1. Significant results and outcomes:

Y2 of PRF project is primarily aimed at the development of highly catalytically active transition metal dichalcogenides (TMDs) such as MoS$_2$ nanostructures through a hydrothermal synthesis route. Basic (electro)catalytic properties of some of the synthesized TMDs have also been evaluated during this project period. Technical details pertaining to synthesis, characterization, and studies on (electro)catalytic properties are presented in the following sections.

1.1. Synthesis and characterization of transition metal doped transition metal dichalcogenide (TM-doped TMD) layered nanostructures by the hydrothermal method:

Transition metal dichalcogenide (TMD) materials have shown significant potential over the past decade owing to their excellent electrical, optical, mechanical, and (electro)chemical catalytic properties[1, 2]. Among various synthesis processes for TMDs, hydrothermal method draws much attention because of the ability to scale-up the production and better control over the sum of layers if growth happens via solution-mediated synthesis[3]. The intrinsic essence of enhancing catalytic activity of TMDs materials is the modulation of electron density of catalytically active sites within that. Doping TMD with transition metals such as Ni is expected to alter the electronic density of Mo and S atom and therefore modulating the electrocatalytic activity of the in-plane atoms.

Synthesis of transition metal doped MoS$_2$ was carried out as follows: For the preparation of different TM-doped MoS$_2$, ammonium thiomybdate [(NH$_4$)$_2$MoS$_4$] was added to DMF solution of 4.25 $\times$ 10$^{-5}$ mol corresponding Nickel metal ion [Ni(NO$_3$)$_2$]. The mixture was sonicated at room temperature for ~5 min to achieve a clear and homogeneous solution. The reaction solution was then transferred to a 100 mL Teflon-lined autoclave container and then heated in an oven at 200 °C for 10 h. Then the product was collected by centrifugation at 8000 rpm for 20 min, washed with DI water, and recollected by centrifugation. The washing step was repeated at least three times to ensure that most DMF was removed. Finally, the product was re-dispersed in 10 mL of DI water, frozen by liquid nitrogen, and lyophilized overnight. Then, the black powder was calcined in a tubular furnace at 400 °C for 3 h in Ar gas atmosphere (heating rate: 10 °C/min). Pure MoS$_2$ was synthesized by the same procedure except for adding metal ion. As synthesized TM-doped MoS$_2$ nanosheets, along with their bulk counterpart (without TM doping of MoS$_2$), were systematically characterized using transmission electron microscopy (TEM) and X-ray photoelectron microscopy (XPS). The TEM images show that TM doped-MoS$_2$ (Figure 1a & 1b) is composed of distinct ripples and corrugations, which implies the ultrathin structure of the sample with a layer spacing of 0.57 nm assigned to the (002) crystalline plane of MoS$_2$. The amount of Ni incorporation in Ni-MoS$_2$ is calculated by EDAX and was found to be 3.31 at% (Figure 1c). Whereas, undoped MoS$_2$ structures consists of very few ripples with layer spacing of 0.64 nm (Figure 1d & 1e). The appearance of small nanosheets with sharp edges in TM-doped MoS$_2$ indicates a high crystallization of the product and such structures are expected to be enriched with catalytically active edge sites[4]. We have also synthesized other TM-doped MoS$_2$ nanosheets by the hydrothermal method. Co-doped MoS$_2$ crystals can be synthesized by adding small amount of CoCl$_2$ powder in the mixture of transition metal oxide. We chose CoCl$_2$ compound as the precursor of the Co dopant due to its relatively low melting temperature (740 °C) and obtained high crystalline flakes of Co-doped MoS$_2$.

1.2. Electrochemical properties

Before attempting the hydrodesulfurization (HDS) process with TMDs catalysts, we have screened their (electro)catalytic activity towards hydrogen evaluation (HER) and oxygen evolution reaction (OER). Both evolution
Reactions were performed in alkaline conditions (1 M KOH) using linear sweep voltammetry (LSV) with a conventional three-electrode setup at a scan rate of 5 mV/s. Figure 2a shows the comparative LSV recorded during HER on TM-doped MoS2 along with its counterpart catalysts. During the cathodic sweep, TM-doped MoS2 showed minimal onset potential for hydrogen reduction (η = 150 mV vs. Reversible Hydrogen Electrode (RHE)) and for oxygen evolution (η = 350 mV vs RHE), as shown in Figure 2b, followed by a sharp rise in current. Whereas, its counterpart’s Ni nanoparticles and 1T-MoS2 (without TM doped) displayed the onset potential and HER catalytic current at > 300 mV vs. RHE. The obtained results denote a high (electro) catalytic nature of TM-doped MoS2 on both reactions. The reduced overpotential for hydrogen reduction on TM-doped MoS2 was likely due to the exposure of highly active edge sites and changes in atomic structures of MoS2 nanosheets while TM-doping, which decreases the hydrogen adsorption energy on catalytically active edge sites. To further corroborate the catalytic activity, we performed Tafel analysis on the obtained polarization curves with iR-correction as demonstrated in Figure 2c and 2d. It was found that TM-doped MoS2 exhibited a Tafel slope value of 115 mV/dec and 99 mV/dec for hydrogen and oxygen evolution reactions respectively. The obtained Tafel slope values were very low compared to its counterpart catalyst samples. Similarly, the exchange current density (j0) was calculated from the extrapolation of the X-axis in the Tafel plot, and it was found that TM-doped MoS2 show higher j0 compared to its counterparts. From the Tafel and exchange current analysis, it is evident that atomic engineering of MoS2 nanostructures with TM doping exhibits enhanced (electro) catalytic activity kinetics compared to other samples and previous reports in the literature.

2. Impact of the research

As a part of this research, PI has started working on novel AFM based in-situ Scanning Electrochemical Microscopy coupled with Raman spectroscopy (SECM-Raman) tool to evaluate (electro) catalytic activity materials in nanoscale perspective. Currently, one Ph.D., student and one postdoctoral researcher have gained operating skills on this novel tool, through which they are deepening their basic understanding of HDS catalysis reactions with the developed catalyst materials. This novel characterisation tool has exposed PI not only to HDS and nanomaterials but also to other electrochemistry related areas such as batteries wherein understanding electrode/electrolyte interfaces is critical in designing better materials that can enhance energy density and safety. We hope this would bring new knowledge not only to our students but also to the entire electrochemistry community.

3. Plans for the next reporting period to accomplish the goals

Physico-chemical transformations of pristine and doped MoS2 based nanostructures in HDS process will be evaluated using novel in-situ AFM-based SECM-Raman technique in upcoming months. HDS performance studies will be conducted on the best identified HER catalysts. The collected data and analysis will be reported in the final report.

4. References:


