

Project Title: Three-Dimensional MoS₂ Nanostructures for Deep Hydrodesulfurization Catalysis

Principal Investigator: Dr. Leela Arava, Department of Mechanical Engineering, Wayne State University, Detroit, MI 48202

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 MoS₂ 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 MoS₂ was carried out as follows: For the preparation of different TM-doped MoS₂, ammonium thio molybdate [(NH₄)₂MoS₄] was added to DMF solution of 4.25×10^{-5} mol corresponding Nickel metal ion [Ni (NO₃)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 MoS₂ was synthesized by the same procedure except for adding metal ion. As synthesized TM-doped MoS₂ nanosheets, along with their bulk counterpart (without TM doping of MoS₂), were systematically characterized using transmission electron microscopy (TEM) and X-ray photoelectron microscopy (XPS). The TEM images show that TM doped-MoS₂ (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 MoS₂. The amount of Ni incorporation in Ni-MoS₂ is calculated by EDAX and was found to be 3.31 atom % (Figure 1c). Whereas, undoped MoS₂ 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 MoS₂ 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 MoS₂ nanosheets by the hydrothermal method. Co-doped MoS₂ crystals can be synthesized by adding small amount of CoCl₂ powder in the mixture of transition metal oxide. We chose CoCl₂ 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 MoS₂.

1.2. Electrochemical properties

Before attempting the hydrodesulfurization (HDS) process with TMDs catalysts, we have screened their (electro)catalytic activity towards hydrogen evalution (HER) and oxygen evolution reaction (OER). Both evolution

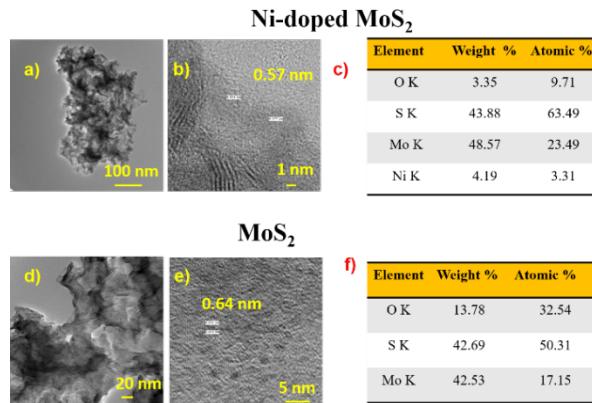


Figure 1 (a) &(b) TEM images of Ni doped MoS₂ (c) elemental compositions of Ni doped MoS₂ (d) & (e) TEM images of undoped MoS₂ (f) elemental compositions of undoped MoS₂.

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 ($\eta = 150$ mV vs. Reversible Hydrogen Electrode (RHE)) and for oxygen evolution ($\eta = 350$ 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 99mV/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 (j_0) was calculated from the extrapolation of the X-axis in the Tafel plot, and it was found that TM-doped MoS₂ show higher j_0 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) catlaytic 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 caltalysis reactions with the developed catalyst materials. This novel charecterization 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:

- (1) Benck, J.D., et al., *Catalyzing the hydrogen evolution reaction (HER) with molybdenum sulfide nanomaterials*. Acs Catalysis, 2014. **4**(11): p. 3957-3971.
- (2) Chhowalla, M., et al., *The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets*. Nature chemistry, 2013. **5**(4): p. 263.
- (3) Wang, H., et al., *Synthesis, properties, and optoelectronic applications of two-dimensional MoS₂ and MoS₂-based heterostructures*. Chemical Society Reviews, 2018. **47**(16): p. 6101-6127.
- (4) Yan, Y., et al., *Recent Development of Molybdenum Sulfides as Advanced Electrocatalysts for Hydrogen Evolution Reaction*. ACS Catalysis, 2014. **4**(6): p. 1693-1705.

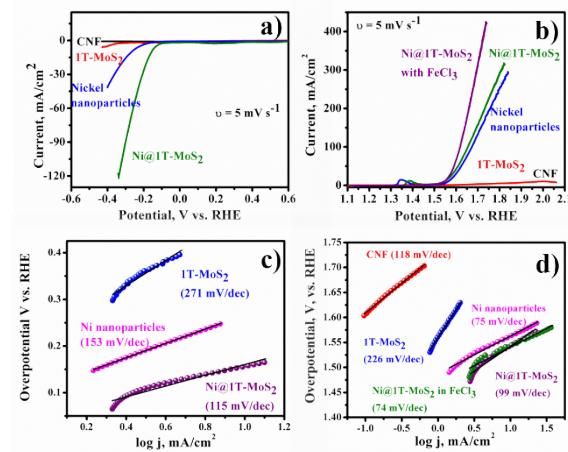


Figure 2. (a) & (c) HER polarization curves of various electrocatalysts as indicated and their corresponding Tafel plots derived from early stages of HER respectively; (b) & (d) OER polarization curves of various electrocatalysts as indicated and their corresponding Tafel plots derived from early stages of OER respectively.

Figure 2a and 2b show HER and OER polarization curves, respectively, for various electrocatalysts. The curves are plotted against Potential (V vs. RHE) and Current (mA/cm²). The curves for TM-doped MoS₂ (blue) show significantly lower overpotentials compared to their counterparts (red, green, purple). Panel (c) shows the corresponding Tafel plots (Overpotential V vs. RHE vs log j, mA/cm²) for HER, and panel (d) shows the Tafel plots for OER. The Tafel slopes and exchange current densities (j_0) are summarized in the following table: