Electronic Supplementary Information

Beneficial effect of Re doping in the electrochemical HER activity of MoS_2 fullerenes

Manjeet Chhetri[a], Uttam Gupta [b], Lena Yadgarov [c], Rita Rosentsveig [c], Reshef Tenne [c], C.N.R. Rao* [a, b]

a. New Chemistry Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P. O., Bangalore 560064, India.
b. Chemistry and Physics of Materials Unit, Sheikh Saqr Laboratory, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P. O., Bangalore 560064 , India.
* E-mail: cnrrao@jncasr.ac.in
c.Department of Material Science and Interfaces, Weizmann Institute, Rehovot 76100, Israel.

Calculation of TOF

The Turn over Frequency of hydrogen evolution was estimated using the calculation of number of active sites on the electrode based on method described in details below. However the inferences from these calculations can only be considered as an estimate because of the assumptions made.

(1) The origin of active site for HER is not unambiguously known.
(2) The theoretical calculations does not account for the loss in the surface area upon the attachment of the particles on the electrode and among themselves.

TOF was calculated using the current density at an overpotential of 0.5V (vs Ag/AgCl, 3 M NaCl).

1. Theoretical calculation of active sites induced by Re presence in the IF

Assuming that Re-doped and undoped IF-MoS_2 nanoparticles (NPs) have a **radius** of **70 nm** and a **hollow core** of **6 nm** the surface area of the (spherical) IF NP is: $S = 4\pi r^2 = 4\pi 70^2 = 6.16e4 nm^2 = 6.16\text{e-}10 cm^2$

The volume of the IF nanoparticle (V_{IF}):

$$V = \frac{4}{3}\pi(r_{sphere}^3 - r_{core}^3) = \frac{4}{3}\pi(70^3 - 3^3) = 1.44e6nm^3 = 1.4e-15cm^3$$

The mass of the single IF can be calculated using the specific gravity of bulk MoS_2 which is 4.8 g/cm^3. Assuming that compared to bulk the packing density of the IF is 75%the weight of IF is $5.18x10^{-12}$mg.

$$m_{NP} = \rho V = 4.8 \times 0.75 \times 1.44 \times 10^{-15}\, g.cm^{-3}.cm^3$$

$$m_{NP} = 5.18 \times 10^{-12}\, mg$$

In the experiment 2 mg of the IF were dispersed in 200 µL solution of which 5 µL were used, i.e. 0.05 mg of the IF were used for each electrode. Thus the number of IF in the electrode is $0.05/(5.2x10^{-12}) = 9.6x10^9 \approx 10^9$nanoparticles in each electrode.

$$N_{cells} = \frac{V_{IF}}{V_{cell}} = 1.34 \times 10^7$$

$$N_{Mo\ atoms\ in\ IF} = 1.34 \times 10^7 \times 2 = 2.69 \times 10^7$$

$$N_{S\ atoms\ in\ IF} = 1.34 \times 10^7 \times 4 = 5.37 \times 10^7$$

Area of electrode is 0.07065 cm^2.

Also, Molar Volume (M_v) = 44.46 cm^3/mol

Molar Mass (M_m) = 160.07 g/mol

Surface area of the nanoparticle: $S_{IF} = 6.16 \times 10^{-10}\ cm^2$

Volume of the IF nanoparticle: $V_{IF} = 1.43 \times 10^{-15}\ cm^3$

The mass of catalyst deposited on the electrode per cm^2 = 0.707 mg/cm^2

The density (d) of bulk $MoS_2$is 4.8g/cm^3 (or 3.6g/cm^3 for IF-MoS_2) and the packing density as assumed earlier as 0.75 compared to bulk,

Surface area per mg of 70 nm of diameter (S_A)= S_{IF} x 1/V_{IF} x 1/d

$$S_A = 6.16 \times 10^{-10}\ cm^2 \times 1/1.43 \times 10^{-15}\ cm^3 \times 1 cm^3/3.6\ g = 119.7\ cm^2/mg$$

Average surface (A_S) atoms per cm^2 for 4H-MoS_2 = (n x 6.022 x 10^{23} atoms x 1/M_v)$^{2/3}$

$$= 0.707 \times (6 \times 6.022 \times 10^{23}\ atoms \times 1/44.46\ cm^3)^{2/3} = 1.32 \times 10^{15}\ cm^{-2}$$

Surface atoms per testing area (S_t) = S_A x A_S

$$= 119.7 \times 1.32 \times 10^{15}$$

$$= 1.58 \times 10^{17}$$

$$TOF^*(s^{-1}cm^{-2}) = \frac{1}{2e^-} \times (current\ density@-0.5\ V) \times \frac{1}{F} \times 6.022 \times 10^{23} e^- \times 1/S_t \quad (1)$$ [2,3]

(F= Faradays Constant =96485 C)

$$TOF^* = \frac{12.43 \times 6.022}{2 \times 96485 \times 1.58} \times 10^{23} \times 10^{-17} s^{-1}$$

$$TOF^* = 0.245\ s^{-1}$$

Summary of calculation:

	Undoped	Doped
Current Density at 0.5 V	2×10^{-3}	12×10^{-3}
TOF* ($s^{-1}cm^{-2}$)	0.04	0.24
Exchange current density (i_o)(A/cm^2)	1.54×10^{-6}	4.74×10^{-6}

The exchange Current density was calculated from the Tafel equation[4],

$$\eta = a + b \log i$$

Where b is the Tafel slope, $a = 2.3\frac{RT}{\alpha F}\log(i_0)$ and α is the charge transfer coefficient.

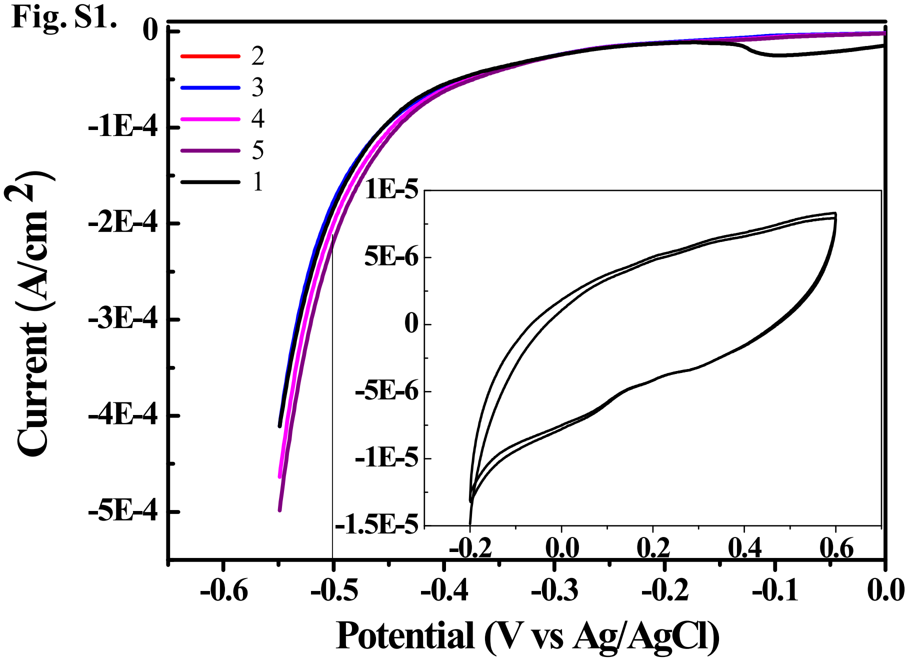

Figure S1: Linear sweep voltametry curve (LSV) and cyclic voltametry (CV) of FL-MoS_2. The numbers correspond to the cathodic polarization cycle number.

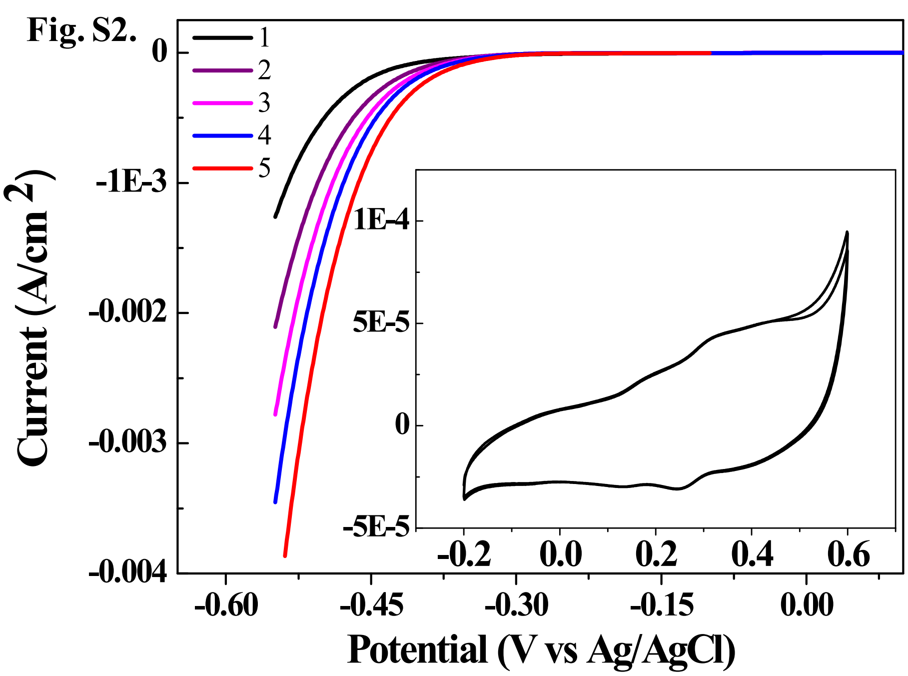

Figure S2: Linear sweep voltametry curve (LSV) and cyclic voltametry (CV) of IF-MoS_2.The numbers correspond to the cathodic polarization cycle number.

Fig. S3.

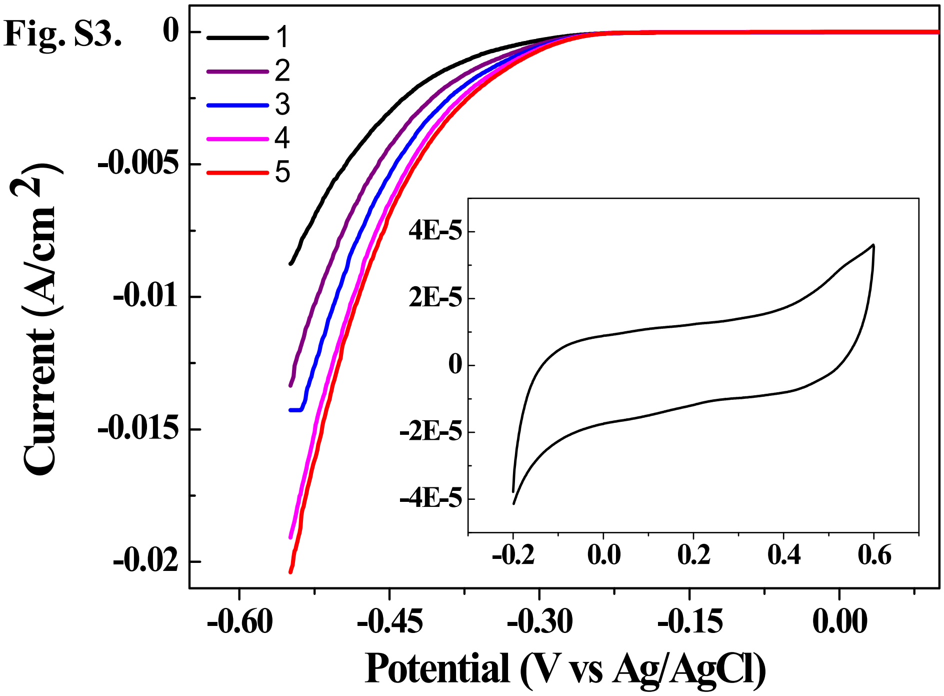

Figure S3: Linear sweep voltametry curve (LSV) and cyclic voltametry (CV)of Re-doped-IF-MoS_2. The numbers correspond to the cathodic polarization cycle number.

Fig. S4.

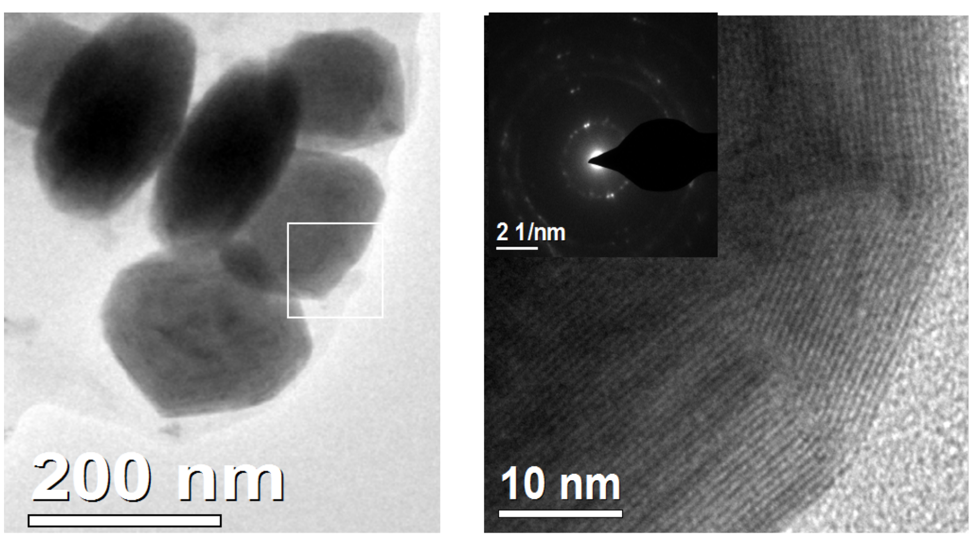

Figure S3: TEM and HRTEM of Re-doped-IF- MoS_2 after 1000 cycles. The and inset shows electron diffraction of the studied electrode material after 1000 cycles

Comparison of MoS_2 based catalysts with the present work

Serial No.	Compound	Overpotential (V w.r.t. Ag/AgCl) [V vs RHE*]	Tafel Slope mv/dec	Reference
1	Pt(20 wt%)/C	0.24 [0.01]	---	Present Work
2	IF-$Re_xMo_{1-x}S_2$	0.28 [0.05]	128 (at low potential)	Present Work
3	IF-MoS_2	0.38 [0.15]	98	Present Work
4	FL-MoS_2	0.38 [0.15]	172	Present Work
5	Bare GCE	0.36 [0.14]	---	Present Work
6	2H-MoS_2	0.43 [0.20]	117	J. Am. Chem. Soc. 2013, 135, 10274
7	1T-MoS_2	0.42 [0.19]	43	J. Am. Chem. Soc. 2013, 135, 10274−10277
8	Vertically aligned MoS_2 (edge terminated)	0.45 [0.22]	86	Nano Lett. 2013, 13, 1341
9	Ultra thin Oxygen incorporated MoS2 @ (4.18% Oxygen)	0.35 [0.12]	67	J. Am. Chem. Soc. 2013, 135, 17881

References:

(1) Hassel. O. 1925 for MoS_2, P 63/mmc; Formula Units per Cells.

(2) Popczun, E. J., McKone, J. R., Read, C. G., Biacchi, A. J., Wiltrout, A. M., Lewis, N. S., &Schaak, R. E. (2013). Nanostructured nickel phosphide as an electrocatalyst for the hydrogen evolution reaction. *J. Am. Chem. Soc.*, *135*(25), 9267-9270.

(3) Wang, H., Tsai, C., Kong, D., Chan, K., Abild-Pedersen, F., Nørskov, J. K., & Cui, Y. (2014). Transition-metal doped edge sites in vertically aligned MoS2 catalysts for enhanced hydrogen evolution. *Nano Research*, *8*(2), 566-575.

(4) Electrochemical Methods: Fundamentals and Applications, Bard, A.J. Faulkner, L.R., Wiley, 2000, ISBN 9780471043720.