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Noteworthy effects of p- and n-type doping in IF-MoS$_2$ on the hydrogen evolution reaction.

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Abstract: In this report we describe a systematic study of the effects of p- and n-type doping on the hydrogen evolution reaction (HER) of the inorganic fullerene (IF), MoS$_2$. Active edge site enriched IF-MoS$_2$ promoted by strategically introducing Nb (p-type) and Re (n-type) dopants (below 500 ppm) enable facile HER over a range of pH values. Experimental results suggest that while Nb doping on IF-MoS$_2$ leads to better electrocatalytic HER activity in the alkaline medium with an onset potential difference of 80 mV, Re doping gives excellent activity in the acidic medium. The present work presents a systematic study of HER activity by finely tuning the activity in different electrolyte media with varied pH values through deliberate doping of parent catalyst with p- and n- type materials. The doped IF-MoS$_2$ catalysts exhibit excellent catalytic activity even with sea water as an electrolyte.

Introduction

Study of the hydrogen evolution reaction for producing H$_2$ from water has great significance because of its crucial role in the energy and environmental scenario. Of the various electrocatalyst investigated for HER, MoS$_2$ turns out to be a promising material, as borne out by the Sabatier volcano plot. Because of the low hydrogen binding energy and cost effectiveness, MoS$_2$ has a potential to be a strong candidate for industrial scale electrochemical hydrogen production. MoS$_2$, analogues to graphene, is a two-dimensional (2D) hexagonal layered structure with covalently linked S-Mo-S intra-layers held together by weak van der Waals force. The intrinsic problem of MoS$_2$ for electrocatalytic hydrogen evolution reaction is the low electronic conductivity between two nearby S-Mo-S layers which can be 2200 times poorer, compared to that through the basal planes[1], which suggests that single layer of MoS$_2$ would be an ideal catalyst for high current density and electrochemical applications. Experimental[2] and computational[3] studies show the significance of active edge sites in the catalytic activity of the 2D MoS$_2$ sheets,

instead of the basal planes. Despite the possible drawbacks, when appropriate modifications are induced, MoS$_2$ can have higher activity in electrochemical reduction of water to hydrogen evolution. Different efforts have been developed to improve transition metal sulphide based electrocatalysts involving thin films[4, 5], Nanoparticles (NP)[3, 6, 7] nanowires[8], chemically exfoliated sheets[9-11], amorphous and doped MoS$_2$[12-15] and mesopores[16]. The general strategy applied to improve the electrocatalytic performance of MoS$_2$ is by increasing the number of edge site density. Thus, vertically aligned or stacked[4] or fullerene-like MoS$_2$ have been synthesized to maximize the density of exposed edges[17, 18]. Increasing the number of edge sites increases the current density. However, the underlying problem of the onset potential needs to be addressed. Doping of the catalyst with a suitable atom can reduce the binding energy of hydrogen adsorption (ΔG_{H^*}). A recent study by us on IF-MoS$_2$ doped with Re, as low as 100 ppm, has revealed a reduction in the onset potential by ~240 mV at pH-0.3 (compared to undoped IF-MoS$_2$)[15] .We found that Re-doping increased the free charge carriers by 10^{16} -10^{17} cm^{-3} in the conduction band of MoS$_2$. These free charge carriers lie close to the surface of MoS$_2$ fullerene (IF) and increase the n-type character and electrical conductivity[19, 20]. However there is no systematic study in designing the strategy to improve the HER activity in both acidic and basic medium based on the nature of dopants. The present study shows how electrochemical activity can be tuned at different pH by introducing p- and n-type dopants in IF-MoS$_2$.

p- and n- type doping were induced on IF-MoS$_2$ by in-situ doping of fullerene-like nanoparticles of MoS$_2$ with Niobium and Rhenium atoms respectively. Nb-doped IF-MoS$_2$ were synthesized by using Nb$_2$O$_5$ and MoO$_3$ as Nb and Mo precursors respectively. The key point of the present approach is the development of a particular composition of the mixture Nb:Mo oxide precursor. The preparation of this complex oxide includes several stages and results in the formation of a solid solution of molybdenum and niobium oxides (described in the experimental section).

The concept of n-type Re-doping in IF-MoS$_2$ and its achievement is already reported[19, 20]. Niobium is located to the left of molybdenum in the periodic table and would therefore induce p-type doping. In mixed Mo$_{1-x}$Nb$_x$S$_2$ (x< 1 wt%), the bottom of the valence band corresponds to 3p-S and 4d-Mo(Nb) hybrid states and the upper part of the $4d_z^2$ Mo (Nb) states[21-23]. The number of valence electrons in MoS$_2$ is sufficient to fill the valence band completely, rendering MoS$_2$ a semiconductor with an indirect bandgap of

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1.23 eV and a direct bandgap at the Gamma point of 1.92 eV. However, NbS_2 has one electron less per metal atom so that the top of its valence band is half filled with metallic behavior. Consequently, substituting molybdenum by niobium is expected to lead to p-type doping of the nanoparticles [21, 22], which would acquire positive charge on their surface. To control the position of the Fermi level, exquisite control of the doping level below 1000 ppm is necessary, which is not trivial. Unlike the case of rhenium doping of IF-MoS_2, Nb_2O_5 is not volatile at the reactor temperatures of 800-900°C needed to sulfidize the MoO_3 nanoparticles. Therefore, congruent evaporation of the minor phase (Nb_2O_5), like the case of ReMo is not possible [19, 20]. A new strategy for the Nb doping of IF-MoS_2 nanoparticles was therefore developed[19] to ensure uniform doping density in the MoS_2 of nanoparticles through careful control of the reaction conditions. The analysis of minute amounts of the dopant atoms (<500 pm) in the nanoparticles is a difficult task. The Re- and Nb- doping level in the IF-MoS_2 nanoparticles was determined using inductive coupled plasma mass spectrometry (ICP-MS) analysis[12, 14, 15]. Due to this difference in the dopant nature of Nb and Re, we observe different activities of modified MoS_2.
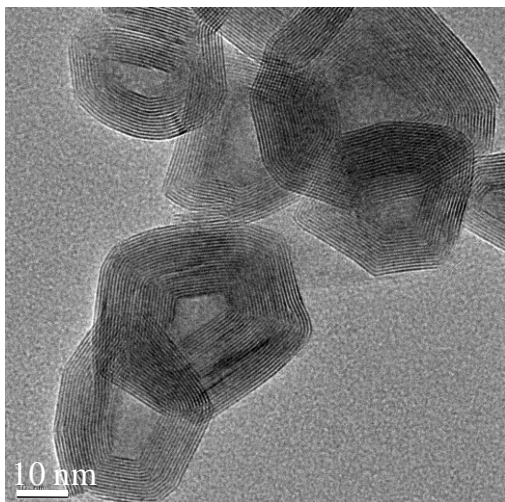
Results and Discussion

Figure 1: HRTEM of Nb-doped IF-MoS_2, (spacing between fringes is 0.63nm.)

The inorganic fullerene structure of MoS_2 imparts it a higher density of active edge sites in comparison to few-layer (FL) MoS_2[20]. The morphology of Nb-doped IF-structures were examined by the TEM and HRTEM. In figure 1 we show a typical HRTEM image of the fullerenes. Because of the onion like morphology, active edge sites in

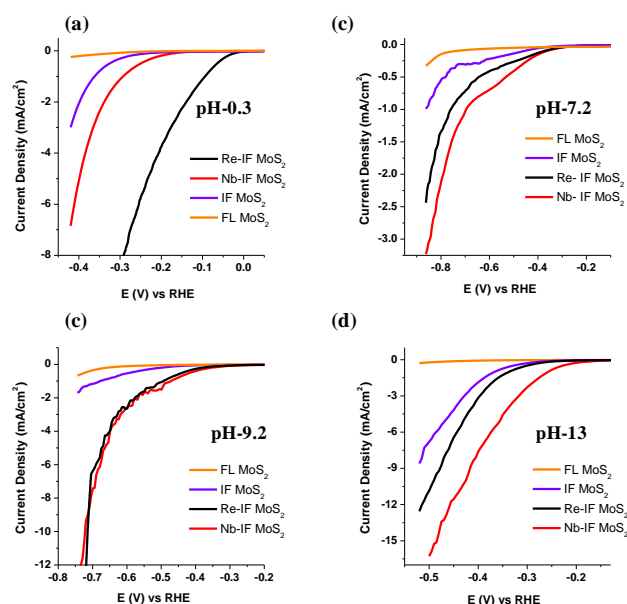the catalyst increases and hence higher electrocatalytic activity is anticipated.

Figure 2: The LSV polarization curves for the various catalysts (FL-, IF-, Re-doped and Nb-doped MoS_2) measured at 5 mV s^{-1} at pH (a) 0.3, (b) 7.2 (c) 9.2, and(d) 13 of the electrolyte.

Electrocatalytic hydrogen evolution activity was studied by linear sweep voltammetry (LSV) by sweeping the working electrode in the cathodic direction to overcome the innate overpotential in the process of hydrogen ion reduction. The potentials reported here are with respect to the reversible hydrogen electrode (RHE) unless mentioned otherwise. The onset potential gives the measure of overpotential involved in the process of HER. A comparative analysis of the onset potentials for the three electrocatalysts shows that the activity of Re and Nb-doped IF-MoS_2 differ at different pH of the electrolyte. The inference and the detailed discussion of this observation is given in the later part of article. In acidic pH, the overpotential is less for Re-doped IF-MoS_2 than the undoped and Nb-doped counterparts. The onset potential difference (OPD) between Re- and Nb-doped IF-MoS_2 is ~170 mV at pH-0.3. As the pH of the electrolyte increases (7.2, 9.2 and 13), the overpotential for Nb-doped IF-MoS_2 becomes less than that of the Re-doped IF-MoS_2 (OPD of ~ 0-70 mV) (Figure 2). The features in the trend in activity suggests improvement in HER activity in both acidic and basic media by the modification in MoS_2 (from few-layer (FL) to IF structure) and doping with Re and Nb atoms. A detailed listing of the onset potentials is given in Table 1 clearly. Modification of the properties of MoS_2 by doping can lead to changes in the electronic structure which are necessary for HER [15].

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From the earlier works of Trassatti [24] and Norskov [25] on the volcano plot for hydrogen evolution, one can predict the higher activity of Re in comparison to Nb in the acidic medium as observed in the present study. However the effect of nanoclusters or low doping of metals on the substrate was not considered, and there would be additional effects caused by local strain[26] on the adsorption-desorption process in HER. The dopant sites act as active sites for catalysis. If the volcano plot (Sabatier's principle) is considered, the activity of the metals, which lie in the ascending region is controlled by desorption of the product whereas those lying in the descending region is limited by the activation of the reactant[25]. It is important to note that the descending region of volcano plot is mainly occupied by metals which form oxide films during the evolution of hydrogen. This implies that by changing the experimental condition, the activity of Nb for HER can be enhanced and hence we propose that this is why the activity of Nb-doped IF-MoS$_2$ is higher than that of the Re-doped counterpart in the basic medium. At pH-7.2, the onset potential for Nb- and Re-doped samples is -0.36 V whereas that for the undoped sample it is -0.44 V suggesting an improvement in overpotential difference (OPD) by 80mV. The improvement in the onset overpotential difference with Nb-doped MoS$_2$ fullerene over Re-doped and undoped IF-MoS$_2$ samples is 10 mV and 130 mV at pH-9.2; 73 mV and 93 mV at pH-13 respectively (Figure 2 and Figure 5a). The question of the activity of Nb doped sample being better than that of Re doped counterpart in basic medium is worth investigating. The same observation of a difference in HER activity was noticed in previous studies by Nenad et al[27]. However the investigation was based on transition metals with primary interest in the interrelationship between the type of electrode and the HER activity at higher pH. HER activity at higher pH is dictated by the hydrogen binding energy (HBE) and also by its relation to the kinetic energy necesary for the dissociation of water[27, 28]. We also made a simillar observation which gives insight about the relation between the type of electrode and the HER activity at different pH values. Therefore the mechanism of HER in both acidic and basic medium is expected to be different depending on the nature of the MoS$_2$ based catalyst.

The reduction of hydrogen ion at the cathode is a function of pH of an electrolyte and usually follows Nernst equation,

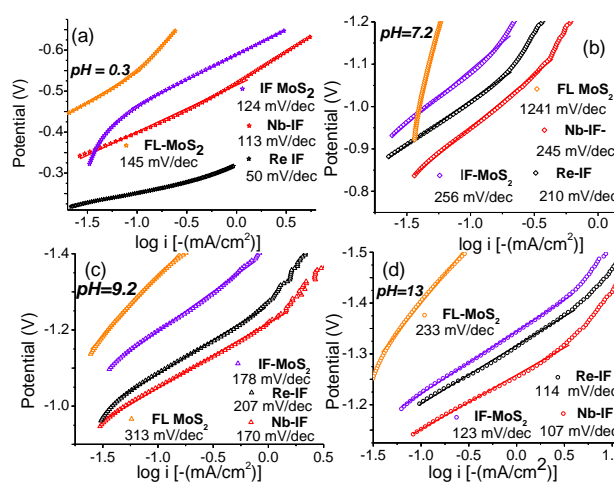$$E = E^O – 0.0592 \times pH \text{ (at 298 K)} \quad - (1)$$

Figure 3: pH dependent Tafel slope analysis of various catalyst (FL-, IF-, Re-doped and Nb-doped MoS2) in HER at pH (a) 0.3, (b) 7.2 (c) 9.2, and (d) 13. (the potential here is w.r.t Ag/AgCl, 3 M NaCl)

Here, E^O is the standard reduction potential of hydrogen. The cathodic potential increases with the pH, but shows a deviation from the Nernstian trend due to the effects on minute dopants on the MoS$_2$ matrix. The values of the overpotential at a current density of 5 mA/cm^2 with a turnover frequency (TOF) of 0.11s^{-1} (calculations are shown in the electronic supplementary information) is listed in Table S1. The trend in the values as a function of pH of the electrolyte was found to be the same as that of the onset
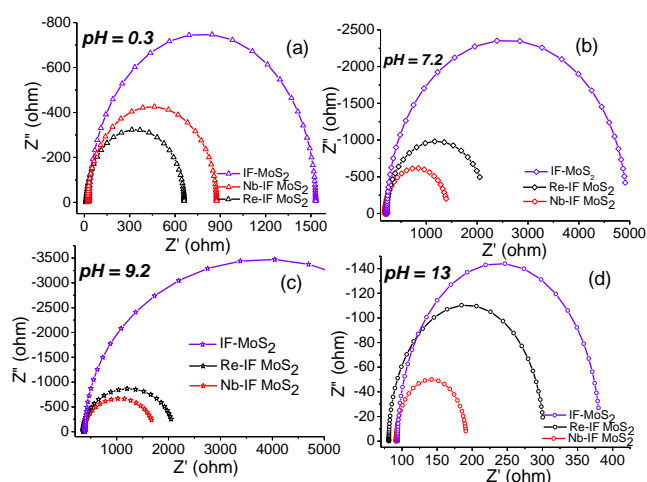

Figure 4: Electrochemical impedance spectroscopy (Nyquist plot) of various catalyst (FL-, IF-, Re-doped and Nb-doped MoS$_2$) at onset potential at different pH (a) 0.3, (b) 7.2 (c) 9.2 and (d) 13

potentials. The improvement in the overpotential towards the less cathodic potential indicates the enhancement in activity due to modification of MoS$_2$ through structural

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alteration as in the case of the fullerenes and through doping. While the Nb-doped IF-MoS$_2$ shows improved performance in HER at higher pH values Re doped sample shows the opposite. The activity comparison is further manifested by Tafel slope analysis obtained from the LSV curves.

To understand the mechanism involved in hydrogen evolution mechanism, we have examined the Tafel slopes, obtained from Butler-Volmer equation:

$$\eta = b \, log \, (i/i_o) \quad - (2)$$

Here η is the overpotential and i_o is the exchange current density and b is the Tafel slope. The results obtained (see Table 1.) clearly indicates that by Nb-doping we have further enhanced the HER activity in basic medium. The values of the Tafel slope are 107 mV/dec, 170 mV/dec and 245 mV/dec at pH 13, 9.2 and 7.2 respectively for Nb-doped IF-MoS$_2$ (Figure 3 and Figure 5b). Except for pH-0.3 the values of tafel slope for Nb doped sample indicates its superior activity in comparison to Re doped sample in basic medium (see table 1). The hydrogen evolution by cathodic reduction of H$^+$ ion from the electrolyte occurs as,

$$2H^+ + 2e^- \rightarrow H_2 \quad - (3)$$
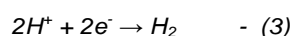
In this process the electrode encounters a significant charge transfer resistance (R$_{ct}$) at the electrode-electrolyte interface, which also depends on the electrolyte used. This hinders HER activity of the electrocatalyst. We have examined the R$_{ct}$ by electrochemical impedance spectroscopy (EIS), and the results are listed in table 1. As the pH of electrolyte increases the R$_{ct}$ at the electrolyte/electrode interface changes for both the catalysts. The lower R$_{ct}$ values for Nb-doped IF-MoS$_2$ in comparison to the Re-doped counterpart at higher pH explain the better activity of Nb-doped sample (Figure 4 and Figure 5c). The stability of the catalyst in nearly neutral pH (~7.2) was studied by accelerated cyclic voltammetry test (0.25 to -0.5 V) for 1000 cycles (Figure S1). The activities before and after these cycles remained same which suggests high stability of the catalyst.

The mechanism of hydrogen evolution in acidic and basic media are given below

$$H^+ + e^- \rightarrow H_{ads} \, (acidic) \quad - (4)$$
$$H_2O + e^- \rightarrow H_{ads} + OH^- \, (alkaline) - (5)$$
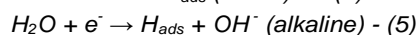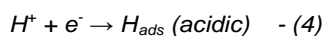
H$_{ads}$ is the surface adsorbed hydrogen which leads to H$_2$ in further steps (Tafel and Heyrovsky) depending upon the particular mechanism followed. Unlike the case of Re, the 4d orbitals in Nb are compact and hence interaction with H$^+$ ions falls off quickly with distance. The electron

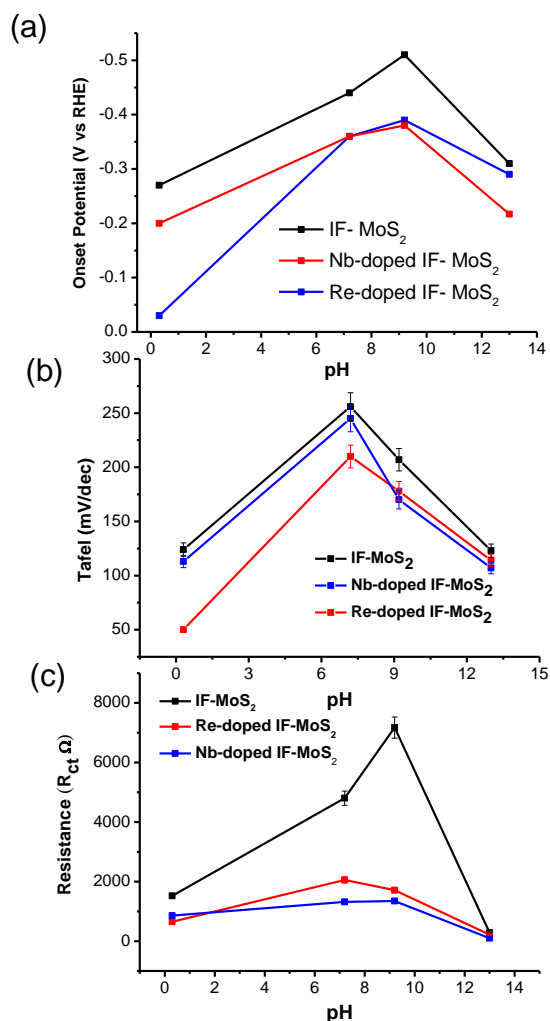transfer rate at the electrode/electrolyte interface is therefore sluggish.

Figure 5: Comparative analysis of p and n type of dopant in IF-MoS$_2$ for HER as a function of pH of the electrolyte (a) onset overpotential (b) Tafel slope and (c) charge transfer resistance (R$_{ct}$).

In alkaline medium, on the other hand, H$_2$O interacts with the catalyst in the electrode/electrolyte interface; due to the p-type nature of the Nb, interaction with H$_2$O is expected to lead to enhanced charge transfer and activity in alkaline medium in comparison to Re-doped IF-MoS$_2$ (n-type dopant). Nb has more vacant d-orbitals compared to that of Re. Hence, the lower R$_{ct}$ for Re-doped IF at pH=0.3 and opposite at higher pH.

We have investigated the nature of these dopants (p- or n- type) and found that Re acts as a n-type dopant whereas Nb acts as p-type dopant. The trends in activity

and the R_{ct} value therefore is expected to reverse as the pH increases. Another factor to note is the low concentration of dopant and its effect on the electronic properties and local strain at the dopant site of IF-MoS$_2$. The concentration of free charge carriers in the conduction band can be increased by Re- and Nb- doping at 10–500 ppm (by 10^{16}–10^{17} cm^{-3}) [19, 20]. As a result, the surface of IF- MoS$_2$ consists of n-type or p-type carriers, which improve the conductivity of pristine MoS$_2$ and reduces the charge-transfer resistance in electron transfer reactions.

Table1. Comparison and summary of results between undoped, Re and Nb-doped and IF-MoS$_2$.

Sample	pH	Onset (V) vs RHE	Tafel (mV/dec)	R_{ct} (ohm)
Nb-IF	13	-0.21	107	100
	9.2	-0.38	170	1348
	7.2	-0.36	245	1320
	0.3	-0.2	113	860
Re-IF	13	-0.29	114	220
	9.2	-0.39	178	1712
	7.2	-0.36	210	2055
	0.3	-0.03	50	649
IF	13	-0.31	123	288
	9.2	-0.51	207	7172
	7.2	-0.44	256	4801
	0.3	-0.27	124	1525

The summary of the results obtained from the above study is given in Figure 5 and table 1.. The figure is discussed with other results for understanding the activity of both the samples. The onset potential vs pH for undoped, Re and Nb doped MoS$_2$ is shown in Figure 5a. The onset potential increases with pH with a maximum at 9.2 and decreases at 13.0. Both undoped and Nb-doped MoS$_2$ are p-type and have similar values at the extreme pHs values (0.3 and 13) while the Re being n-type dopant shows a noticeable differences. The Tafel slope and charge transfer resistance

(R_{ct}) at varying pH values suggests that the Nb-doped fullerene is better than the Re-doped one at alkaline pH while the reverse holds at acidic pH (Figures 5b and c). With this strategy of doping it appears that one should be able to tune HER activity of MoS$_2$ fullerenes over a range of pH values. A comparative study of other types of modifications in MoS$_2$ based catalysts and the present study is given in table S2.

An important focus in the design of catalysts for hydrogen production is the practical application and its economic viability. A realistic catalyst must be efficient in the practical situation. One way to look into the problem is by using abundant seawater (1/3 abundance in earth) as the electrolyte. The bottleneck to this idea is the presence of other cations and anions and their possible effects on the kinetics of HER at the cathode. This happens because the incipient adatoms may be adsorbed on the active sites thereby reducing the activity. We have examined hydrogen production from sea water (Arabian Sea coast) by these two catalysts. Interestingly, with Re-doped and Nb-doped IF-MoS$_2$ catalysts are specific for hydrogen production at pH close to 7 (~6.8) (Figure S2).

Conclusions

The present study demonstrates how doping MoS$_2$ based fullerene with minute concentrations of p- and n-type dopants (~500 ppm) gives rise to excellent electrochemical catalytic activity in HER. It is noteworthy that Nb- and Re-doped IF-MoS$_2$ catalysts are active in both acidic and basic media, with Nb-doping being superior to Re-doping in alkaline media. Similar studies can be performed with IF-sulfides of W, Ti, Ta etc and understand their role in HER. We propose this study will help in better designing strategies of electrocatalysts for various practical applications like PEM electrolyzers, PEMFC etc that can operate in wide range of pH values depending on the need of situation.

Experimental Section

Synthesis of Nb-doped IF-MoS$_2$: The mixed oxides of Mo and Nb were prepared using high purity grade precursors from Aldrich. Thoroughly ground weighted and mixed powders of MoO$_3$ (99.5%) and Nb$_2$O$_5$ (99.9%) were heated in nitrogen flow in quartz crucibles, for 18 hours at a temperature of 973°C.The boat with crucibles was then moved out of the furnace and cooled naturally to room temperature in nitrogen flow. The subsequent conversion of the Nb-Mo oxide cake into the Nb doped IF-MoS$_2$ nanoparticles (Nb: IF-MoS$_2$) possesses some similarity to that of pure (undoped) IF-MoS$_2$ NP or Re:IF-MoS$_2$ NP (Synthesis of IF-MoS$_2$ and Re-doped IF-MoS$_2$ is previously reported [19, 20, 27].

The synthesis may be separated into four consecutive steps: Evaporation of the Nb-Mo oxide cake at temperature about 810 °C, Partial reduction

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of the oxide vapor with consequent condensation into Nb-doped MoO_{3-y} nanoparticles, Fast sulfidization of the first few layers of the oxide nanoparticles in the volume of the reactor, Further sulfidization of the nanoparticles proceeding on the collecting quartz wool filter and subsequent annealing in the presence of H_2S /H_2 at 870-900 °C for 35-40 h. It should be noted that about 70% of the product is high quality IF nanoparticles, the rest being larger IF nanoparticles and platelets of MoS_2.

Characterization: The sample was characterized using high resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), and X-ray fluorescence (XRF.). Details of the method of analysis will be discussed elsewhere [28].

Electrochemical characterization: The electrochemical HER activity of the electrocatalysts, FL-MoS_2, IF-MoS_2, Re-doped IF-MoS_2 and Nb-doped IF-MoS_2 was studied by cyclic voltammetry (CV), linear sweep voltammetry (LSV), and electrochemical impedance spectroscopy (EIS). Electrochemical workstation (CHI760E) fitted with a three electrode system: a glassy carbon electrode (GCE) (3 mm in diameter) as working electrode, a platinum coil electrode as the counter and Ag/AgCl (3 M NaCl) as the reference electrode was used for all the measurements. Before the measurements GCE was cleaned by sequential polishing using alumina powders and polishing pad (CHI120 electrode polishing kit). 1 mg of catalyst dispersed in 200 µL of nafion solution (5 wt% nafion: IPA: H_2O = 0.05:1:4 (v/v/v)) is named as the catalyst ink here. 2.5 µL of this ink was drop-casted on the polished GCE and was allowed to dry. The Electrolytes used (different pH solutions) was saturated with N_2 gas by purging for 30 minutes prior to measurements. To remove any impurities from the electrode surface, initially the electrode was scanned between 0 V to 0.8 V for 10 cycles. The potentials with respect to RHE was converted by the following formula from the Nernst equation.

$$E\,(\text{RHE}) = E\,(\text{Ag/AgCl}) + E°\,(\text{Ag/AgCl}) + 0.059 \times \text{pH}$$

Acknowledgements

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ARTICLE

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The Doping Effect: Reduction of overpotential in electrocatalytic hydrogen evolution reaction and fine tuning of the hydrogen evolution activity over a range of pH can be achieved by p- and n-type doping of MoS2 fullerenes.

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Noteworthy effects of p- and n-type doping in IF-MoS2 on the hydrogen evolution reaction

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