Electronic Supplimentary Information

Electrochemical Synthesis of Luminescent MoS_2 Quantum Dots

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Experimental Methods:

1. Synthesis of MoS_2 quantum dots through electrochemical exfoliation. MoS_2 quantum dots were synthesized through an electrochemical route. MoS_2 flakes, Ionic Liquids such as Bis (trifluoromethane)sulfonimide lithium (LiTFSI) salt, 1-Butyl-3-methylimidazolium chloride ([BMIM]Cl) from Sigma Aldrich, were used as received. In a typical experiment, MoS_2 discs (diameter 1cm) made from commercially available MoS_2 powder flakes, were placed in an electrochemical cell 1 cm apart, in aq. Lithium bis(trifluorosulfon)imide (LiTFSI) or 1-Butyl-3-methylimidazolium chloride ([BMIm]Cl) of various concentrations *viz*. 0.1, 1 and 5 wt.%. A constant DC potential of 5 V is applied between the MoS_2 discs at room temperature. The reaction mixture was collected after 3 h and centrifuged using vivaspin centrifugal concentrators at 6000 rpm for 1 h to remove any traces of bulk MoS_2.

2. Structural characterizations and Electrochemical HER measurements of MoS_2 quantum dots. The structure and composition of the exfoliated MoS_2 QDs were characterized using various microscopic and spectroscopic tools including high resolution transmission electron microscope (HRTEM), Atomic force microscope (AFM), X- ray photoelectron spectrometer (XPS), UV- Vis photo-spectrometer, and Fluorescence spectrometer. HRTEM images of MoS_2 QDs of varying sizes were obtained using JEOL JEM 2100 (200 kV) with a LaB_6 electron gun and JEOL 2100 Field Emission Gun Transmission Electron Microscope. AFM images were taken using Bruker Multimode 8. XPS measurements were carried out using

PHI Quantera XPS. Shimadzu UV- 3600 UV- Vis spectrometer was used to collect the absorption spectra of the synthesized MoS_2 QDs. Photoluminescence emission spectra were recorded on spectro-fluorimeter (Horiba JobinYvon- Fluorolog 3).

Electrochemical measurements. The electrocatalytic performance of MoS_2 QDs towards the Hydrogen evolution reaction (HER) was evaluated using a three electrode system with 0.5M H_2SO_4 as electrolyte. As synthesized MoS_2 QDs with 5 wt% nafion solution were drop-casted onto a freshly polished glassy carbon (GC) electrode and dried at room temperature, which acts as the working electrode. A Pt wire auxiliary electrode and a Ag/AgCl were used as counter and reference electrodes respectively. The performance of the catalyst towards hydrogen evolution was measured using linear sweep voltammetry by applying a potential ranging from +0.2V to -0.45V *vs.* standard hydrogen electrode (SHE) with a very slow scan rate of 2 mVs^{-1}.

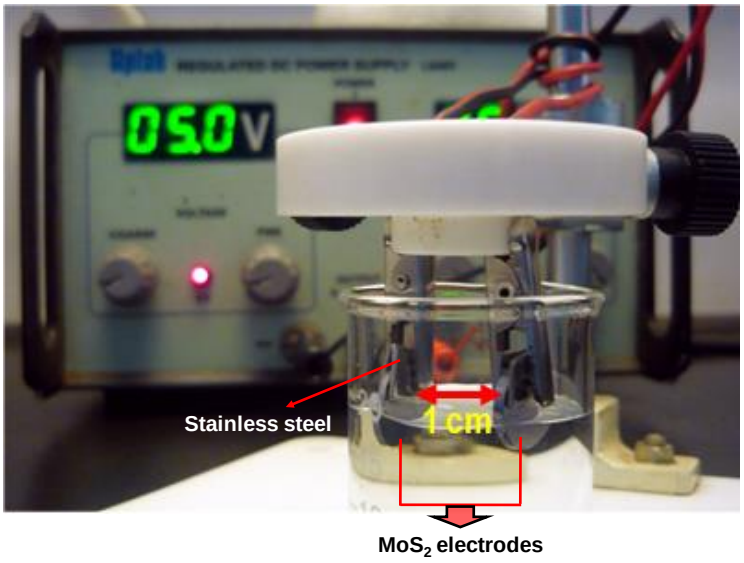

Fig. S1 Experimental set up for the electrochemical exfoliation of MoS_2 nanoclusters.

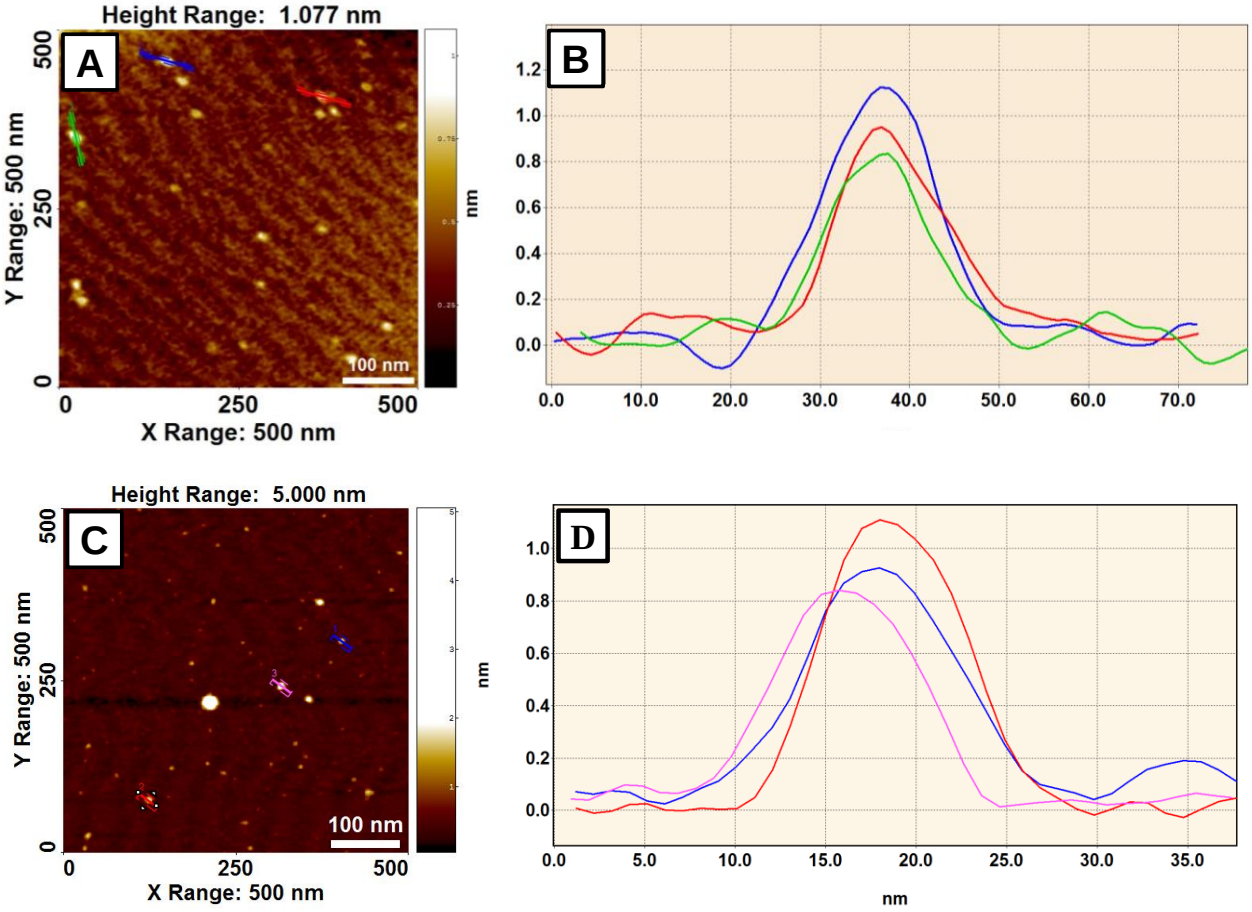

Fig. S2. Electron AFM images of electrochemically exfoliated MoS2 QDs. AFM analyses show particles with uniform thickness distribution for all the samples. (A) and (B), respectively, show AFM images and corresponding height profile of MoS2 QDs synthesized using aq. [BMIm]Cl electrolyte with 0.1 wt%. (C, D), respectively, show AFM images and height profile of similar particles obtained with 1.0 wt% concentration of aq. [BMIm]Cl electrolyte.

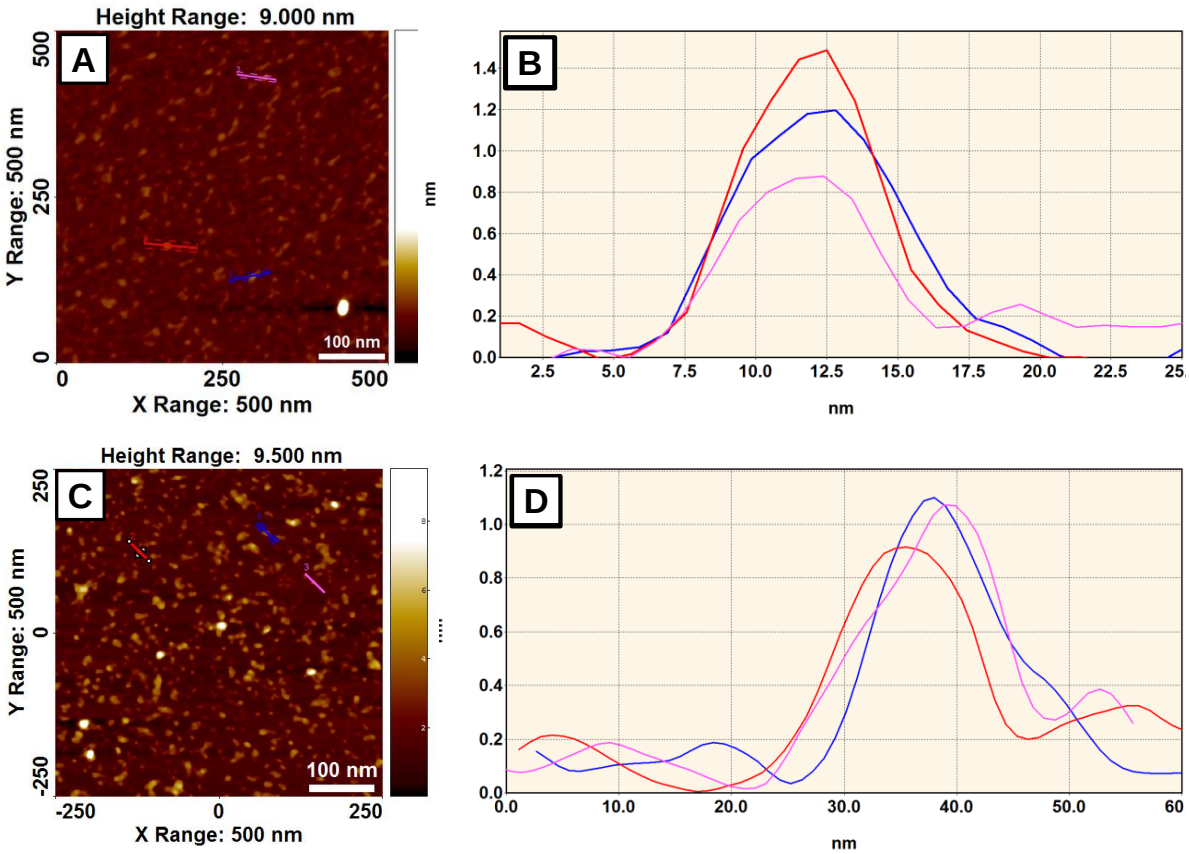

Fig. S3 AFM image of the MoS_2 clusters formed using LiTFSI 0.1 wt. % (A) and its corresponding height profile (B). C and D correspond to the AFM image and height profile of MoS_2 clusters respectively, obtained using 1wt. % aq. LiTFSI electrolyte.

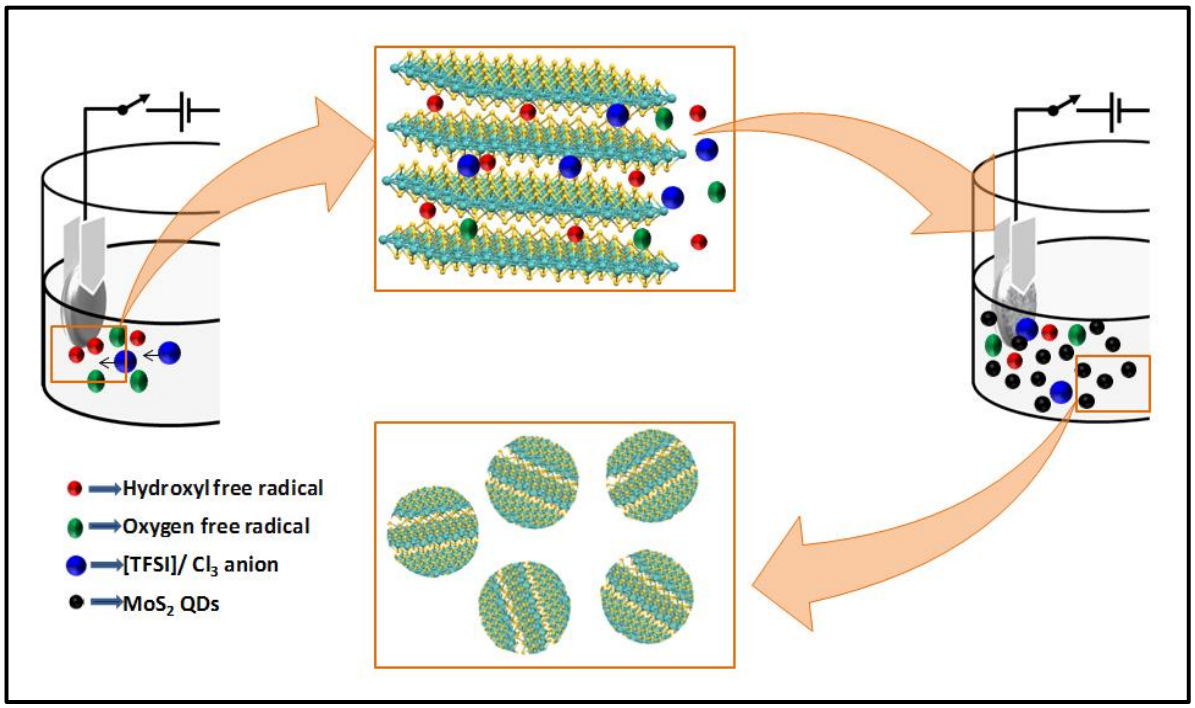

Fig. S4. A schematic representation of the electrochemical exfoliation of MoS_2 pellets in LiTFSI/ [BMIm]Cl based aq. Electrolyte. Hydroxyl and oxygen free radicals generated under the applied DC voltage trigger the initial cleavage of MoS_2 sheets. As the time progresses, the MoS_2 anode swells by the incorporation of $TFSI^-$ anions and MoS_2 QDs start dissolving in the electrolyte [Sizes mentioned are not to the scale].

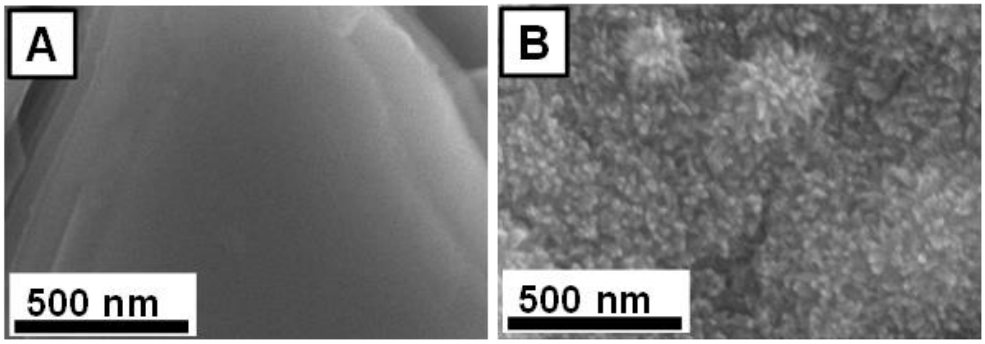

Fig. S5 SEM images of the bulk MoS_2 anode surface before the electrochemical exfoliation and after the electrochemical exfoliation. Surface roughening results from the etching of MoS_2 nanoclusters from the surface of the anode.

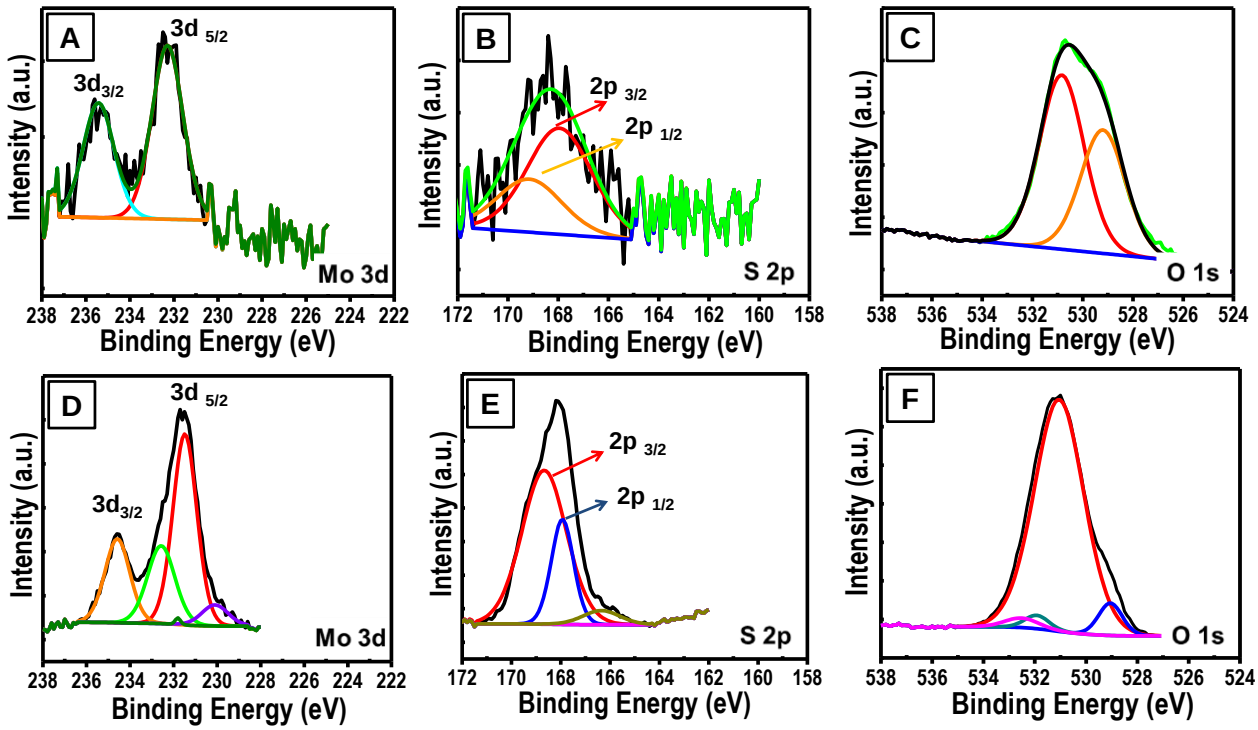

Fig. S6 The XPS spectrum of MoS_2 QDs synthesized using [BMIm] Cl 1 wt% (A, B & C) and LiTFSI 1 wt% (D, E & F) at a potential 5V. Slightly oxidized nature of Mo 3d (D); existence of S-O bond of S 2p (E) and O 1s (F).

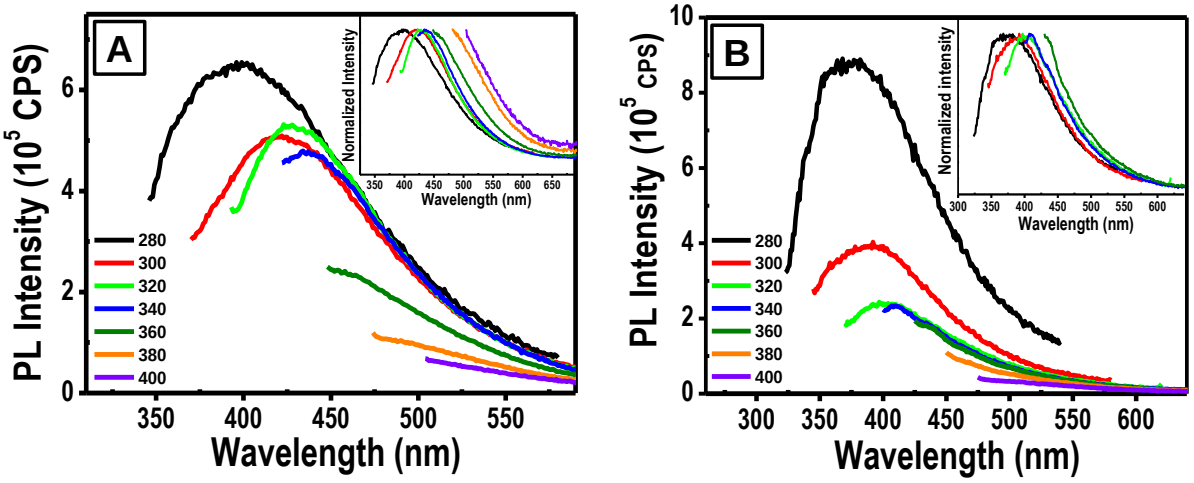

Fig. S7 A and **B** show photoluminescence spectra of MoS_2 QDs obtained at an applied DC voltage of 5 V with 0.1 wt% and 1 wt% concentration of [BMIm]Cl. Excitation wavelengths are varied and normalized excitation dependent emission spectra are shown in the corresponding inset.

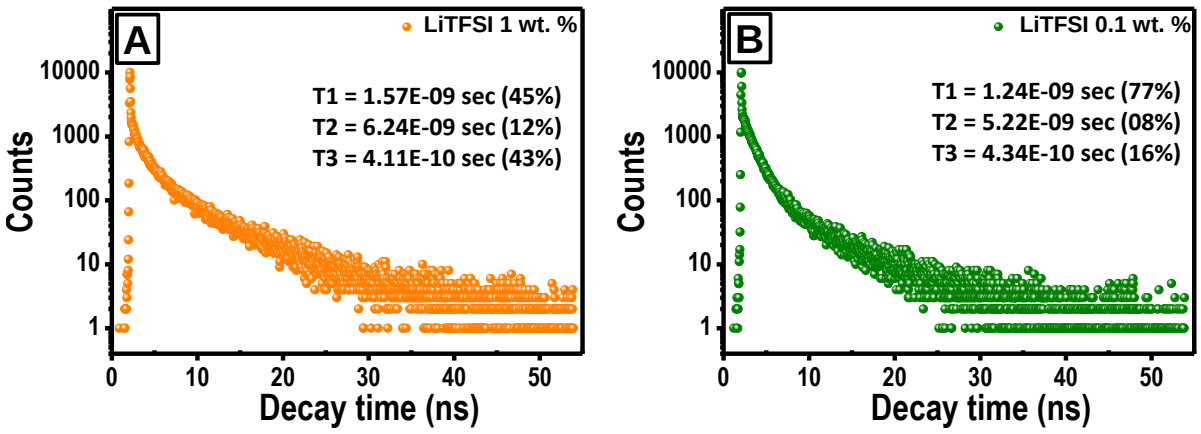

Fig. S8 Time resolved Photoluminescence of MoS_2 QDs synthesized using aq. LiTFSI electrolytes of concentration 1.0 (A) and 0.1 wt. % (B) measured at room temperature.

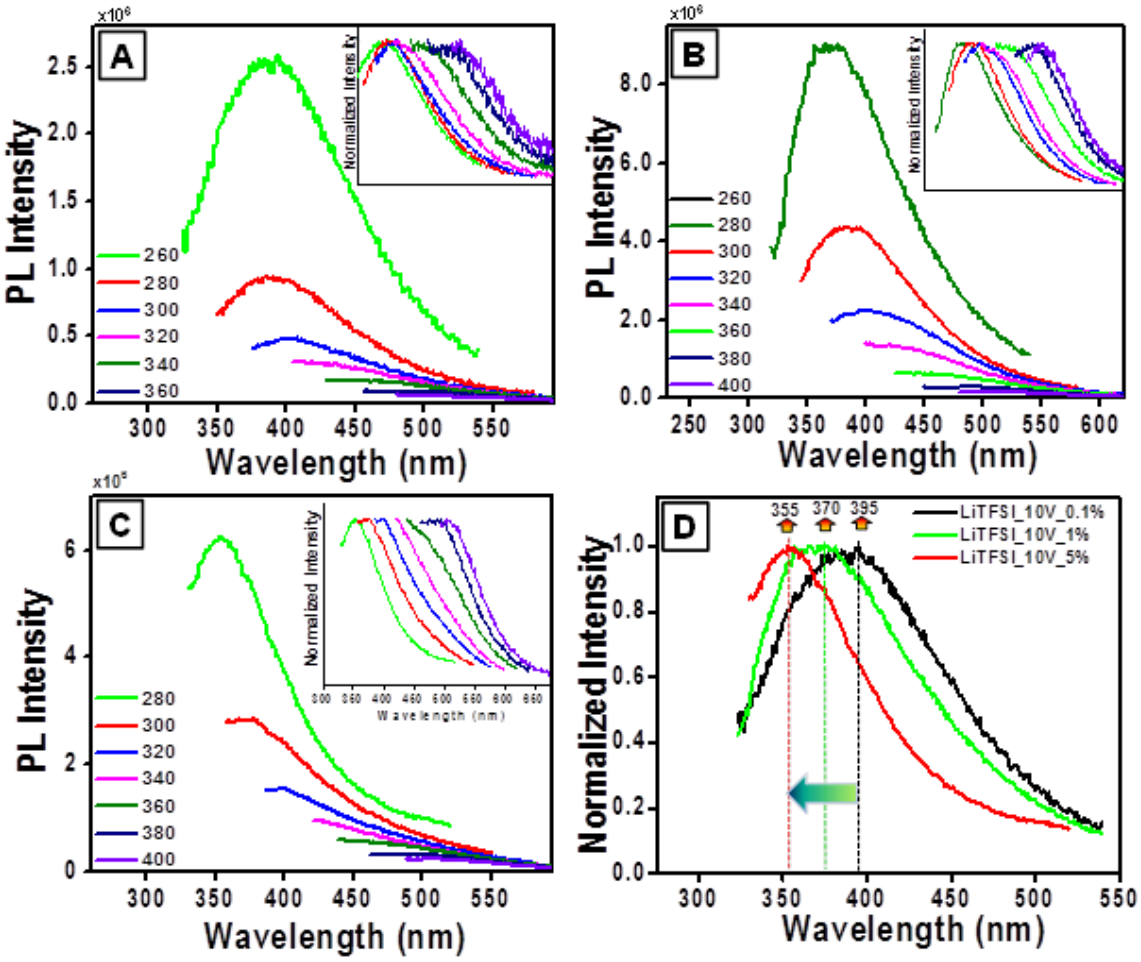

Fig. S9. Excitation dependent photoluminescence spectra of MoS_2 QDs synthesised by electrochemical exfoliation of bulk MoS_2 electrodes in aq. LiTFSI of various concentrations *viz*., 0.1, 1.0 and 5 wt% at 10V are shown in A, B and C respectively. D shows the comparison of the normalized photoluminescence spectrum of MoS_2 QDs obtained at an applied potential of 10V at various concentration *viz* 0.1, 1 and 5 wt. %.