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Supplementary information

Amorphous molybdenum sulfide quantum dots: an efficient hydrogen evolution electrocatalyst in neutral medium

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Table-S1: Comparison of onset potentials for different MoS_2 based nano materials

Materials	Onset Potential (mV)	Tafel Slope (mv/dec)	References	Medium
MoS_3 on glassy carbon	171-203	86	Chem. Sci., 2012, 3, 2515	pH 7
MoS_2/N-doped graphene aerogel	236	-	J. Mater. Chem. A, 2014, 2, 13795	pH 7
$CuMoS_4$ on glassy carbon	135	-	Energy Environ. Sci., 2012, 5, 8912–8916	pH 7
Fe-MoS_3	137-176	95	Chem. Sci., 2012, 3, 2515	pH 7
Ni-MoS_3	110-144	96	Chem. Sci., 2012, 3, 2515	pH 7
Cu-MoS_3	87-122	87	Chem. Sci., 2012, 3, 2515	pH 7
Ni-Mo-S nano sheets on carbon fiber cloth	132	85.3	*Science Advances*, DOI: 10.1126/sciadv.1500259	pH 7
Amorphous MoS_x on carbon fiber	205	46	*Energy Environ. Sci*. 2012, 5, 6136−6144.	0.5 M H_2SO_4
Amorphous MoS_x/Graphene/Ni-foam	109	42.8	*Chem. Commun.*, 2015, 51, 6293-6296.	0.5 M H_2SO_4
Monolayer MoS_2 quantum dots	120	69	*RSC Adv.,* 2015, 5, 97696-97701	0.5 M H_2SO_4
Monolayer MoS_2 /WS_2 composite Quantum Dots	120	69-75	Adv. Funct. Mater. 2015, 25, 1127–1136	0.5 M H_2SO_4
MoS_2 quantum dot decorated RGO	64	63	J. Mater. Chem. A, 2015, 3, 21772	0.5 M H_2SO_4
Tungsten Phosphide Submicroparticles	54	57	ACS Catal. 2015, 5, 145149	pH 7
Tungsten Phosphide Nanorod	100	125	ACS Appl. Mater. Interfaces 2014, 6, 21874	pH 7
Amorphous MoS_x quantum dots	**65**	**73.9**	**Present work**	**pH 7**

Table-S2: Comparison of exchange current density (j_0) values

Material	j_0 (μA/cm^2)	References
Oxygen incorporated MoS_2 nanosheets	12.6	*J. Am. Chem. Soc.*, 2013, *135* (47), 17881–17888
Defect-rich MoS_2 nanosheets	8.9	*Adv. Mater.*, 2013, 25, 5807–5813
Defect-free ultrathin MoS_2 nanosheets	3.16	*Adv. Mater.*, 2013, 25, 5807–5813
Active edge MoS2	7.9	Science, 2007, 317, 100–102
MoS_x	1.59	*Nano Lett.*, 2014, *14* (3), 1228–1233
S-rich MoS_2	0.4	*J. Mater. Chem. A*, 2015,3, 15927-15934
MoS3 on glassy carbon	0.89	*Chem. Sci., 2012, 3, 2515-2525*
Amorphous MoS_x quantum dots	8.71	**Present work**

Photoluminescence Study of quantum dots:

To establish the quantum dot behavior, we have measured the fluorescence property of these MoS_x nano particles. It shows quite weak blue photo luminescence (PL) spectra at ~ 430 nm when excited at 360 nm wavelength. As the nano particle is amorphous in nature it gives very weak PL compared to crystalline MoS_x nanoparticles as shown in **Fig S1**. The most striking feature of quantum dots is that they show excitation dependent PL property due to splitting of the energy band gap[1-4] and our material also shows such excitation dependent photoluminescence behavior as shown in **Fig. S2**. With the increase in excitation wavelength the peak position is gradually red shifted. It is noted that the band gap of monolayer MoS_2 is ~ 1.9 eV (direct band

gap), whereas it is found to be ~ 2.9 eV for our material. Therefore, a huge blue shift (~ 1 eV) and splitting of energy levels giving rise to excitation dependent PL confirming the quantum confinement of the electronic wave functions in the as synthesized material. This strongly resembles the quantum dot behavior of our MoS_x nano particles.

