Enlargement of Interlayer Spacing of Molybdenum Disulfide on Graphene Oxide for the Hydrogen Evolution Reaction

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Abstract- Molybdenum disulfide is a prominent substance in experiments on hydrogen evolution reaction (HER) due to the lower binding energy of the material. It has been recently considered as a promising non-precious metal alternative to platinum with high HER activity. The most stable form of molybdenum disulfide among three specific phases is 2-H MoS_2, and it has a hexagonal phase structure but only edge-sites are activated across the basal plane. Here, we have hypothesized that the concentration of GO will influence the interlayer spacing of MoS_2 on the GO. In this work, we studied the formation of MoS_2 using various concentrations of GO (6 mg, 12 mg, and 18mg) along with other precursors. (Ammonium Molybdate, Thioacetamide, and Urea). The impact of the mass ratio of MoS_2 to rGO during the synthesis process was then extensively examined, utilizing a variety of analytical methods such as SEM, PXRD,and Raman. The intercalation of rGO nanosheets into the MoS_2 nanosheets results in a 3D hierarchical floral architecture in the MoS_2/rGO nanocomposite. Moreover, the sharp, uniformly distributed MoS2 nanostructures observed at the higher amount of GO (18mg) and also the X-ray diffraction pattern show that a polycrystalline, hexagonal structure with a larger interlayer spacing of 9.39 A^0 for the same sample. Raman results of the material confirmed the structure and GO-3 sample has a less number of defects Additionally, GO-3 had the lowest onset over potential for HER, according to the electrochemical analysis.. Finally Interlayer space enlargement happened due to the intercalation of GO into the MoS_2 layers during the hydrothermal process, which led to the creation of a 3D hierarchical floral structure of MoS2 with a greater activity for HER.

Keywords: Hydrogen Evolution, Molybdenum Disulfide, Interlayerspace

I. Introduction

Global warming has been identified as the huge environmental problem that people have to face in next two decades and it refers to the gradual rise in the overall temperature of the atmosphere of the Earth. Carbon dioxide is one of the main gas components contributing to the daily increment of global warming and the Rate of the carbon dioxide emission has been increased due to the higher usage of fossil fuels. In that case numerous researchers have concentrated on the production of alternative energy sources such as Hydrogen. In that purpose renewable energy sources like solar are used for the formation of hydrogen through the electrochemical or photochemical water splitting reaction. But the electrochemical water splitting reaction should be catalysed due to their kinetic and thermodynamic barriers of the reaction. Platinum is the most appropriate catalyst could be used for the Hydrogen Evolution Reaction (HER) because it can easily override the both barriers of kinetics and thermodynamics. But, Platinum cannot be used in the industrial scale due to the low cost and low availability. That is the main reason for focusing on the Alternative catalysts for HER.

Molybdenum disulfide is a commonly used material in research related to electrochemical hydrogen production. Because it has a lower binding energy value, it is more near to zero as compared to the platinum metal. We hypothesized in this study that changing the ratio of GO to MoS_2 would have a significant impact on interlayer spacing and the HER catalytic performance of the MoS_2/rGO nanocomposites. MoS_2 has three major structures, which are identified as 1T-MoS_2, 2H-MoS_2 and 3R-MoS2. But 2-H MoS_2 is the most stable form that has activated edge-sites and an inactive basal plane. Therefore, enhancing and opening edge-sites into the reaction site is important for the synthesis of reactive materials. Here we have investigated the influence of rGO on the interlayer spacing of MoS_2 to form the best material for the hydrogen evolution reaction. 3R-MoS2.But 2H-MoS2 is the most stable form and only the edge sites are activated here.

II. Materials And Methods

A. Synthesis of Molybdenum Disulfide-Graphene Oxide Nanocomposites

GO was synthesized from natural graphite powder by a modified Hummers' method [1]The MoS_2/Graphene Oxide nanostructures are synthesized by a hydrothermal method using Graphene Oxide, Ammonium molybdate tetrahydrate $(NH_4)_6Mo_7O_{24}.4H_2O$, thioacetamide and urea as starting precursors under 6-7 PH of conditions. GO (10, 15, 20 mg) powder was added into deionized water Under ultrasonic dispersion for 60 min to get the dispersion solution at room temperature After being dissolved in graphene mixture under continuous stirring for 2 hours. The resulting solution is then put in a 25 mL Teflon-lined stainless-steel autoclave at a temperature of 180 ˚C for 24 hours. Then it is allowed to cool

down to room temperature. The finally obtained product is collected by centrifugation and washed several times using water and ethanol Finally, The precipitates are then vacuum dried for 2 hours. The reactions which occur during above procedure are written as follows

III. Results And Discussion

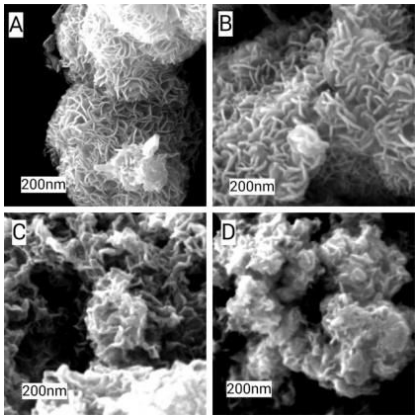

Figure 01: SEM images of MoS_2 nanoparticles on graphene ,(A,B,C) Samples prepared by using 18mg, 12mg, 6mg of graphene oxide respectively (D)Pure MoS_2

