070-0957). Using EVA software, semi-quantitative phase analysis of the raw sample was performed. The raw sample consists of 86% ammonium tetrathiomolybdate and 14% ammonium molybdenum oxide hydrate. The SAED (selected area electron diffraction) pattern of the raw sample confirms its polycrystalline nature (the inset of figure 2a). The XRD pattern of thermally heated sample at 230°C shows less crystalline nature. As we increase the sample temperature to 300°C, there is no diffraction peak is observed. This signifies that the formed product is amorphous in nature. As the sample temperature is increased further to 360°C, a significant transformation from amorphous phase to crystalline phase has occurred.

Using EVA software, the degree of crystallinity was calculated from XRD spectral data using the equation

\[ X_c(\%) = \frac{A_c}{A_c + A_a} \]  

Where, \( A_c \) is the area under crystalline region, \( A_a \) is the area under amorphous region [17]. As Sample temperature is increased from 300°C to 410°C, degree of crystallinity is also increased from 18.5% to 53.4% which are shown in table 1.

| Sample temperature(°C) | Degree of crystallinity |
|-------------------------|------------------------|
|                         | Crystalline region(%)  | Amorphous region(%) |
| 300                     | 18.5                   | 81.5                 |
| 360                     | 26.4                   | 73.6                 |
| 410                     | 53.4                   | 46.6                 |

**Fig 4a.** XRD spectra of a) Raw b)230°C c) 300°C d)360°C e)455°C f)700°C(MoO₃). **Fig 4b.** XRD spectra of the sample at 360°C for holding time of 0min,5min,10min,15min,20min,25min,30min,40min respectively. **Fig 4c.** Magnified XRD spectra of the sample at 360°C for 10min holding time.
2.1.2. Effect of holding time of heating on crystallinity

When the holding time of the sample at 360°C was increased from 1 minute to 40 minutes, the crystallinity of the material increased. Besides the phase of MoS₂, the additional peaks of MoO₃ phase were also observed, which is evident from XRD graph. When holding time of the sample was 10min, the average size of the nanorods on MoS₂ nanosheet was found to be 10nm which is shown in fig 6b. The effect of time which influences the structural and morphological properties of the sample was characterized by XRD and SEM and is shown in fig 3. No significant changes in the size of the nanorod are observed when holding time of the sample is up to 10mins. Beyond that, it is observed that as we increase the time of heating, size of the nanorod also increases. The optimized conditions used for this hybrid nanostructure synthesis was found to be 360°C for 10 min.

The magnified view of diffraction data of sample heated at 360°C for 10min is shown in Fig 4c. The main diffraction peaks are located at 14.3°, 28.8°, 33.5°, 48.8° and 58.7° which correspond to (102), (004), (101), (105) and (110) planes of the standard XRD data of MoS₂ respectively. This indexed diffraction pattern matches well with standard PDF (Powder diffraction file) of hexagonal structure of MoS₂ (0037-1492). Besides peaks of MoS₂, extra peaks are observed at 23.3°, 27.3° and 34.3°, which correspond to (110), (021) and (140) plane of orthorhombic structure of MoO₃ (PDF number 074-7383). Using EVA software, the semi-quantitative value of sample heated at 360°C for 10min, is found to be 63.2% MoS₂ and 36.8% MoO₃.

| Temperature (°C) | BET surface area | Pore volume | Pore size |
|------------------|------------------|-------------|-----------|
|                  | Single point adsorption total pore volume of pores | Adsorption average pore width (4V/A by BET) |          |
| 300 °C           | 2.7307 m²/g      | 0.012003 cm³/g | 175.8247 Å |
| 360 °C           | 5.2061 m²/g      | 0.029937 cm³/g | 230.0191 Å |
| 445 °C           | 1.0976 m²/g      | 0.004531 cm³/g | 165.1266 Å |

BET surface area measurements like BET surface area, pore volume and pore size are shown in Fig5. Table 2 represents the surface area of the sample heated at different temperature points. At 300°C, BET surface area, pore volume and pore size of the sample is found to be 2.7307 m²/g, 0.012003 cm³/g and 175.8247 Å respectively. It can be seen from Table 2, pore volume, pore size and BET surface area of the sample increases with increasing heating temperature. The BET surface area, pore volume and pore size of the sample is increased till 360 °C, which is due to the growth of nanorods on MoS₂ nanosheet which was supported by SEM analysis (Fig 3d). As the temperature of the sample is further increased from 360°C, particle size is also increases which decreases the gas adsorbed volume. This decreased adsorbed volume with increasing temperature, causes a substantial decrease in surface related parameters of the sample, which is also observed. The BET surface area and pore volume of sample decreases with increasing temperature which is due to increasing the particle size and degree of agglomeration by the effect of heating [18].
Fig 5. Nitrogen adsorption/ desorption isotherms of sample heated at different temperatures 300°C, 360°C and 445°C respectively.