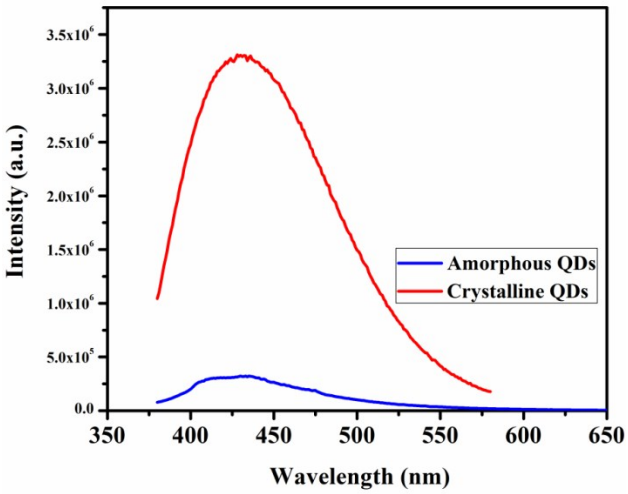

Fig. S1: Comparison of PL spectra between crystalline and amorphous MoS_x quantum dots

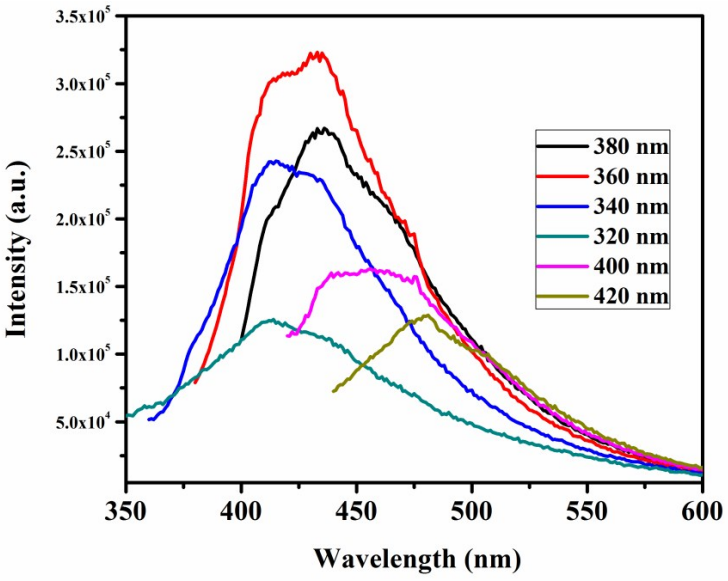

Fig. S2: Excitation dependent PL spectra of amorphous MoS_x quantum dots

HER study of MoS_x quantum dots in different medium:

***In 0.5 M H_2S0_4 medium*:**

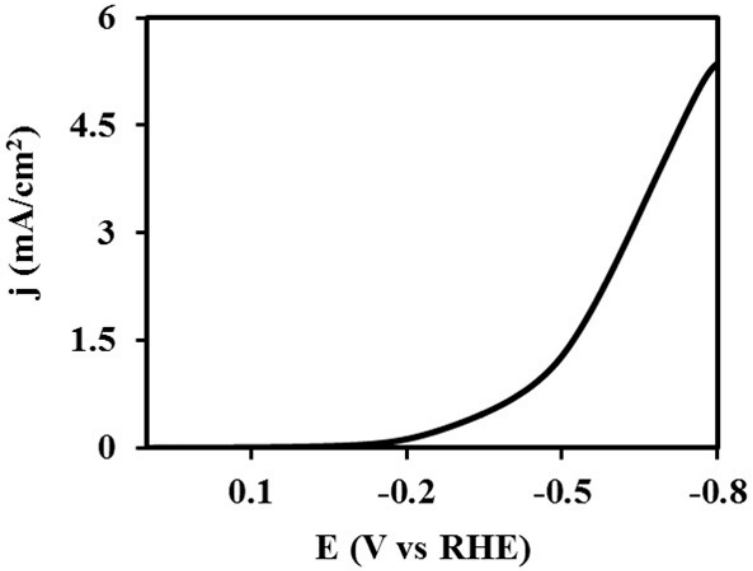

Fig. S3: HER activity in acidic condition

***In 1 N NaOH medium*:**

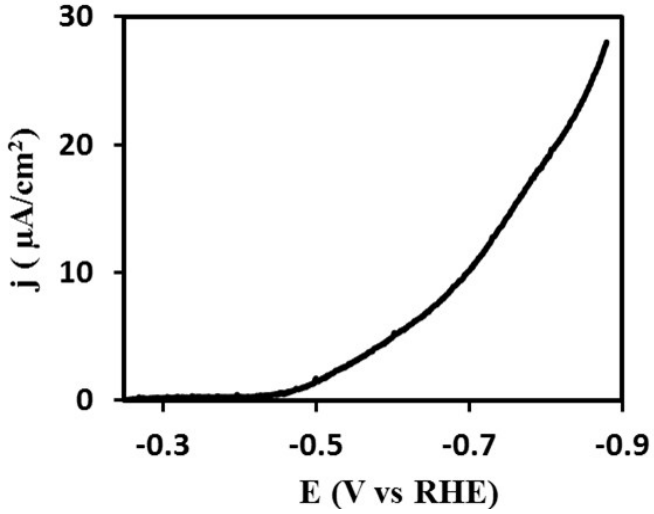

Fig. S4: HER activity in basic condition

***Determination of TON and TOF*:**

Turn over frequency is determined from the double layer capacitance (C_{dl}) of the MoS_x film modified ITO electrode. C_{dl} could easily be determined from the current density of the modified electrode where no faradaic current is observed. The difference between the anodic and cathodic current at 0.08 V vs RHE is plotted against scan rate as shown in **Fig. S3**. From the slope of this linear fit the double layer capacitance of the modified electrode is easily determined to be ~ 765 μF/cm^2. The area-averaged capacitance depends on the electrode materials. The TOF has been determined from the double layer capacitance of the MoS_x surface (C_{dl} = 765μF/cm^2) and charge consumed (22.18 C) which is converted to the number of electrons passes through the electrode per second.[5] The total charge consumed during bulk electrolysis at particular time consumption is taken from **Fig. S4**. The number of electrons could be converted to number of hydrogen per second dividing it by 2, as each molecule of hydrogen generation involves 2e$^-$. Using these results, the TON has been determined to be 1.13×10^4 and TOF is 2.83 s^{-1} at 480 mV overpotential.

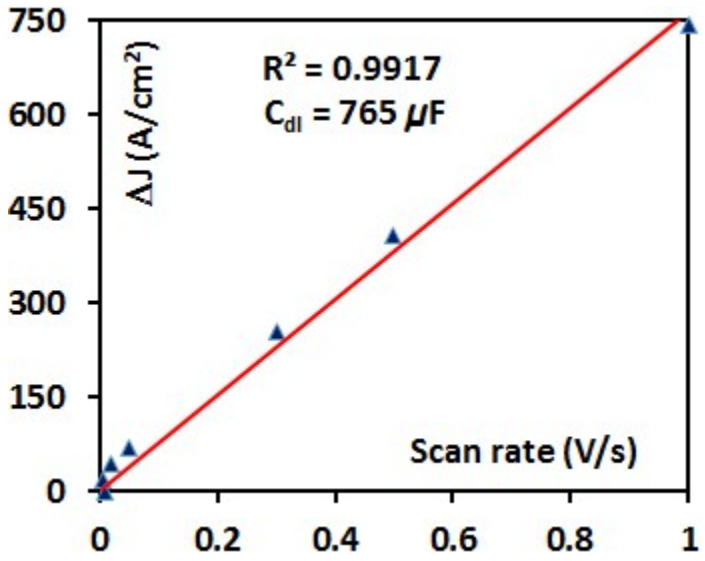

Fig. S5: Plot of difference between cathodic and anodic current against scan rate.

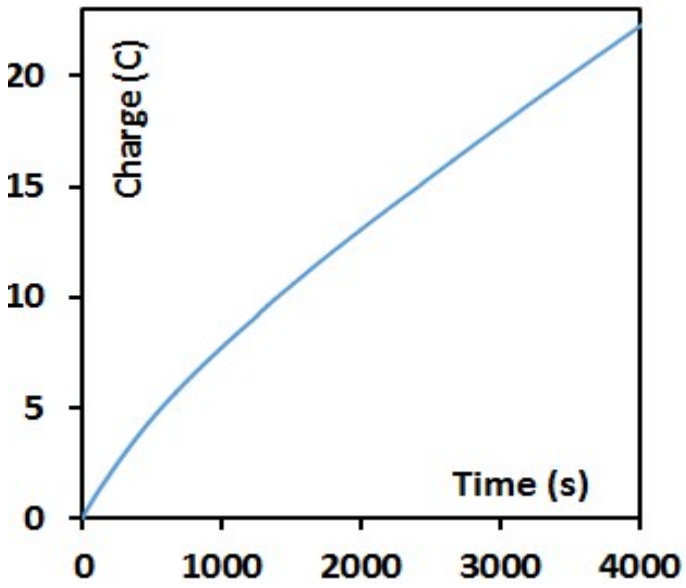

Fig. S6: Consumption of charge at particular time interval during bulk electrolysis.

***Tafel plot at lower over potential*:**

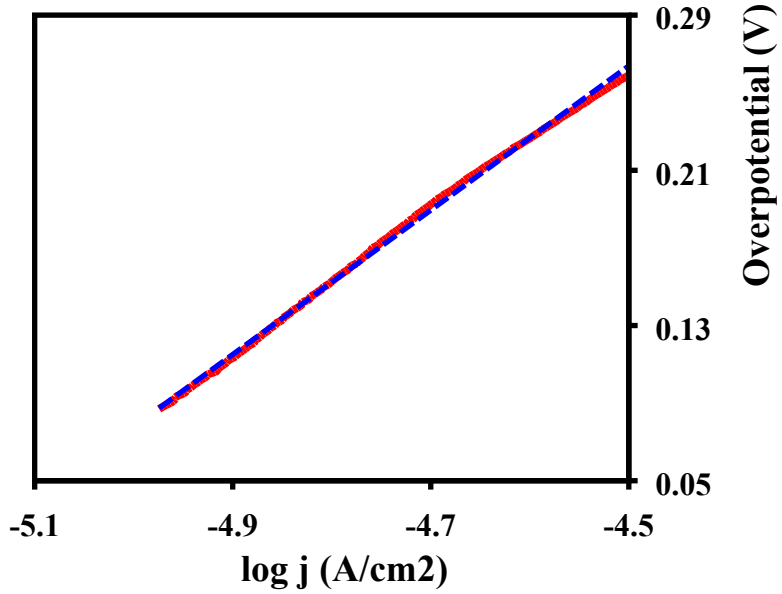

Fig. S7: Tafel plot of MoS_x quantum dots in pH 7 at lower over potential region.

***LSV experiment on bare ITO plate*:**

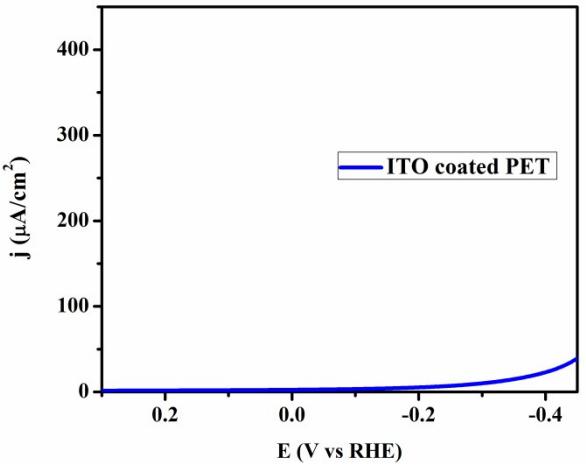

Fig. S8: LSV experiment over bare ITO coated PET plate at pH7.

