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The Effect of Hydrothermal Duration on the Formation of Activated Edgesites of 2-H Molybdenum Disulfide and the of Hydrogen Evolution Performances of the Material

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Abstract – Molybdenum disulfide (MoS_2) is a nontoxic, environmentally friendly, abundant semiconducting material which is widely used in the areas of hydrogen storage, gas sensing and, solid super lubricant. It has three major phases called 1-T MoS_2, 2-H MoS_2 and 3-R MoS_2. Among them 2-H MoS_2 form is the stable form which has a hexagonal phase structure with an activated edge. Therefore, Activation of the material is possibly changing by making differences on nature of material edges. In this work, we report that influence of duration of hydrothermal process toward the growth of edge sites of 2-H molybdenum disulfide nanocomposites. In this study, we have synthesized three 2-H MoS_2 nanostructures by facile hydrothermal route by using Ammonium molybdate, Thioacetamide, and urea as the basic precursors. All the samples were prepared at 200 °C temperature by changing the duration of hydrothermal process as 24h, 36h and, 48h. The samples were characterized by powder X-ray diffraction (PXRD) and Scanning electron microscope (SEM) for the phase confirmation and morphological characterizations respectively. Next, Electrochemical characterizations were carried out by using linear sweep voltammetry under the basic medium. Powder X-ray diffraction results confirmed that the prepared three products were at the Hexagonal phase of MoS_2 with minor level of impurity. The SEM images show that the as-prepared structures have a Plate-like structure with sharped edges. Then the Linear sweep voltammetry of the materials verified that the high number of sharped edges of MoS_2 nanocomposites leads to excellent activity for Hydrogen evaluation reaction (HER). When compared to others, 48 h material has a higher number of sharped edge sites and the best performances in HER. Finally, the sharpness and amounts of edge sites are possible to control with the duration of hydrothermal process and 2-H MoS_2 with more number of sharped edge sites were found to increase the performances of HER.

Keywords: Edge sites, Global warming, hydrothermal synthesis, Hydrogen Evolution, Molybdenum disulfide

1. INTRODUCTION

Global warming has been identified as one of the major environmental issue that people will face over the next two decades, and it refers to the gradual increase in the overall temperature of the Earth's atmosphere. Carbon dioxide is one of the primary gas components contributing to the daily increasing global warming, and the rate of carbon dioxide emission has increased as the use of fossil fuels has increased. In that case, many researchers have focused on the development of alternative energy sources such as hydrogen and solar panels. Therefore, the potential use of H_2 as a future sustainable fuel (Alimohammadi et al. 2018) (McCrory et al. 2015) would play a crucial role in providing a carbon neutral or carbon free energy source. In this case, the solar power is used in this process to create hydrogen via the electrochemical or photochemical water splitting reaction. However, due to the reaction's kinetic and thermodynamic barriers, the electrochemical water splitting reaction must be catalyzed and this reaction is highly pH dependent (Jiao et al. 2015) and there are only few materials that have an ability to successfully catalyse the reaction. The development of Hydrogen evaluation reaction (HER) catalysts that can reduce water under basic conditions would be a valuable contribution since they would operate in the same pH range as the Oxygen evaluation reaction OER catalyst.

The mechanism for hydrogen evolution reaction follows either Volmer-Heyrvosky or Volmer-Tafel.

Volmer step:	$H^+ + e^- + * \rightarrow H^*$
Heyrovsky step:	$H^* + H^+ + e^- \rightarrow H_{2(g)}$
Tafel Step:	$2H^* \rightarrow H_{2(g)}$ or $H_2{}^*$
Desorption:	$H_2{}^* \rightarrow H_{2(g)}$

Where, * is indicating the reaction site and H^* is the absorbed H^+ to the site and it is the initial step

of the mechanism and the second step would be a Heyrovsky or Tafel but rarely it can be a tafel. Additionally, the intermediate H^* would obtain at the water desolution in the alkali medium. That step is the rate determination step of the mechanism due to the energy barrier (Zhang et al. 2016) that created by the OH^- ions in the solution. In this scenario only the limited catalytic material would be used as an effective catalyst to perform the hydrogen evolution reaction.

