# Nanoheterostructures based on the Layered Transition Metal Dichalcogenide Molybdenum Diselenide for Catalytic and Optoelectronic Applications

**Synopsis of the Thesis**

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Two dimensional (2D) transition metal dichalcogenides (TMDs) have made a smooth entry into the elite class of materials due to the perfect amalgamation of unique and tunable material properties such as quantum-well structures with broad range of indirect to direct band gap crossover, thickness dependent band transitions, in-plane charge carrier mobility, high specific surface area, and enhanced spin-orbit coupling. The applications of these materials are highly dependent on the surface sites, *viz.* terrace sites and edge sites. Terrace sites at basal planes are terminated with less number of dangling bonds and are useful for various applications in optoelectronic devices, supercapacitors, spintronic devices whereas the edge sites on the side surface have more number of dangling bonds which are active sites for catalytic reactions and ion batteries. The work in this thesis emphasizes on how to utilize these different surface sites for various catalytic and optoelectronic device applications *via* developing various synthetic protocols. Synthesis of defect-rich and vertically aligned $MoSe_2$ nanosheets for hydrogen evolution reaction and counter electrode in dye-sensitized solar cells (DSSCs) has been carried out. Further, we have shown how to utilize these defects for designing nanoheterostructures with different materials for photonic device applications. Lattice matched heterostructures have been grown epitaxially and also it has been possible to combine materials with completely different lattice structures by means of bifunctional ligands. A number of applications such as dye-sensitized solar cell (DSSC), quantum-dot sensitized solar cell (QDSC), hydrogen evolution reaction (HER), oxygen evolution reaction (OER) and photodetectors, to name a few, have been attempted with these nanoheterostructures.

The thesis has been divided into the following chapters:

## Chapter 1: Introduction

In this chapter, extensive literature survey on TMD, plasmonic, and perovskite materials is presented. The chapter also describes about the different surface sites of TMDs and the current limitations of these materials. In this chapter we have also discussed the various mechanisms of TMD based materials for applications in catalysis and optoelectronic devices. This chapter also comprises the objectives of the present thesis work.

## Chapter 2: Materials and Methods

Methods used for the syntheses of nanosheet morphology of TMDs and their nanostructures are described in this chapter. The detailed method for the functionalization of 2D TMDs with various thiol containing ligands are discussed. This chapter also includes the methodology for the preparation of electrocatalysts, fabrication procedures of dye/quantum dot sensitized solar cells, photodiodes. Brief accounts of the X-ray diffraction, absorption spectroscopy, steady state/time resolve fluorescence spectroscopy, Raman spectroscopy, FTIR spectroscopy, transmission electron microscopy, elemental analysis techniques used to characterize the newly synthesized materials are provided.

## Chapter 3: Colloidally Synthesized Defect-Rich $MoSe_2$ Nanosheets for Superior Catalytic Activity

The presence of defects and the role of thickness towards the catalytic processes are realized. In this chapter, we report a colloidal synthesis of 2H-$MoSe_2$ nanosheets (NSs) having large number of defects and vertically aligned edges, where the thickness is varied by changing the amount of coordinating solvent. The Se-vacancies in these NSs introduce defect sites which are corroborated by the presence of additional vibration modes in Raman spectra. These NSs exhibit thickness dependent electrocatalytic hydrogen evolution reaction (HER) performances with a low overpotential (210-225 mV) at 10 $mA/cm^2$ current density and a small Tafel slope (54-68 mV/decade). The combined effects of thickness dependent hopping mechanism, conductivity and the larger electrochemical surface area (ECSA) value are contributed for better catalytic activity of lower monolayer NSs. Moreover, these $MoSe_2$ NSs are also employed as counter electrodes for the fabrication of dye sensitized solar cells (DSSCs) via a cost-effective and simplified procedure. The power conversion efficiencies of $7.02 \pm 0.18\%$, comparable with Pt counter electrode ($7.84 \pm 0.10\%$) could be routinely achieved. These results demonstrate a novel synthetic strategy to prepare layered transition metal dichalcogenides with superior catalytic applications.

## Chapter 4: $MoSe_2$-$Cu_2S$ Vertical p-n Nanoheterostructures for High-Performance Photodetector

Heterostructures based on atomically thin two dimensional layered transition metal dichalcogenides are highly promising for optoelectronic device applications owing to their tunable optical and electronic properties. Hence, a colloidal synthetic route is devoloped using defect–passivation to synthesize $MoSe_2$–$Cu_2S$ nanoheterostructures (NHSs). For the design of $MoSe_2$–$Cu_2S$ NHSs, defect-rich $MoSe_2$ NSs are employed so that the $Cu_2S$ islands grow vertically on top of the defect sites present on the $MoSe_2$ surface, thereby forming vertical p-n junctions having plasmonic characteristics. These $MoSe_2$–$Cu_2S$ nanoheterostructures have been used to fabricate photodetectors with superior photo response characteristics. The fabricated device exhibits a broadband spectral photoresponse over the visible to near infrared range with a highest peak responsivity of 410 $mAW^{-1}$ at -2.0 V and over 3000-fold photo-to-dark current ratio. The superior device performance of $MoSe_2$-$Cu_2S$ over only $MoSe_2$ devices is due to the combined effect of the pronounced light-mater interaction, passivation of surface defects, and formation of p-n junction.