The morphology and nanostructure of the as-prepared samples were examined using scanning electron microscopy (SEM). SEM (FESEM-LEO 1525) was used to evaluate the morphology and structure of the samples in order to verify the sharpness and extent of MoS_2 development on the different amounts of graphene oxide. According to the figure:01 the stark morphological contrast emphasizes the key role of GO as a support material for mediating the formation of nanomaterials. To begin with, as shown in Figure 01 (D): MoS_2 has a diameter of between 100 - 150 nm and the structure is like 3D flowers. However, the edge sites were not cleaned and have a staggered structure with no discernible strata. However, when GO got involved, these layers began to diverge, and at 18 mg of GO, they were properly divided equally and dispersed as intended.

The MoS_2/rGO hybrid was characterized by X-ray diffraction (XRD), and the set of diffraction peaks indicated the Nano sized MoS_2 crystal with hexagonal structure. For pure MoS_2, the diffraction peaks are well matched with the JCPDS Card No. 37-1492[2]. The peaks appear at 14.2 º, 33.5 º, and 59.3º corresponding to (002), (100), and (110) planes, respectively. For MoS_2/rGO only the GO peak has disappeared and all the other characteristic peaks of MoS_2 are present. Enlargement of the interlayer spacing of the MoS_2 has been proved by XRD patterns of MoS_2/rGO. In comparison to the pure MoS_2, Peak value corresponding to the (002) plane in MoS_2/rGO3 has shifted from 14.2˚ to 9.411˚ and interlayer spacing values has risen from 6.22A˚ to 9.39A°. Furthermore, the interlayer space has also increased with an increment of GO ratio as a result of GO intercalation into the layers of MoS_2[3]. The layed-like structure of MoS_2/rGO, which possesses a hexagonal phase, was confirmed by the Raman spectra of three different materials. E2g1 and A1g peaks representing in-plane and out-of-plane vibrations were seen At 181 cm^{-1} and 320 cm^{-1}, respectively, The number of defects in the material is correlated with the intensity ratio between the G peak and D peak. They claim that the sample made with 6 mg of graphene oxide had the highest number of defects. Additionally, the peak at 786 cm^{-1} is related to the Mo- C bonding.

Linear sweep voltammetry was used to test the hydrogen evolution capabilities of nanocomposites in an acidic environment. The results were confirmed that the activity of the materials is able to increase by increasing the number of edge sites by enlarging the interlayer space value of MoS_2. According to the LSV the sample with the largest interlayer space also had the lowest onset over potential (0.276 V) at a current density of 4.4 mA/cm^{-2}.

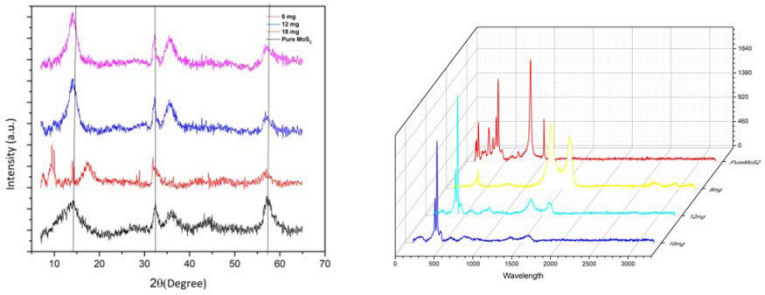

Figure 01: XRD and Raman patterns of pure MoS_2 and MoS_2/rGO hybrids

IV. Conclusion

In conclusion 3D hierarchical MoS_2.rGO nanocomposites have successfully synthesized by the one pot hydrothermal method exhibits the interlayer spacing of 9.39 A^0. The addition of GO increased the interlayer space of MoS_2/rGO. It has been wider with more clear, sharped active edge sites which have contributed to the hydrogen evolution activity.

References

[1] L. Zou *et al.*, "Results in Physics MoS 2 / RGO hybrids prepared by a hydrothermal route as a highly efficient catalytic for sonocatalytic degradation of methylene blue," *Results Phys.*, vol. 14, no. February, p. 102458, 2019, doi: 10.1016/j.rinp.2019.102458.

[2] W. Dong, H. Liu, X. Liu, H. Wang, X. Li, and L. Tian, "Defective-MoS_2/rGO heterostructures with conductive 1T phase MoS_2 for efficient hydrogen evolution reaction," *Int. J. Hydrogen Energy*, vol. 46, no. 14, pp. 9360–9370, 2021, doi:10.1016/j.ijhydene.2020.12.087.

[3] J. Xie *et al.*, "Controllable Disorder Engineering in Oxygen-Incorporated MoS_2 Ultrathin Nanosheets for Efficient Hydrogen Evolution," *J. Am. Chem. Soc.*, vol. 135, no. 47, pp. 17881–17888, Nov. 2013