Theoretically, the water reduction reaction occurs at 0.00 V (Alimohammadi et al. 2018), but due to those kinetic and thermodynamic barriers, additional potential has be supply to overcome the potential barriers of the reaction in an alkali medium. The excess voltage is known as the "over potential," (Philosophy 2019) and the material with the lowest over potential is the best hydrogen evolution catalyst. When using a catalyst, the most important parameter as to consider is Gibbs binding energy and it provides the information about the attraction H^+ ions to the surface of the catalyst. Figure 1 illustrates the comparison of catalytic activity vs. binding energy of earth abundant metals including Molybdenum disulfide (MoS_2). The catalyst which exhibits the binding energy nearly equal to the zero are the best catalyst for the hydrogen evolution reaction while other metals have poor catalytic activity. According to the volcano plot as shown in Figure 1, metals which has lower binding energy, such as Pt, Pd and Pd has the best catalytic activity for the HER because it has ability to overcome kinetic and thermodynamic barriers due to its lower binding energy. However, Platinum cannot be used on a large scale due to its low cost and scarcity. As a result, scientists have focused on alternative catalyst for HER.

Water Oxidation:

$$2H_2O \rightarrow O_2 + 4e + 4H^+ (1.23\ V)$$

Water Reduction:

$$4H^+ + 4e^- \rightarrow 2H_2 (0.00\ V)$$

Overall Water splitting reaction:

$$2H_2O \rightarrow 2H_2 + O_2 \quad (\Delta G = 237.2\ kJ/mol)$$

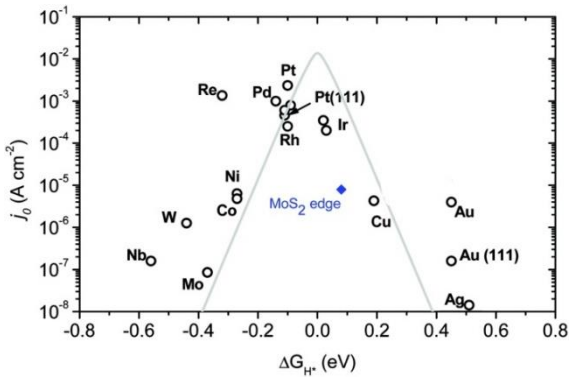

Figure 1: Volcano plot of earth abundant metals and Molybdenum disulfide

According to the volcano plot as shown in Figure 1, MoS_2has a lower binding energy which is near to the zero and, MoS_2has been investigated due to the wide range of applications in the field of electrochemistry including hydrogen evolution reaction (Sun et al. 2017), super capacitance(Krishnamoorthy and Kumar 2014)) and gas sensing applications (Chaudhary, Khanuja, and Islam 2018). MoS_2 is a low-cost, earth-abundant material with a lower binding energy. That was the major reason for choosing MoS_2 as an alternative catalyst for the HER.

Recently, several methods have been investigated for the synthesis of MoS_2. Among several known methods, one pot hydrothermal method is an easy and highly efficient chemical process (Philosophy 2019) that can be used to prepare nanostructures of metal oxides such as MoS_2. Moreover, the hydrothermal process has a few advantages over other chemical methods, such as chemical vapor deposition and chemical bath deposition (Online et al. 2017). It is able to produce nanostructures which are not stable at the higher temperatures, as well as it is a well-known green method due to the closed system conditions throughout the synthesis procedure. Hence, in this study, we have used a hydrothermal synthetic method for the formation of MoS_2 nanocomposites.

MoS_2 exists in several polytopes (Ding et al. 2015) of semiconducting 2-H MoS_2 which have

trigonal prismatic coordination around Mo and two S-Mo-S units. In this form, only the edge S atoms have binding energy nearly to zero (JELLINEK, BRAUER, and MÜLLER 1960) and only the edges are activated and the whole basal plane is almost inactive for HER. On the other hand, in 1-T MoS_2, both the basal plane and edges are activated in the same manner. Metallic 1-T MoS_2 has an octahedral coordination of S atoms around Mo (Attanayake et al. 2020). But the 1-T phase is less stable than the 2-H phase. Thus, the activation of 2-H material is depending upon the number of open edge sites and it makes the material with lower over potential value. Moreover, most of the studies regarding to the 2-H MoS_2 have focused to obtained the more number of edge-sites in their nano structures.