***Faradaic Efficiency calculation*:**

No of moles of H_2 produced during bulk electrolysis = 8×10^{-4}

Charge consumed = 22.18 C

$$\textbf{F. E (\%)} = \frac{100 \times H_2 \text{ produced (mol)} \times 2 \times 96500}{\text{Charge consumed (C)}}$$

= ~70%

Study of amorphous MoS_x quantum dots film after HER experiment:

***Morphological study*:**

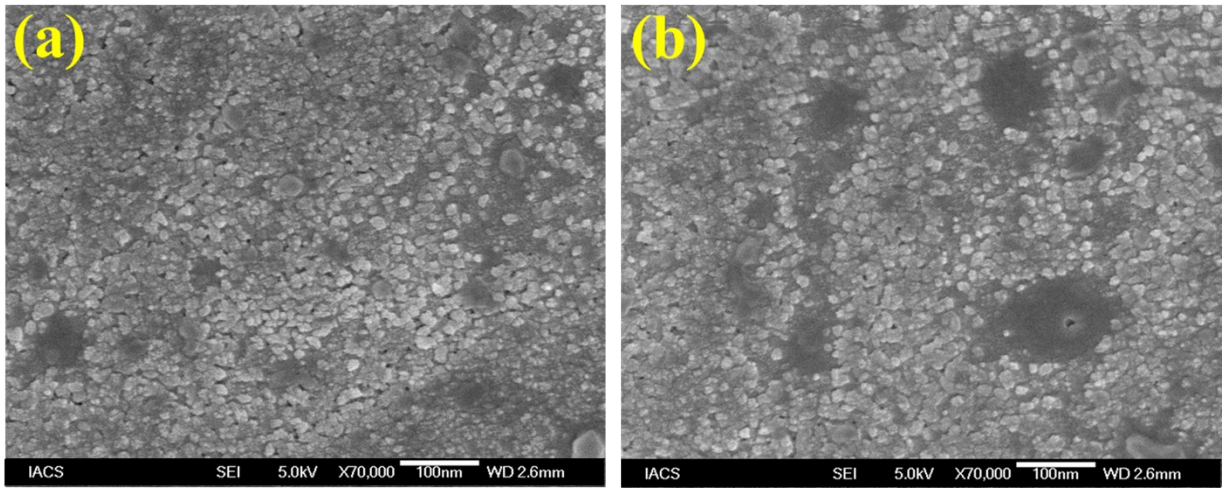

Fig. S9: SEM images of MoS_x quantum dots (a) before and after HER experiment.

***Structural study*:**

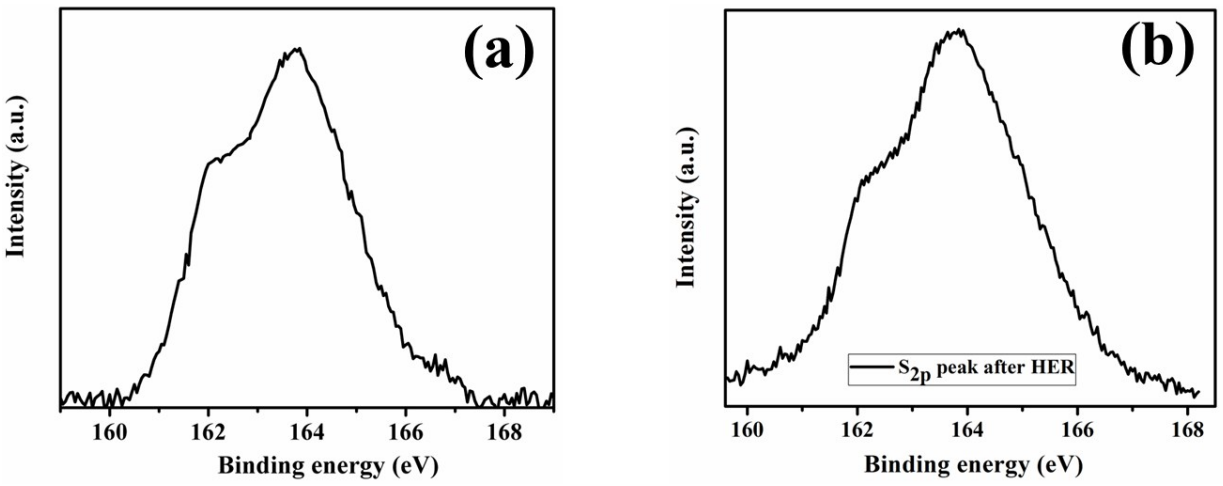

Fig. S10: XPS profile of S 2p in MoS_x quantum dots (a) before and (b) after HER.

