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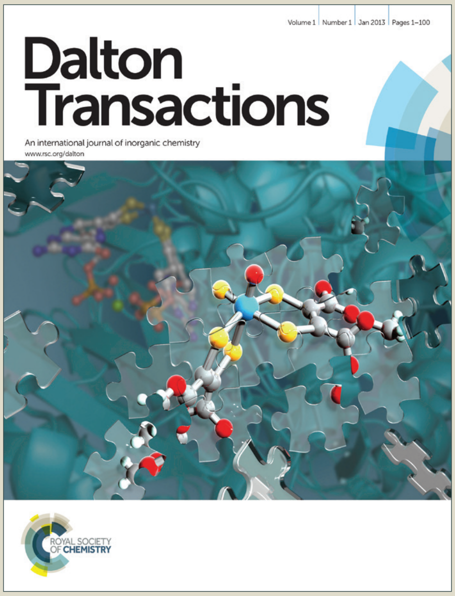

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ARTICLE

Beneficial effect of Re-doping on the electrochemical HER activity of MoS_2 fullerenes

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Electrochemical generation of hydrogen by non-precious metal electrocatalysts at a lower overpotential is a thrust area of research directed towards sustainable energy. The exorbitant costs associated with Pt based catalysts is the major bottleneck associated with the commercial scale hydrogen generation. Hence strategies for the synthesis of cost effective and stable catalysts is craving its way for prospective 'hydrogen economy'. In this report, we highlight the novel and general strategy to enhance the electrochemical activity of molybdenum disulfide (MoS_2) in the fullerene structure (IF-). In particular, pristine (undoped) and Rhenium-doped nanoparticles of MoS_2 with fullerene-like structure (IF-MoS_2) were studied and their performance as catalysts for hydoregen evolution reaction (HER) was compared to that of 2H-MoS_2 particles (platelets). The current density of IF-MoS_2 is higher by one order of magnitude as compared to few-layer (FL-) MoS_2 due to the enhanced density of edge sites. Furthermore, Re-doping as low as 100 ppm in IF-MoS_2 decreases the onset potential by 60-80 mV and increases the activity by 60 times compared to FL-MoS_2. The combined synergistic effect of Re-doping and the IF-structure not only changes the intrinsic nature of MoS_2 but also increases its reactivity. This strategy highlights the potential use of IF-structure and Re-doping in electrocatalytic hydrogen evolution using MoS_2 based catalysts.

Introduction

Splitting of water by the hydrogen evolution reaction (HER) or the oxygen evolution reaction (OER) addresses the problem of cleaner and sustainable energy. Splitting of water by electro-, photoelectro- or photo-catalysis promises clean technology for the hydrogen economy. Pt-based electrochemical cells are efficient, but their mass production is limited by the high cost and scarcity of the metal. Efforts have, therefore, been made to develop inexpensive and environmentally-safe electrocatalysts based on metal alloys[1], metal oxides [2], metal dichalcogenides [3], nitrides[4], carbides[5], phosphides[6], borides [7], enzymes[8]and bioinspired electrocatalysts [9]. According to the Sabatier plot, of all the recently developed materials molybdenum disulphide (MoS_2) is as good as Pt, in terms of favourable Gibbs Free energy for hydrogen adsorption (ΔG_{H*}) and hydrogen binding energy (HBE). By appropriate synthetic modifications, MoS_2 can emerge as a competitive candidate for electrochemical hydrogen production. MoS_2 has the two-dimensional (2D) hexagonal layered structure, analogous to graphene, with S-Mo-S layers held together by weak van der Waals forces. There have been efforts to optimize MoS_2 based electrocatalysts involving nanoparticles [10], nanowires [11], thin films [12], mesopores[13], amorphous and doped MoS_2 [14], and by the chemical exfoliated sheets [15]. However MoS_2 has a poor conductivity between the two adjacent S-Mo-S layers which can be as low as 2200 times compared to that along the basal plane[16]. This is an inherent bottleneck for MoS_2 to be effectively used as an electrocatalyst. This implies that single layer MoS_2 would be an optimal morphology for valuable electrochemical applications. Experimental [17] and computational[10] studies have highlighted the importance of active edge sites in the catalytic activity of the 2D MoS_2 sheets, while the basal surfaces are inert in electrochemical HER. The general strategy to improve the electrocatalytic activity of MoS_2 is by increasing the proportion of edges per mole MoS_2. Thus vertically aligned [12] or fullerene-like MoS_2 have been grown to maximise the exposure of edges [18]. An increase in the number of active sites can also be achieved by increasing the intrinsic activity of the catalyst by doping it with an atom which optimises the H^+ ion adsorption/desorption process thereby reducing the ΔG_{H*}. As for example doping of MoS_2 with Re-atoms at 10-100 ppm can increase the free charge carriers by 10^{16}-10^{17} in the conduction band. These charge carriers lie on the surface of inorganic fullerenes (IF) or nanotubes of MoS_2 and increase the

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x n-type character and conductivity of the pristine IF-MoS_2 and rhenium doped analogues [19]. It should be emphasized that both experiment and theoretical calculations show that Re-doping level in excess of say 500 ppm (0.005 at %) in IF-MoS_2 nanoparticles leads to segregation of the rhenium atoms and appreciable changes in their electronic structure. Therefore, much effort has been invested in controlling the Re-level in the nanoparticles to below 200 ppm [19] The Mo-substitutional site of the Re atoms in the lattice, i.e. $Re_{Mo,}$ which is essential for its electronic character as electron donor. It was carefully confirmed through high resolution (aberration corrected) transmission electron microscopy (TEM); X-ray absorption fine structure (XAFS) and X-ray absorption near edge structure (XANES) analyses.[19] Excess Re atoms in the 2H-MoS_2 lattice (trigonal biprismatic coordination) was shown to convert it into the 1T phase with octahedral coordination and metallic character.[20] In the present work, we highlight for the first time the beneficial effects of incorporating Re-atoms in IF-MoS_2 on the electrochemical HER activity.

Experimental

Materials: $(NH)_4Mo_7O_{24}.4H_2O$ (99% pure) and Thiourea (99%) purchased from Merck India and SD Fine chemicals limited for the synthesis of FL-MoS_2. For preparation of electrodes 5 wt% Nafion solution was procured from Sigma Aldrich. For pH dependent studies, Sulphuric acid (98% pure) and KOH (min 85% assay) was procured from S.D Fine chemicals (India) and for pH 7.2 and 9.2 buffer solution was procured for Merck India.. For the synthesis of the undoped and Re-doped MoS_2 nanoparticles chemicals (Molybdenum (VI) oxide and Rhenium (VI) oxide) were procured from Sigma-Aldrich.

Synthesis of undoped and Re-doped IF-MoS_2: The synthesis of the undoped IF-MoS_2 was performed in a quartz reactor at 800-830^{o}C. Here evaporated MoO_3 powder was reacted with H_2S gas in a reducing atmosphere. Subsequently, a final annealing step was carried out for 25-35 h at 870 ^{o}C. This synthesis is described in great detail in Ref. [19]. The Re- doped IF-MoS_2 powder was prepared from the pre-prepared densified (Re-doped) oxide precursor in an analogous procedure to that of the undoped IF-MoS_2. An auxiliary reactor was used to prepare the $Mo_xRe_{1-x}O_3$ powder which served as a precursor for the synthesis of the doped IF-MoS_2.This synthesis procedure is described in details in the Ref. 20.

Synthesis of FL-MoS2 (Few-Layer): Few-Layer MoS_2 was synthesized using $(NH)_4Mo_7O_{24}.4H_2O$ and excess of Thiourea in molar ratio of 1:48 under N_2 environment at 800^{o}C.

Characterization: Characterization: The synthesized IF-MoS_2 nanoparticles were characterized by Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained using a FEI-Technai microscope working at 200 KeV, FEI Tecnai F30-UT high-resolution transmission electron microscope (HRTEM) operating at 300 kV. Specimens for TEM and HRTEM were prepared by evaporating a drop of ethanol suspension of the nanocrystals onto a holey carbon coated copper grid.

Extensive characterization of the undoped and Re-doped IF-MoS_2 nanoparticles has been carried out. Methods such as X-ray diffraction (XRF); energy dispersive X-ray spectroscopy (EDS) within the TEM; X-ray photoelectron spectroscopy (XPS) and others were extensively used throughout this work. Nonetheless, these methods are unable to resolve and accurately determine the Re-content in the lattice below 0.1 at%. Therefore, extensive analysis of the samples by inductive coupled plasma mass spectrometry (ICP-MS) has been carried out and to a lesser extent also time of flight secondary ionization mass spectrometry (ToF-SIMS). The analysis is described in detail in Refs. 19 and will not be repeated here.

Electrochemical measurements: The electrochemical HER activity of the catalysts was tested by Cyclic Voltammetry (CV), Linear Sweep Voltammetry (LSV) and Electrochemical Impedance Spectroscopy (EIS) techniques. The measurements were performed on electrochemical workstation (CHI760E and RRDE-3A) using three electrode system – a glassy carbon electrode (GCE) (3 mm in diameter) as substrate for working electrode, Ag/AgCl (3 M NaCl) was used as the reference electrode and a platinum wire as the counter electrode. Prior to use, the GCE was mirror polished by sequential use of 1 μ, 0.3 μ, 0.05μ alumina powders and nylon polishing pad. Catalyst ink for the working electrode was prepared by dispersing 2 mg of IF-MoS_2, Re-doped IF-MoS_2 and FL-MoS_2 (FL- few layers) in 200 μL of nafion solution (5 wt% nafion: IPA: H_2O = 0.05:1:4 (v/v/v)). 5 μL of this ink was drop-casted on the polished GCE and was allowed to dry overnight under ambient atmosphere. The electrolyte used for the reaction and the analysis was 0.5 M H_2SO_4saturated with Argon gas purging for 20 min to remove all dissolved gases present. The catalyst surface was cleaned electrochemically by cyclic voltametry in the potential range of 0.1 to 0.8V for 20 cycles prior to measurements. The HER activity of at different pH (0.5 M H_2SO_4, 0.1 M KOH, pH= 9.2 and pH=7.2 buffer solutions.) was studied for Re-doped sample.

Results and discussion

The morphology of the few layer- FL-MoS_2, IF-MoS_2 was revealed by TEM and are shown in Fig. 1.

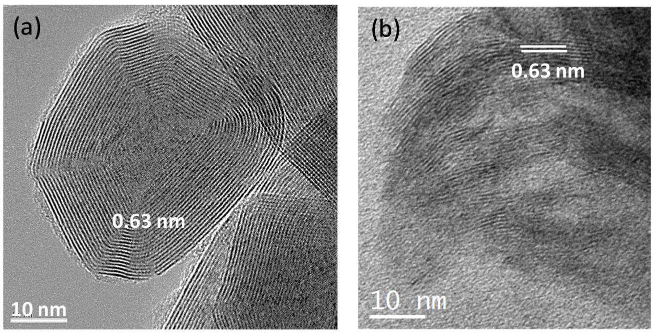


Fig. 1 HRTEM of (a) Re-doped IF-MoS2 and (b) FL-MoS2.

The inorganic fullerene form of MoS_2 has higher density of ordered edge sites compared to FL- MoS_2 (from Fig. 1) studied using SEM and TEM. Representative micrographs of the nanoparticles are shown in Fig. 1. The Inorganic fullerene form of MoS_2 has higher density of ordered edge sites compared to FL- MoS_2 (from Fig. 1).

Electrocatalytic HER activities of few-layer (FL) MoS_2, IF-MoS_2 and Re-doped IF-MoS_2 were studied using a mirror polished glassy carbon electrode (GCE). The measurements were done in a 0.5M H_2SO_4 solution using a rotating disc three-electrode cell setup (Ag/AgCl as reference electrode) with internal resistance correction. From the LSV plot in the cathodic polarization we observe that the onset potential for HER with few-layer MoS_2 (FL-MoS_2) is -0.39V vs Ag/AgCl with a current density of 0.21 mA/cm^2 at 0.5V (Fig. S1). For IF-MoS_2 the onset potential is -0.36V and a current density of 2.0mA/cm^2 at 0.5V (as shown in Fig. S2).

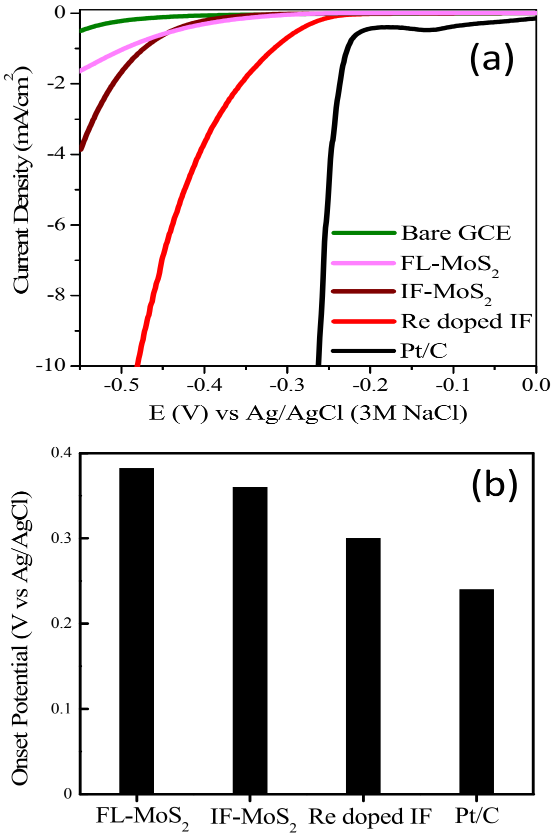


Fig. 2: (a) The LSV polarization curves for the various catalysts measured at 5mV/s. (b) The bar graph comparing the onset potential for HER activity of the catalysts.

The current density increases with each cycle for both IF-MoS_2 and FL-MoS_2 and saturates after 5th LSV cycle probably due to gradual displacement of SO_4^{2-} ions by H^+ ion on the electrode surface with increasing cathodic polarization in the range -0.1 to -0.3V. The current density of IF-MoS_2 is about 10 times higher than FL-MoS_2 is attributed to the higher density of exposed edge sites per mole of MoS_2, due to its onion like ring structure. Similar results have previously been obtained for MoS_2 by improving the density of density of edge sites [10, 17]. In contrast to FL-MoS2, IF-MoS_2 with onion like rings has maximal edge sites, and hence the total surface area exposure for a given mass of a catalyst is more. As a result of this IF-MoS_2 increases the efficient charge flow from the electrode to the surface active sites of the IF-nanoparticles. This would in turn lead to lower a charge transfer resistance for hydrogen evolution as seen from the Nyquist plot (Fig. 3). As seen from the plot, the series resistance of the cell, which encompasses the conductivity of the nanoparticles and the charge transfer resistance (R_{CT}) is the lowest for the Re-doped IF nanoparticles. The improved conductivity of the Re-doped nanoparticles[20] was discussed in detail before (see reference 20).

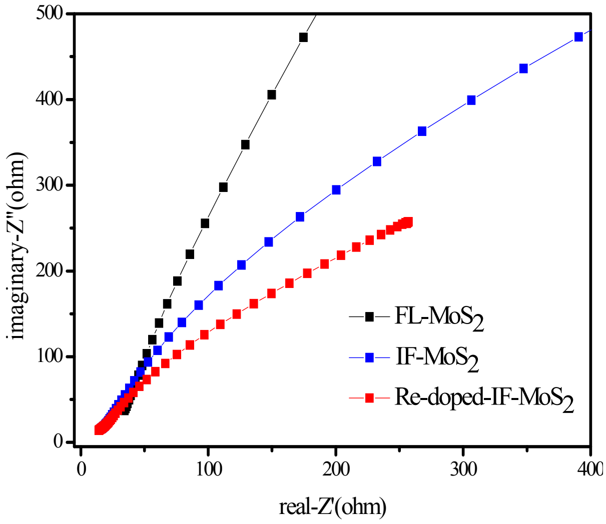


Fig. 3: The comparison of FL-MoS_2, IF-MoS_2 and Re-doped IF-MoS_2 in Nyquist plot.

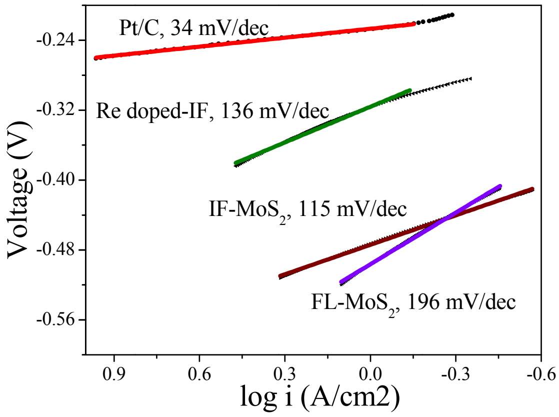
The IF-MoS_2 thus is the preferred structure in comparison to FL-MoS_2. IF-MoS_2 is an attractive catalyst structure for electrochemical HER as the onion like rings has maximal edge sites exposure for a given mass of a catalyst due to the higher density of edge sites and low charge transfer resistance for electron transfer reactions. Though IF-MoS_2 increases the current density, it is still low for practical applications. It is reported that on Re-doping with at as low as few tens to 100 ppm leads to an increased the density of free carriers in the conduction band of MoS_2 at room temperature which resides on the nanoparticle surface or close to it[19]. This extra charge would be expected to lead to a further decrease in the charge transfer resistance thereby reducing the overpotential for electrochemical HER. [19]. As a proof of concept, we have investigated electrocatalytic HER activity of various catalyst under similar conditions as that of IF-MoS_2. As seen from Fig 2 and Fig S3 we observe a drastic reduction of the onset potential (-0.3 V) for Re-doped MoS_2 by 60 and 80mV with respect to both IF- and FL- MoS_2. The shift in the onset potential is indicative of reduced charge transfer resistance from the catalyst electrode to the solution and thus facilitating HER, as seen from the Nyquist plot (Fig. 3). The onset potential of Re-doped MoS2 was comparable to 20 wt% Pt/C(0.24 V), the standard electrocatalyst for HER (from Fig.1).

The overpotential to obtain a current density of 10mA/cm^2 and 20 mA/cm^2 were found to be 0.48 V and 0.54 V. The turn over frequency (TOF) of Re doped IF-MoS$_2$ was calculated to be 0.2 and 0.4 s^{-1} cm^{-2} respectively. The detailed calculations are described in the supporting information on the assumption that the surface atoms on the catalyst to be the sites of hydrogen evolution. (Fig. S3)

In comparison to FL- and IF- MoS$_2$ Re-doped IF-MoS$_2$ showed enhanced current density at an overpotential of 0.5V by 67 times and 6 times respectively (Fig. 1). The detailed calculations are shown in ESI. Density functional theoretical (DFT) calculations indicates that upon doping (randomly) Re in MoS$_2$ a new impurity band appears at -0.2 eV below the conduction band of MoS$_2$, the new band is associated with the Re 5d orbital. As the dopant level increases the new impurity band gets populated with high density of n-type dopants. Re-doping of 10-100 ppm creates n-type charge carrier density of 10^{16}-10^{17}/cm^3 in the conduction band of the IF-MoS$_2$ at room temperature. The activation energy of the dopant atoms is as low as 0.1-0.2 eV thereby decreasing the onset potential and increases the current density [19].

In order to elucidate the electron transfer mechanism for HER, we have calculated the Tafel Slope by the current potential relationship derived from Butler-Volmer equation,

$$\eta = \mathbf{b}\log\left(\frac{i}{i_0}\right) \quad (1)$$



Here η=is the overpotential, i the current density, i$_o$ the exchange current density, and b the Tafel slope. Tafel slope is the measure of potential required to increase or decrease the current density by ten-folds[20]. Fig. 4, compares the Tafel slopes for all the three samples.

Fig 4: The comparison of Tafel slopes of FL-MoS$_2$, IF-MoS$_2$ and Re-doped IF-MoS$_2$.

The Tafel Slope of FL-MoS$_2$ was 196mV/dec, for IF-MoS2 was 115mV/dec and for Re-doped MoS$_2$ was 136mV/dec.

Although the Tafel slope of IF-MoS$_2$ is smaller than that of Re-doped IF-MoS$_2$, the current density of the Re-doped IF-MoS$_2$ at lower overpotential is much higher than that of IF-MoS$_2$. This indicates that the Re-doped nanoparticles are a much better catalyst than the undoped IF-MoS$_2$. The value of the Tafel slope is closer to 120mV/dec, theoretically calculated value for HER on Pt-catalyst. This analysis suggests that the HER proceeds probably through the Volmer-Herovsky mechanism. Comparison of the catalytic activity with other MoS$_2$ based catalysts can be done by turn over frequency (TOF) which is the amount of hydrogen generated per active sites on the catalyst.

Another crucial parameter for the practical applicability of a catalyst is the stability test. The stability of the catalyst under study was tested by CV in the potential range of -0.3 to 0 V at a scan rate of 100mV/s. The HER activity of Re-doped IF-MoS$_2$ is found to be as good as the initial value after 1000 cycles (Fig 5).

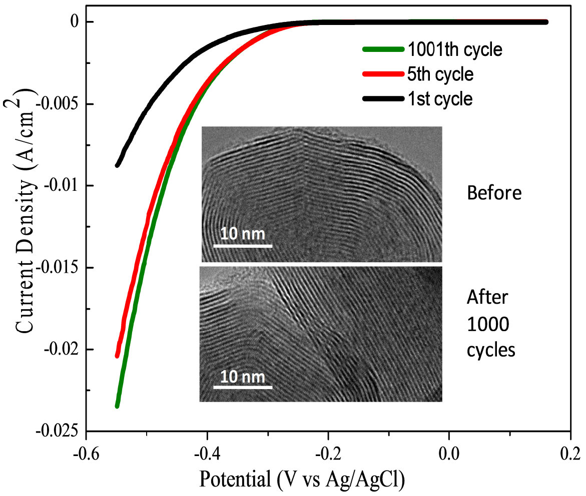


Fig. 5.The linear sweep voltammetry (LSV) curve after 1st, 5th and 1001th cycle and inset shows HRTEM of Re-doped IF-MoS2 after 1000 cycles.

Over a period of time, the catalyst loses its activity due to corrosion under the harsh acidic conditions or due to agglomeration and Ostwald ripening of the catalytic particles thereby decreasing the active surface area.

In case of IF-MoS$_2$the stability is attributed to the structural morphology of the IF-structure which is retained even after 1000 cycles as shown in Figure S5 and inset of Fig. 5. The combined effect of inorganic fullerene and Re-doping thus give higher current density, lower onset potential and lower charge transfer resistance which improves the electrochemical HER as compared to few-layer MoS$_2$ and IF-MoS$_2$.

HER activity is known to depend on the hydrogen binding energy which in turn varies with the pH values and also on the electrocatalyst[21]. Hydrogen evolution in acidic and basic medium proceeds via following equations,

$$2\,H^+ + 2\,e^- \longrightarrow H_2\ \text{(acidic)}\ (2)$$

$$H_2O + 2\,e^- \longrightarrow H_2 + OH^-\ \text{(alkaline)}\ (3)$$

In order to get an insight into the mechanism of hydrogen evolution by Re-doped IF-MoS$_2$at different Ph values of the electrolyte, we performed linear sweep voltammetry and electrochemical impendence spectroscopy studies as a function of different pH. For practical application of electrocatalysts in HER studies are generally carried out at high or low pH values (ease of use with proton/hydroxide exchange membrane fuel cells and electrolysers). In order to understand the effect of pH on the HER activity of the Re doped IF-MoS_2, we have studied at the HER different pH values- (0.5 M H_2SO_4 (0.3), 0.1 M KOH (13.0), pH= 9.2 and pH=7.2 buffer solutions.) The cathodic potential of HER evolution ideally varies with pH following the Nernstian equation,

$$E = E \; - 0.0592\, pH; at\ 298\ K\ (4)$$

E is the potential at the observed pH and E_o is at pH = 0. From Equation 4, the cathodic shift in slope of the potential should change 0.059 times with respect to unit change in the pH.

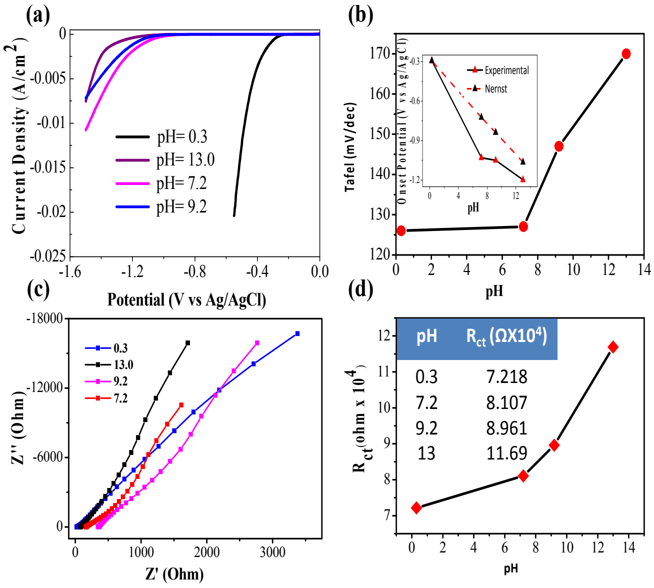


Fig. 6. (a) The linear sweep voltammetry for Re-doped IF-MoS2, (b) change of the Tafel slope and inset shows the onset potential with respect to pH (c) The Nyquist plot and (d) corresponding charge transfer resistance for Re-doped IF-MoS2 at different pH.

Indeed, the cathodic potential shifts to more negative values (as shown in Fig. 6a) with increasing pH. However, there is a deviation from Nernstian trend in Re-doped IF-MoS_2 (as shown in the inset of Fig. 6b) especially at alkaline pH. Fig. 6b gives the variation of the Tafel slope as a function of pH for Re-doped IF-MoS_2. We observe a non-linear relationship in the values of the Tafel slopes as the pH is increased indicating that adsorption and desorption of OH^- ions in the alkaline medium is optimally balanced with the adsorption and desorption of H^+ ions which promotes HER at lower overpotential compared to many of the catalysts reported in the literature [22]. In order to have an idea about the charge transfer resistance in HER at different pH values, we have studied the EIS behaviour at open circuit potential (Fig 6c). Ideally, at higher pH (>9) the resistance corresponding to the HER process is high in comparison to lower pH values which is attributed to the ease of H^+ adsorption on the electrode surface. Re doped IF-MoS_2 shows little variation in the charge transfer resistance (R_{ct}) as the pH was increased (Fig.6d). At higher pH value (>9) the evolution of hydrogen depends on the pH independent conversion of H_2O to H_2 (from Equation 4) [23]. Therefore, at higher pH's, charge transfer resistance is associated with the dissociation of H_2O which in turn is governed by the current obtained from the hydrogen oxidation reaction (HOR). This is in accordance with the previously reported study that the hydrogen binding energy (HBE) might be affecting the HER activity. We predict that Re doped sites might be optimising the HBE at higher pH and thereby resulting in lower R_{ct} for the HER process and hence higher activity. These sites enhance the HER activity by acting as active sites through tuning of HBE.

Conclusions

In conclusion, the present study demonstrates the beneficial effect of Re doping in MoS_2 fullerene for electrochemical hydrogen evolution. Re-doping results in higher current density, lower onset potential and lower charge transfer resistance compared to few-layer MoS_2 and undoped IF-MoS_2. Our study at different pH values suggests the prospect of using Re as the dopant to tune the hydrogen binding energy. It is possible that the oxophilicity of Re modifies the electronic environment around it and facilitates the catalytic substrate with respect to the HER.

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