In this study, we have hypothesized that changes in the formation of edge-sites of 2-H MoS_2 would made by increasing the duration of the hydrothermal process. With the expansion of the hydrothermal process, there is more possibility to grow the edge-sites 2-H MoS_2. Here we report the effect of the duration of the hydrothermal process (24, 36 and48 h) on the synthesis of 2-H MoS_2 with a higher number of exposed edge-sites by the hydrothermal synthesis method and we have discussed the effect of edge-sites on the hydrogen evolution performances of the materials.

2. MATERIALS AND METHODS

Chemicals: Ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, ≥99.0%), Urea and thioacetamide.

Synthesis of Molybdenum disulfide nanocomposites: The precursor solution was prepared according to Philosophy et al with slight modification. At room temperature (27 ℃), 30 mg of ammonium molybdinum tetrahydrate $(NH_4)_6Mo_7O_{24}.4H_2O$, 60mg of thiourea, and 240mg of urea were added into 15 ml of deionized water (DI) under stirring to get a uniformly dispersed solution. After the solution was stirred for 2h, the reaction mixture was put into a teflon lined stainless-steel autoclave with a capacity of 25ml. The autoclave was closed and heated at 200°C for 24h. After, the system was allowed to cooling down to room temperature and after that the sediment was washed with DI water and 20ml of 98% ethanol three times, and then the products were dried at 50°C in a vacuum oven for 3 h to obtain nano sized MoS_2.The above procedure was repeated for different hydrothermal treatment time, s 24, 36, and 48h respectively.

Electrochemical Measurements: The electrochemical performance of prepared MoS_2 was evaluated by using the standard three-electrode system made up of a prepared MoS_2 catalyst ink drop cast glassy carbon electrode as a working electrode, Pt and silver chloride electrode (Ag/AgCl) as the counter and reference electrode (Yang et al. 2021), respectively. At 1 $moldm^{-3}$, the KOH solution potentials were recorded which reference to the reversible hydrogen electrode (RHE) by adding a value of 0.197 V. All the linear sweep voltammetry was recorded at a 10 mVs^{-1} scan rate with a 0.001 of step size in the N_2 sparged basic media.

3. RESULTS AND DISCUSSION

The morphology of the prepared MoS_2 studied using, using Scanning electron microscope (FESEM-LEO 1525) to the confirm of formation of activated edges while Powder Xray diffractogram (Bruker D8 Advance with Cu Kα (λ = 1.5406 Å) using X-ray photons with 2θ intervals from 10° up to 80°) was used to identify the crystalline structure. The linear sweep voltammetry was used to study the electrochemical performance. Because the activation energy and over potential toward hydrogen evolution reactions in 2-H MoS_2 are directly influenced by their inactive basal plane and activation of edge sites, SEM images were used to identify the effect of hydrothermal reaction duration of preparation on the morphological differences of the synthesized materials.