Electrochemical measurements with amorphous MoS_x quantum dots on Cu foil:

We have also carried out electrochemical measurements with MoS_x quantum dots on Cu foil. It shows similar HER activity compared to ITO coated PET substrate. It also shows 65 mV onsets potential during HER at pH 7.

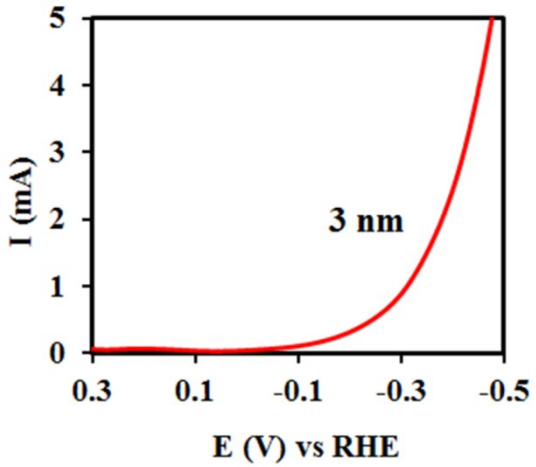

Fig. S11: Polarization curve of amorphous MoS_x quantum dots on Cu foil substrate.

Nyquist plots of amorphous MoS_x quantum dots on Cu foil substrate:

To decrease the R_{ct} value of the material, we have drop casted this material on Cu foil as it is more conducting substrate. The nature of plot is quite similar compared to our previous results with ITO coated PET substrate as shown in **Fig. S5**. Here, the material shows low charge transfer resistance (R_{ct}) of 283 Ω at 70 mV overpotential. With increasing bias it drastically decreases to 30 Ω at 570 mV overpotential. As the Cu foil is more conducting than PET substrate, electron transfer rate during the HER is quite fast compared to PET, resulting such low R_{ct} value. But the major drawback for this substrate is its non-flexibility to use. In recent times, as most of the people are trying to design some flexible electrodes for HER process, it is quite challenging to

use Cu foil as substrate. To avoid this, we have used ITO coated PET substrate as an electrode in spite of its slightly higher R_{ct} value (604 Ω) during HER.

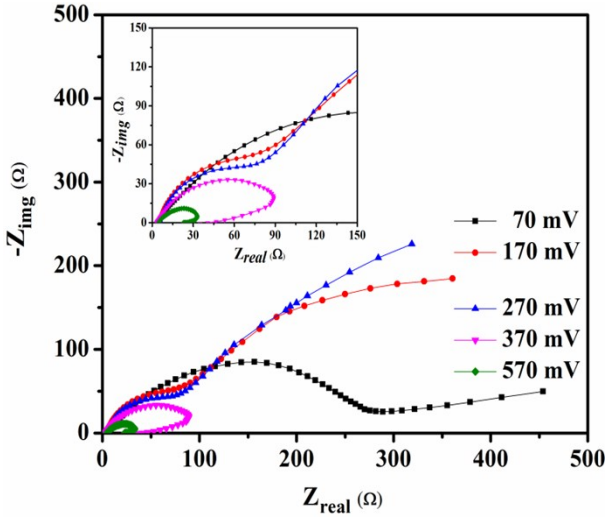

Fig. S12: Nyquist plot of MoS_x quantum dots on Cu foil substrate.

Characterization of amorphous MoS_x nanoparticles with larger particle size:

***XRD study*:**

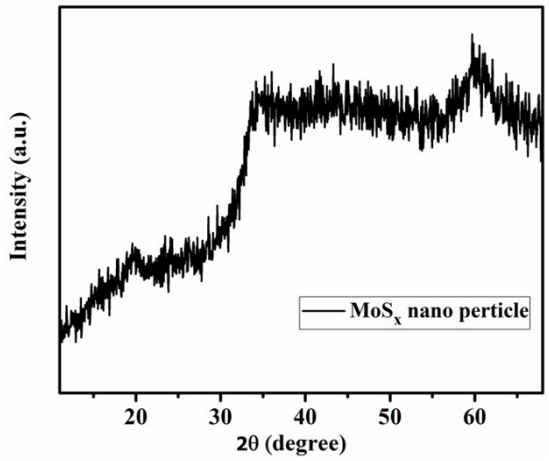

Fig. S13: XRD patterns of amorphous MoS_x nanoparticles.

***XPS study*:**

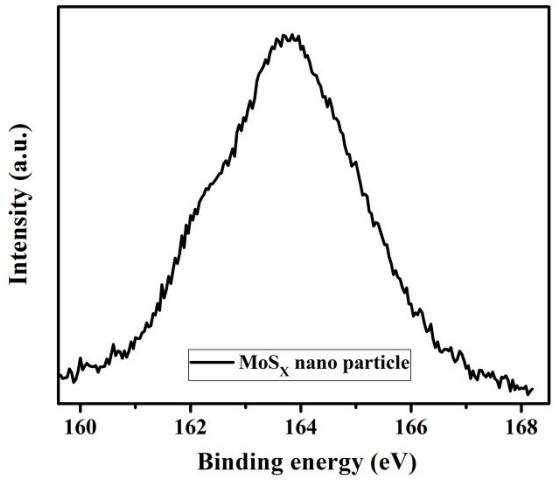

Fig. S14: XPS spectra of S 2p of amorphous MoS_x nanoparticles.

***Raman study*:**

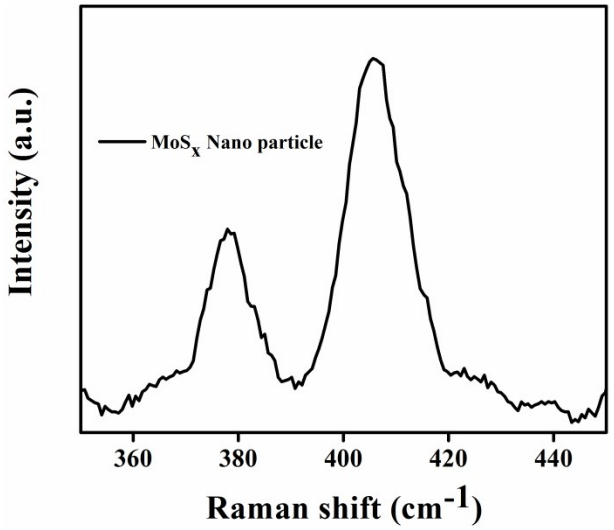

Fig. S15: Raman spectra of amorphous MoS_x nanoparticles.

Stability curve of MoS_x nano particle during bulk electrolysis:

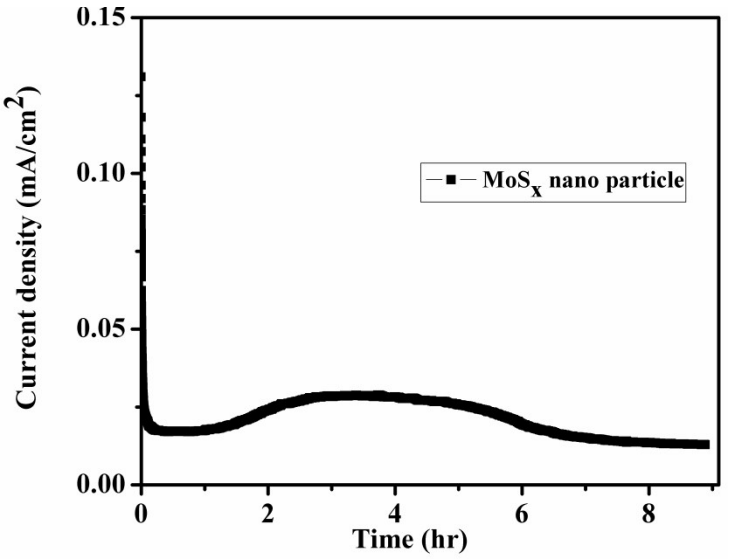

Fig. S16: Durability test of MoS_x nano particles during bulk electrolysis at pH 7.

References:

1. Gopalakrishnan, D., Damien, D., Shaijumon, M.M.; *ACS Nano*, 2014, *8* (5), 5297.

2. Gopalakrishnan, D., Damien, D., Li, B., Gullappalli, H., Pillai, V.K., Ajayan, P.M. Shaijumon, M.M.; *Chem. Commun.*, 2015, 51, 6293.

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5. Dey, S., Mondal, B. and Dey, A., *Phys. Chem. Chem. Phys*., 2014, 16, 12221.