## Chapter 5: Activation of Basal Planes of $MoSe_2$ nanosheets for Enhanced Electrocatalytic Applications

The oxygen evolution reaction (OER) activity of the TMDs are limited by the inert basal planes. Further improvement of the catalytic activity of TMDs demands the activation of basal planes as well as increase the conductivity. Here we have demonstrated that the design of nanoheterostructures with suitable counterparts is highly useful to activate the inert basal planes of TMDs. By combining experiments and theoretical calculations, we showed that $MoSe_2$-$Cu_2S$ NHSs are efficient materials for OER activity. The first principle calculations show that the inert basal planes of $MoSe_2$ are activated when $Cu_2S$ is grown over the basal planes of $MoSe_2$ NSs. $MoSe_2$-$Cu_2S$ NHSs exhibit more active sites as compared to their individual counterparts as suggested by electrochemical surface area measurements. All these parameters contribute towards better catalytic activity of $MoSe_2$-$Cu_2S$ NHSs due to the synergistic contribution of both materials along with a decrease in the thermodynamic barrier. These materials are also employed as counter electrodes in QDSSCs. The high surface area of the $MoSe_2$ NSs promote high numbers of the $Cu_2S$

active sites spread across the surface NSs. Due to the high surface area and shuttling of electrons across the $MoSe_2$ NSs the PCE is increased by ~ 18% as compared to the PCE of $Cu_2S$.

## Chapter 6: Enhanced Photocurrent owing to Shuttling of Charge Carriers across 4-Aminothiophenol Functionalized $MoSe_2$−$CsPbBr_3$ Nanohybrids

The growth of perovskite over the surface of TMDs for high performance photonic device applications has been a challenging task owing to the distinguishable surface chemistry of these two different classes of materials. In this chapter, we have developed a synthetic route for the design of $MoSe_2$−$CsPbBr_3$ nanohybrid structures using a bifunctional ligand *i.e.* 4-aminothiophenol. Close contact between them is established *via* a bridge that leads to the formation of a donor-bridge-acceptor system. The presence of small conjugated ligands between these two constituents facilitates faster charge diffusion across $MoSe_2$−$CsPbBr_3$ interfaces, which is supported by fluorescence spectroscopic measurements. The density functional theory calculations confirm the Type-II band alignment of the constituents within the MvNHs, where the electrons are transferred from $CsPbBr_3$ nanocrystals into the $MoSe_2$ nanosheets and holes are confined into the $CsPbBr_3$ nanocrystals. The $MoSe_2$−$CsPbBr_3$ nanohybrids show much higher photocurrent in the photodiode configuration ($\sim 2 \times 10^4$-fold photo-to-dark current ratio) as compared to pure $CsPbBr_3$ nanocrystals, and pristine $MoSe_2$ nanosheets owing to the synergistic effect of pronounced light-matter interaction followed by efficient charge separation and transportation. A photoelectrochemical cell is also constructed using these materials to measure the photo current in solution medium.

## Chapter 7: Summary and future Perspective

In this chapter, we have summarized the results of the thesis, emphasizing the use of different sites of TMDs for applications in catalysis and optoelectronic devices. The defect passivated syntheses using different thiols are employed to design NHSs as it builds an intimate contact between the constituents. The mechanisms for the enhancement of catalytic and optoelectronic device performance in each systems are studied in details. In future, these fundamental studies open up the possibility for construction of new NHS systems for catalytic as well as photonic device applications, also study the detailed charge transfer kinetics and surface chemistry at the interfaces.

## Publications:

1. Hassan, M.S.; Bera, S.; Gupta, D.; Ray, S.K.; Sapra, S. $MoSe_2$−$Cu_2S$ Vertical P−n Nanoheterostructures for High-Performance Photodetectors. *ACS Appl. Mater. Interfaces* **2019**, *11*, 4074–4083.
2. Hassan, M. S.; Jana, A.; Gahlawat, S.; Bhandary, N.; Bera, S.; Ingole, P. P.; Sapra, S. Colloidally Synthesized Defect-Rich $MoSe_2$ Nanosheets for Superior Catalytic Activity. *Bull. Mater. Sci.* **2019**, *42*, 74 (1-11).
3. Yadav, Y.; Hassan, M.S.; Verma, P.; Sapra, S. Nickel Selenide Nanoparticles as a Cheap Alternative for Pt-Counter Electrode in Dye-Sensitized Solar Cells. *Journal of NanoScience and Nanotechnology* **2019,** *19*, 375-382
4. Hassan, M.S.; Basera, P.; Bera, S.; Mittal M.; Ray, S.K.; Bhattacharya, S.; Sapra, S. Shuttling of Charge Carriers across 4-aminothiophenol Functionalized $MoSe_2$-$CsPbBr_3$ nanohybrids **(Under revision *ACS Appl. Mater. Interfaces*)**
5. Hassan, M.S.; Basera, P.; Gahlawat, S.; Ingole, P.P.; Bhattacharya, S.; Sapra, S. Activation of Basal Planes of Transition Metal Dichalcogenides for Enhanced Oxygen Evolution Reaction **(Manuscript under preparation)**
6. Hassan M.S.; Soni B.; Sapra S. Effect of Architecture of $TiO_2$ on Photovoltaic Parameters of Dye and Quantum Dot Sensitized Solar Cell (**Manuscript under preparation)**
7. Sarkar, S.S.; Hassan, M.S.; Bear, S.; Sapra, S.; Khatri R.K.; Ray, S.K. Novel $MoSe_2$-$Cu_{2-x}S$/ GaAs heterostructures based self-biased broadband photodetector with high detectivity **(Manuscript under preparation)**
8. Mitra, B.; Singh, M.; Sapra, S.; Vinayak, P. Hassan, M.S. Layered transition Metal Dichalcogenide sensing film based extended gate field-effect transistor (EGFET) for the sensing of heavy metals **(patent submitted, Application No. 201911049144 (FT/IDF/11/2019/160))**