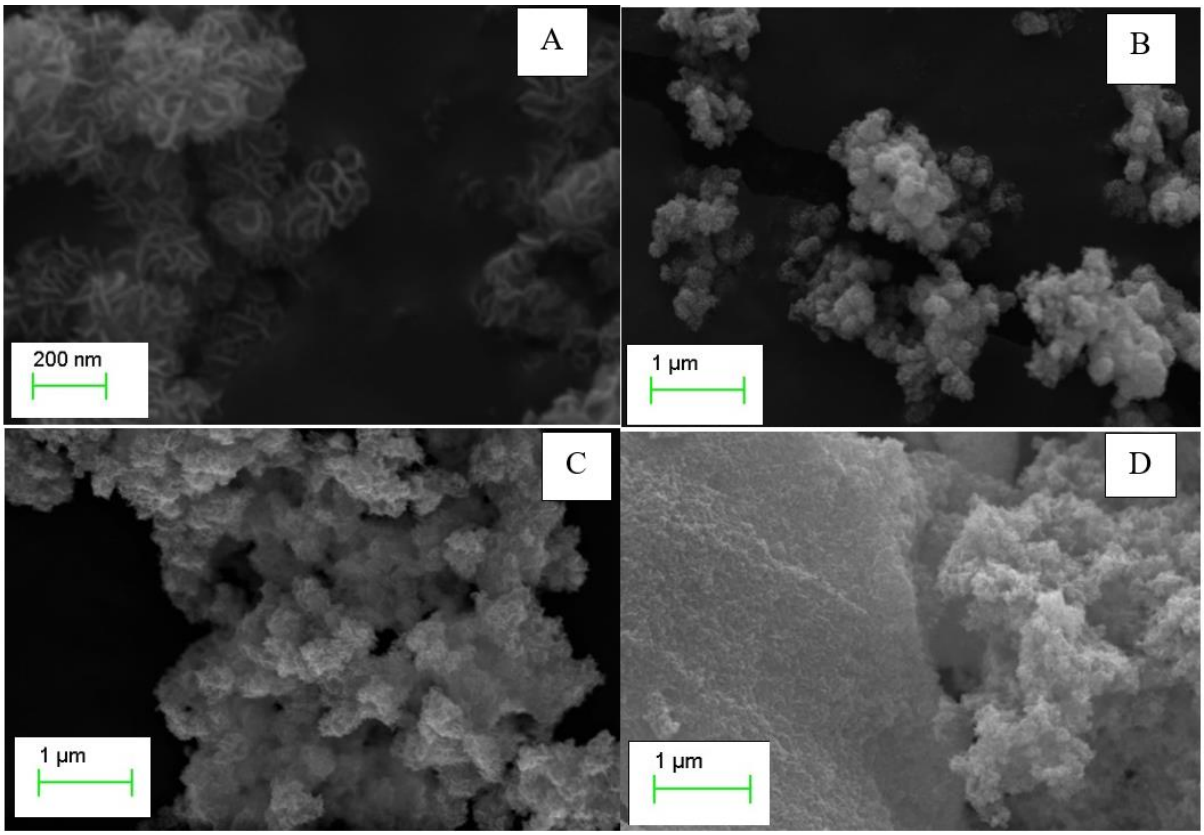

Figure 2: SEM image of the MoS_2 nanocomposites synthesised in (A, B) 48h, (C) 36h, (D) 24h

Table 1: Morphology and the over potential values of the samples

Hydrothermal time	24h	36 h	48 h
Morphology	Lump-liked structure	Lump + crystalline structure	Crystalline structure
Over Potential value/V (Volts)	0.455	0.455	0.355

Figures 2B, 2C and 2D show that SEM images of prepared MoS_2 nanocomposites after 24, 36, and 48h of hydrothermal treatment, respectively. A clear morphological difference was observed for all the prepared samples. With the increment of time, the shape of crystal, and formation of edge-sites were enhanced throughout the nanostructures. Both C and D samples (which are prepared at 24 h and 36 h) were had an improper growth and lump-like structures while B (48 h hydrothermal sample) had a proper growth with sharped edges of 2-H MoS_2. It confirmed that hydrothermal duration of the procedure could make an influence to the growth and morphology of nanostructures and it forms more activated edges on 2H-MoS_2 nanostructure. Therefore, sample prepared at 200 ℃ for 48 h was chosen as most appropriate hydrothermal duration for the preparation of nanostructure with more open edges.

PXRD was taken to confirm the crystalline structure of the MoS_2 as the 2-H MoS_2, which has a hexagonal lattice structure. PXRD analysis (PANalytical PW3040/60) with Cu K radiation (= 1.5406) from 10° to 80° was used to confirm the substance of the MoS_2 powder and it confirmed that it has a hexagonal structure. The diffractogram pattern of the 48-h MoS_2 nano composite is shown in Figure 3. The presence of sharp peaks is an indication of the crystallinity and purity of the sample. In the case of MoS_2,

the peaks found at Figure 3 with values 14.0º 33.5º, 39.6, and 58.7º can be indexed to the (0 0 2), (1 0 0), (1 0 3), and (1 1 0) (Huang et al., 2013) planes of MoS_2, respectively. All these diffraction peaks of MoS_2 can be indexed as hexagonal phases.

