

**Project Title:** Three-Dimensional MoS<sub>2</sub> Nanostructures for Deep Hydrodesulfurization Catalysis

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## 1. Significant results and outcomes

Y1 of PRF project is mainly aimed at the optimization of growth parameters in chemical vapor deposition (CVD) method for the synthesis of transition metal dichalcogenides (TMDs). Basic 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 catalytic properties are presented in the following sections.

### 1.1. Synthesis and characterization of transition metal dichalcogenide (TMD) atomic layers by chemical vapor deposition method (CVD)

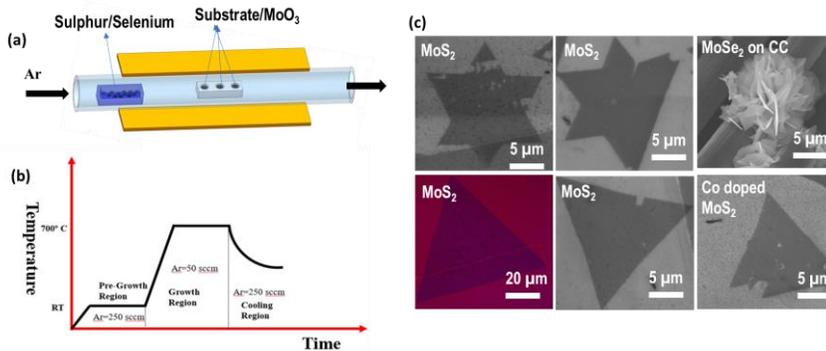
Two dimensional (2D) layered materials have shown significant potential over the past decade owing to their excellent electrical, optical, mechanical, and (electro)chemical properties [1]. In particular, inorganic-based transition metal dichalcogenides (TMDs), commonly represented as MX<sub>2</sub> (M= transition metals, and X= S, Se, Te) compounds, are emerging as potential candidate to replace conventional catalysts [2-4]. To obtain a high quality single atomic layer of MoS<sub>2</sub>, many approaches have been considered in an account like mechanical exfoliation, chemical exfoliation and chemical vapor deposition (CVD). Among all synthesis processes, CVD method draws much attention because of the scaled-up production and give better control over the sum of layers if growth happens via surface-mediated synthesis. All the CVD method reported to date for growing MoS<sub>2</sub> used chemically inert solid-state dielectric substrates [5].

Experimental procedures of CVD grown MoS<sub>2</sub> are as follows: quartz boat consisting of MoO<sub>3</sub> powder were positioned in the middle of furnace whereas Sulphur boat placed at the upstream of lower temperature zone as shown in Figure 1 (a).

Initially, for growing monolayer MoS<sub>2</sub> at different temperature was categorized from 650 °C to 800 °C. The typical process flow of CVD grown MoS<sub>2</sub> as shown in Figure 1 (b), where Ar pass for 250 sccm for 20 mins to remove all environmental gases and then ramp up the temperature till 700 °C in 15 mins. It has been noted that low-temperature growth of MoS<sub>2</sub> showed bulk deposition of material on Si/SiO<sub>2</sub> substrate [6]. In order to obtain a high crystalline monolayer of MoS<sub>2</sub>, the different temperature has been categorized. It is found that at lower temperature i.e., 700 °C shows the peak of MoS<sub>2</sub>, MoO<sub>3</sub> and MoO<sub>2</sub> in X-ray diffraction (XRD) spectra which suggested that the reaction does not take place completely at low temperature. Figure 1 (c) shows the optical image of CVD grown MoS<sub>2</sub> monolayer of size in micrometer at 760 °C. Similarly, we have also successfully synthesized monolayer and few-layer crystalline flakes of MoSe<sub>2</sub> on carbon cloth (CC) by using CVD method at 850 °C. The growth of TMD films through the reduction of transition metal oxide (TMO) (such as MoO<sub>3</sub>) by Selenium vapor on the CC substrate covered in presence of Ar/H<sub>2</sub>. We have also grown heavily doped monolayer and few-layer TMDs by the CVD method. Halide assisted electron-doped MoS<sub>2</sub> monolayer crystals can be synthesized by adding small amount of CoCl<sub>2</sub> powder in the mixture of transition metal oxide. We choose CoCl<sub>2</sub> compound as the precursor of the Co dopant due to its relatively low melting temperature (740 °C). Al<sub>2</sub>O<sub>3</sub> crucible containing CoCl<sub>2</sub> and MoO<sub>3</sub> placed at high temperature zone upstream of the sulfur source at 780 °C, which provides high crystalline flakes of Co-doped MoS<sub>2</sub>.