Fig 6. EDAX spectra of a) Raw b) 360°C c) 455°C.

The EDAX spectra reveal the presence of nitrogen(N₂), oxygen(O₂) Molybdenum(Mo) and sulfur(S) elements in raw sample and besides, the stoichiometric ratio of Mo to S is found to be 1:4 which are shown in Fig 5. As we increase the sample temperature, the stoichiometric ratio of Mo to S is varied. At 455°C, this oxidation process is completed and MoO₃ is formed, which is evident from EDAX spectra. It was found that no stoichiometric change occurs at 700°C, which is confirmed by EDAX data.

Raman spectrum of the MoS₂ based hybrid nanostructure heated at 360°C is shown in fig 7. From the spectrum, the Raman peaks are localized at 146 cm⁻¹, 234 cm⁻¹, 280 cm⁻¹ and 333 cm⁻¹ for the characteristic peaks of metallic MoS₂ [18]. As per previous reports, semiconducting 2H MoS₂ exhibits two dominant vibrational modes of (E₁₂g) and (A₁g), which appear in the range of 370-400 cm⁻¹ [19]. One of the vibrational modes of 2H MoS₂ in the present spectrum is due to the trace amount of 2H MoS₂ in the samples. The small peak at 195 cm⁻¹ is due to the presence of layered structure of MoS₂ [18]. The peaks at 662 cm⁻¹, 811 cm⁻¹ and 993 cm⁻¹ are the characteristic peaks of MoO₃ [18].
3. Optical properties

The absorption spectra of sample 300°C and hybrid nanostructure are shown in fig 8a and fig 8b. The three common peaks are observed from the both spectra, which located at 210nm, 258nm and 327nm respectively. The strong peak at 210nm, which is considered as invalid peak, is due to increased scattering at the edge of the spectrophotometers range [26]. In fig 9b, the two shoulder peaks at 220nm and 263nm are the excitonic nature of MoO$_3$ [27]. The one at 329nm is observed in the near-UV region, which is due to the surface defects [28] and shoulder peak at 375nm may be assigned to the excitonic peaks of MoS$_2$-QDs [28]. In sample 300°C, the feeble absorption peaks observed at 674nm, 608 and 448nm which corresponds to exciton A, exciton B and exciton C of 2H-MoS$_2$ respectively and these values are close to the previous reported papers [29]. This feeble intensity is due to the coexistence of two MoS$_2$ phases (2H - semiconducting and 1T- metallic phase). This coexistence phases are completely transformed into single phase (metallic phase) in hybrid nanostructure. As a result, no significant absorption peaks can be seen in this sample. But the absorption spectrum is monotonically decreasing with increasing wavelength which indicates that the characteristics of nonplasmonic metallic nanostructures [30].
Fig 8 (a) and Fig 8(b) absorption spectrum of sample at 300°C and 360°C respectively (c) direct bandgap energy of MoS$_2$ based hybrid nanostructure.

The bandgap energy of the hybrid nanostructure was determined using Tauc plot drawn using the relation $(\alpha h\nu)^n = A(h\nu - E_g)$ ................................................... (equation 1).

Where $\alpha$ is the absorption coefficient, A is the proportionality constant, $E_g$ is the bandgap energy. $n=2$ in equation 1 gives the direct bandgap energy value and $n=1/2$ gives indirect bandgap energy [31]. According to Beer-Lamberts law, optical absorbance(A) of the solution is proportional to concentration(C) and optical length(l) and is given by

$$A = \varepsilon l C$$ ................................................................. (equation 2).

Here molar absorption coefficient is equal to molar extinction coefficient [32]. $l=1$cm, $C=0.42$ mM. The bandgap energy of the hybrid nanostructure is found to be 2.26 eV.

4. Conclusion

Even though MoS$_2$-MoO$_3$ hybrid nanostructures has been reported for various applications, the synthesizing methods are still complex. Here we have successfully synthesized a novel simple method for the preparation of MoS$_2$ based hybrid nanostructures using single precursor by thermal decomposition method. This method was optimized by varying temperature and heating time. TGA, Electron microscopy, and XRD are the characterization tools used for this optimization studies. Optical properties of this hybrid structure were also studied. The bandgap energy of the hybrid nanostructure is 2.2eV. By tuning the parameters viz temperature and time of heating, the composition of the hybrid nanostructures (ie, the ratio of MoS$_2$ to MoO$_3$) can be varied according to any particular application.
5. References

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