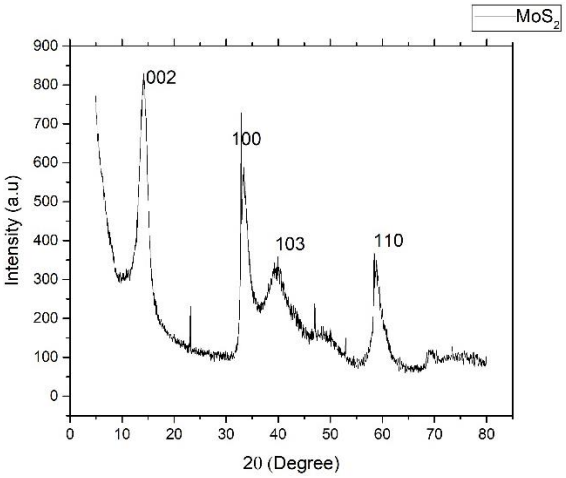

Figure 3: XRD pattern of 48h sample

The Hydrogen evolution reaction (HER) is the cathodic reaction of the water splitting reaction. Theoretically, HER occurs at 0V, but here we have to put some voltage due to the kinetic and thermodynamic barriers of the reaction. That additional voltage is known as the over potential of the reaction. The better materials for the hydrogen evolution reaction should have a lower over potential and it should be a considerable parameter at the comparison of performances of nanostructures. Here, we have studied the hydrogen evolution performances of nano materials which are prepared under the different hydrothermal conditions to study the effect of 2H-MoS_2 edges for the HER. It was done under the basic conditions they were confirmed that number of edges and growth of edges were effected on the activity of the materials. In general, according to the linear sweep voltammetry, 48h of hydrothermally synthesized MoS_2 led to the lowest onset over potential (at a current density of 4.4 mA/cm^{-2}) for the HER. While 24h and 36h materials were at -0.455V, Finally, the best results for the HER reaction were for the MoS_2 nano composite, which was prepared in 48h of hydrothermal duration.

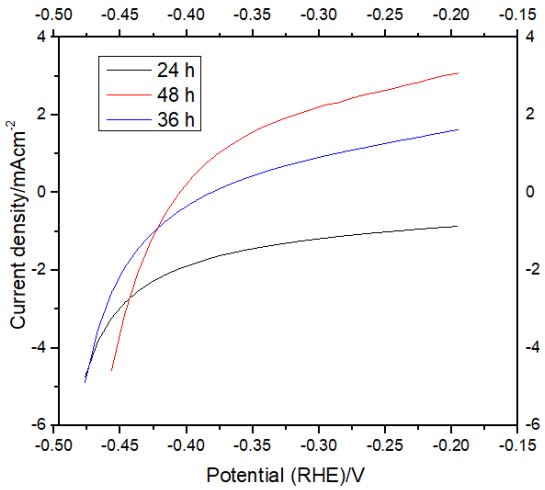

Figure 4: Linear Sweep Voltammetry of prepared three materials

4. CONCLUSION

In summary, we described the effects of hydrothermal duration on the sharpness and number of edges of 2-H MoS_2 nanocomposites. The experimental results showed that 48 h was the ideal hydrothermal reaction duration for preparing 2-H MoS_2 with a higher number of sharp edge sites and 36 h is an appropriate hydrothermal duration for the preparation of more open edge sites within the given period of time. To conclude, by increasing the duration of the hydrothermal process, the number of sharp edge sites is possible to increase. But, with the increment of the hydrothermal process, MoS_2 nanocomposites get more stacked. Our further studies will focus on the methods which can increase the number of open edge sites to activate MoS_2 under the given experimental conditions.

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