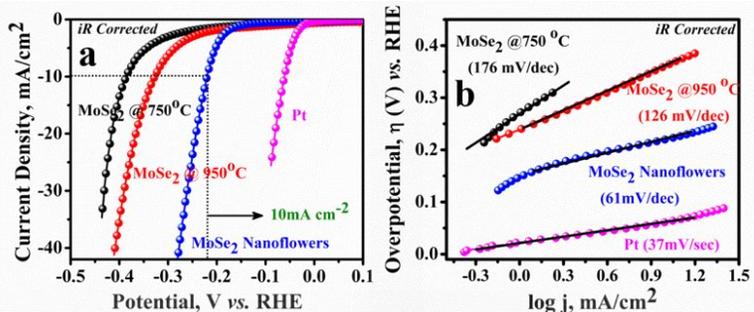
### 1.2. Electrochemical properties

Before evaluating above prepared catalysts for hydrodesulfurization (HDS) reaction, we have screened their catalytic activity towards hydrogen evolution reaction (HER). HER was performed in acidic conditions (0.5 M H<sub>2</sub>SO<sub>4</sub>) using linear sweep voltammetry (LSV) with a conventional three-electrode setup at a scan rate of 1 mV/s. Figure 2a shows



**Figure 1** (a) Schematic diagram of CVD (b) Process of MoS<sub>2</sub> growth at 700 °C (c) Morphology of MoS<sub>2</sub> /MoSe<sub>2</sub> CVD growth on different substrate

the comparative voltammograms of MoSe<sub>2</sub> grown at different temperatures along with a benchmark platinum (Pt) catalyst. During the cathodic sweep, MoSe<sub>2</sub> nanoflowers showed minimal onset potential for hydrogen reduction ( $\eta = 170$  mV vs. Reversible Hydrogen Electrode (RHE)) followed by a sharp rise in current, which denotes a high catalytic nature in HER, whereas, MoSe<sub>2</sub> grown at 750 °C and 950 °C displayed the onset potential and HER catalytic current at  $> 250$  mV vs RHE. The reduced overpotential for hydrogen reduction on MoSe<sub>2</sub> nanoflowers was likely due to the vertical orientation of MoSe<sub>2</sub> nanosheets, which is decreasing 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 2b. It was found that MoSe<sub>2</sub> nanoflowers exhibited a Tafel slope value of 61 mV/decade, which is very low compared to other samples grown at 750 °C (176 mV/decade) and 950 °C (126 mV/decade). Naturally, Pt displays (37 mV/decade) the lowest Tafel slope value among all the electrocatalysts studied for HER. Similarly, the exchange current density ( $j_0$ ) was calculated from the extrapolation of the X-axis in the Tafel plot, and it was found that MoSe<sub>2</sub>/CC (0.85 mA/cm<sup>2</sup>) nanoflowers show higher  $j_0$  compared to the samples grown at 750 °C (0.24 mA/cm<sup>2</sup>) and 950 °C (0.18 mA/cm<sup>2</sup>). In addition, the enhancement of HER kinetics was confirmed from the overpotential measured at 10 mA/cm<sup>2</sup> HER current, and it was found that nanoflower samples require only  $\eta = 220$  mV, whereas MoSe<sub>2</sub> grown at 750 °C and 950 °C needs  $> 350$  mV. From the Tafel and exchange current analysis, it is evident that MoSe<sub>2</sub> with a nanoflower structure exhibits enhanced HER kinetics compared to other samples and previous reports in the literature.



**Figure 2.** (a) HER polarization curve on MoSe<sub>2</sub> nanoflowers (blue) compared with MoSe<sub>2</sub> grown at 750 °C (black), 950 °C (Red), and benchmark Pt/C catalyst (Magenta). Scan rate: 1mV/sec. (b) Tafel plot ( $\eta$  vs  $\log j$ , mA cm<sup>-2</sup>)

## 2. Impact of the research

As a part of this research, PI has set-up novel AFM based in-situ Scanning Electrochemical Microscopy coupled with Raman spectroscopy (SECM-Raman) tool. This novel characterization 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. Currently, one Ph.D., student and one postdoctoral researcher have gained operating skills on this novel tool, though which they are deepening their basic understanding of HDS catalysis reactions. 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 MoS<sub>2</sub> nanostructures in HDS process will be evaluated using novel in-situ AFM-based SECM-Raman technique. HDS performance studies will be conducted on the best identified HER catalysts. The collected data and analysis will be reported in the Y-2 and final report.

## 4. References:

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