Abstract

Transition metal dichalcogenide (TMD) materials have been found to be potential materials for various optoelectronic applications because of their semiconducting nature [1-7]. TMD materials are finding applications in room temperature to moderately high temperature mechanical applications, such as dry solid lubricants, etc. [8-10]. This is due to the ability of its stable layers to glide over one another almost frictionlessly. Being a finite band gap (BG) layered semiconductor (SC) and due to its BG being tuneable, TMD has been studied extensively as a successor of graphene [1, 4, 11-17]. MoS_2 and WS_2 are two members of TMDs family which have been studied broadly in recent years for many applications. Composites of TMDs have great application in photovoltaic cell, battery, transistor, photodetector etc. [5-7, 18, 20]. Synthesis of layered MoS_2/graphene (MoS_2/G) composites, application of MoS_2/TiO_2 nanocomposites, ITO-MoS_2-Au stacked structure in photovoltaic cells, the photocatalytic activity of different composites of MoS_2 and WS_2 in combination with TiO_2, CdS, Graphene etc., have been reported in recent years [19-22]. Application of ternary TMD alloys such as $WS_{2(1-x)}Se_{2x}$ as electrocatalyst for enhanced hydrogen evolution, $MoS_{2x}Se_{2(1-x)}$ and $Mo_xW_{(1-x)}S_2$ nanosheets as electrocatalyst in dye-sensitized solar cell, have been reported recently [23-25]. The study of intercalation of 3d block transition metal in TMDs, doping of potassium in MoS_2 to study superconductivity, intercalation of both organic and inorganic molecules in TMDs as SCs have also been reported[26, 27].

Though bare TMDs, composites, and intercalation of 3d block metals in TMDs have been explored extensively worldwide, there are very few detailed studies of ternary compounds of TMDs. Both MoS_2 and WS_2 have similar structure (trigonal prismatic, Mo^{IV} or W^{IV} and pyramidal, S^{-2}). These TMDs have minimum lattice mismatch and incorporation of Mo, W and S in the formation of intercalated and ternary TMD compound is quite possible. Due to the insertion of guest atoms, ions or molecules such compounds have significantly different functions from those of the parent materials. Since Mo is a 4d block and W is a 5d block element, we are expecting a change in behavior in the ternary compound of Mo, W and S as compared to the pristine MoS_2 and WS_2. We are, therefore, interested in investigating the behavior, both structural and optical, of the mixed TMD

compound of Mo, W and S. In this report, we have not studied the materials in the bulk form but in the form of nanoparticles (NPs). In our study, these TMD compound NPs have been found to be very good photocatalyst and show enhanced luminescence in comparison to their parent materials MoS_2 and WS_2 [28]. We have also performed a density functional theory (DFT) simulation to investigate whether there is any change in behavior when W atom is inserted in MoS_2 lattice. To the best of our knowledge, for the first time, we have compared experimental and theoretical results for W addition in MoS_2 layers in the form of bimetallic ternary compounds.

The first chapter of this doctoral thesis is an introductory chapter which highlights the salient features and fundamental aspects of the ternary compound TMDs. Here we will discuss TMD materials, some important properties and findings of TMD materials and their applications in the light of existing literature and recent reports. We will highlight the advantage of ternary TMD compound NPs over bare TMDs in the chosen field.

In the second chapter, we have reported the synthesis process of MoW-disulfide compounds having different Mo:W molar ratio in particle form in the nanoscale range by using solid-state reactions and provide a comparative analysis of its morphology and optical properties with as-synthesized MoS_2 and WS_2 NPs. The application of solid state reaction in the synthesis of bimetallic ternary compound TMDs is a new approach. We will briefly discuss various characteristic tools employed for characterization of the as-synthesized materials. The synthesized materials are MoS_2 NPs, WS_2 NPs, NPs of two compounds of Mo, W and S namely MoW-diulfide1 in which Mo:W molar ratio is 1:1 and MoW-diulfide2 in which Mo:W molar ratio is 10:1 (taken in the synthesizing process). In each section, a brief description and working process of the different characterization techniques are given.

In chapter 3 different characteristic techniques e.g. X-ray diffraction, Raman spectroscopy, scanning electron microscopy, transmission electron microscopy and energy dispersive X-ray spectroscopy and N_2 adsorption/desorption isotherm analysis are employed to study morphology and compositional properties of the as-synthesized materials. The optical properties of the materials are investigated using UV-visible spectroscopy and photoluminescence spectroscopy. We have observed that there is an enhancement in luminescence in the W incorporated MoS_2 compounds, indicating that it can be a good material for luminescence devices.

In chapter 4 we have studied the photocatalytic behavior of the as-synthesized ternary compound MoW-disulfide1 NPs along with MoS_2 and WS_2 NPs. Since the prepared NPs are SC in nature as depicted in chapter 3, these have potential applications in photocatalytic activity. The multiple BG values of the compound NPs also helps in utilizing a broad range of the solar spectrum and hence in chapter 4 we have studied the photocatalytic behavior of the as-synthesized compound NPs. We have not studied the photocatalytic behavior of MoW-disulfide2 NPs because it does not show any drastic change in optical behavior from its parent material MoS_2 and WS_2 due to having less concentration of W as compared to Mo. A comparative study of photocatalytic activity reveals that the as-prepared compound MoW-disulfide1 NPs shows better photocatalysis than MoS_2 and WS_2 NPs. For the comparison, we have selected rhodamine B and Methyl Orange as the model dyes. We have performed experiments to observe the photocatalytic behavior by degrading the dye solution using the mentioned NPs catalysts. The degradation is observed by monitoring the decrease in the maxima of UV-visible absorption peaks in each experiment. The reusability of the compound MoW-disulfide1 catalyst makes the catalytic process a reliable and cost-effective technique. The as-synthesized ternary compound NPs catalyst has potential applications in the field of wastewater treatment and pollution degradation.

In chapter 5 we have performed DFT simulation to study the effect of addition of W in MoS_2 system and investigated total density of states and partial density of states along with the band structure of the systems having different combination of W, Mo and S. Computational investigation of the effect of W in the MoS_2 system using DFT also reveals that insertion of W makes the compound system behave as direct BG SC, a possible reason for which the enhancement of photoluminescence is observed in the experimental section.

In the final chapter 6, we have highlighted the conclusions drawn from the present investigation. We have summarized several important findings and noted their relevance in probable future works.

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