Electronic Supplementary Material (ESI) for RSC Advances.

Monolayer MoS_2 quantum dots as catalysts for efficient hydrogen evolution

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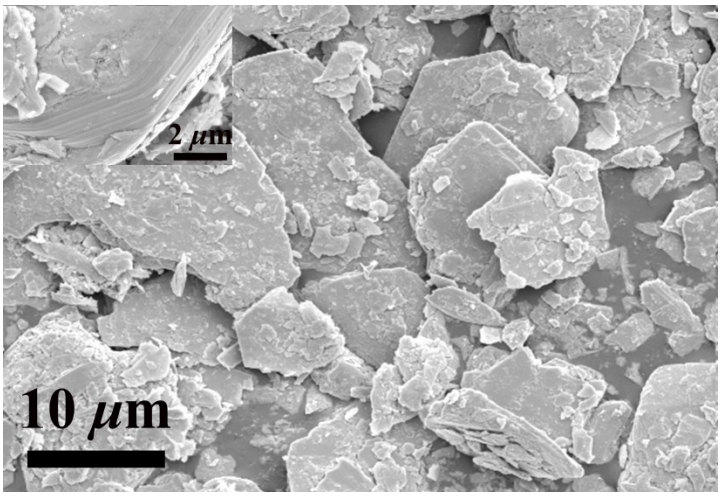

Figure S1. SEM image of bulk MoS_2.

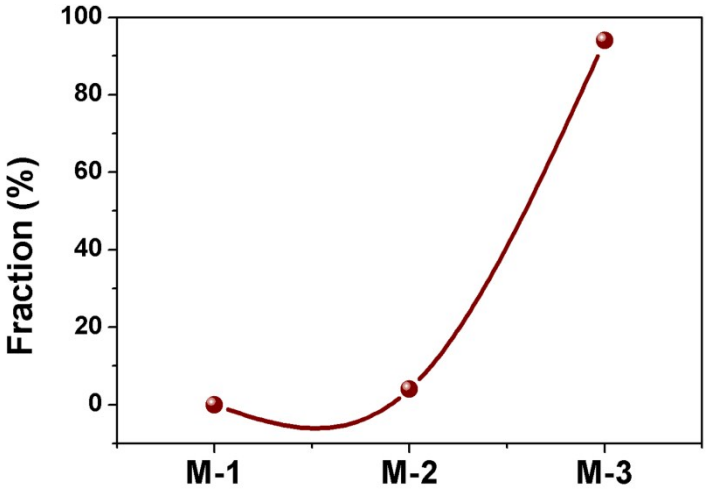

Figure S2. The content of MoS_2 nanosheets that less than 10 nm in lateral size varies with the exfoliation numbers.

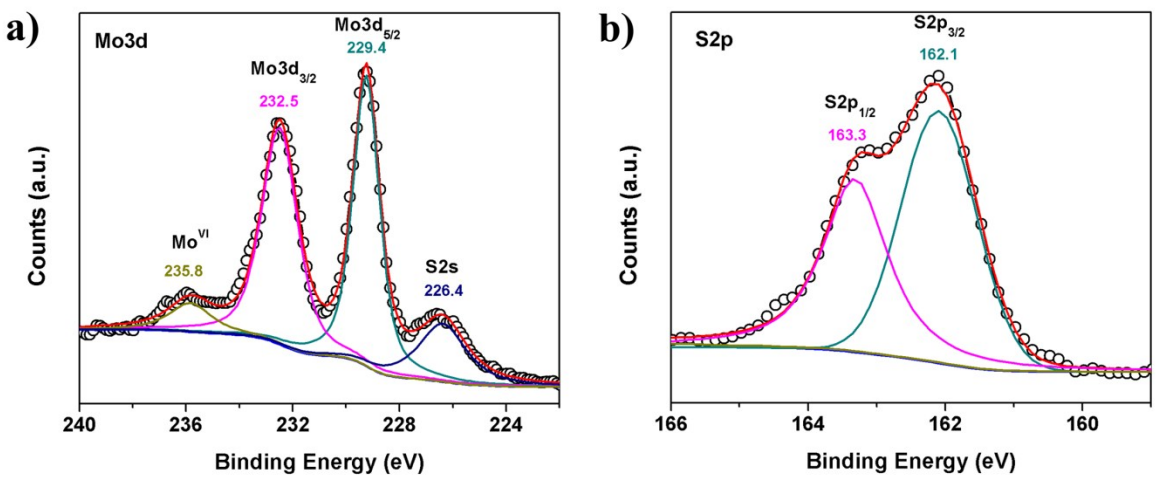

Figure S3. X-ray photoelectron spectra of the Mo 3d a) and S 2p b) regions of the MoS_2 QDs.

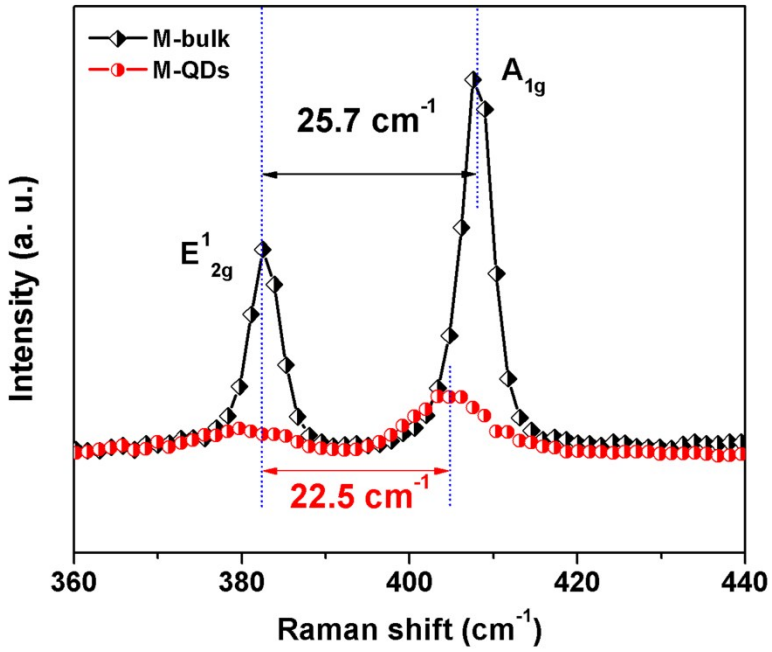

Figure S4. Raman spectra recorded using a 532 nm laser for bulk MoS_2 and MoS_2 QDs.

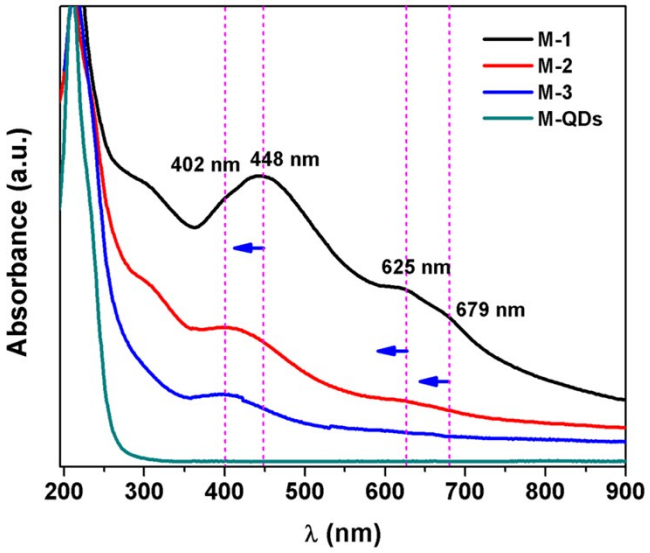

Figure S5. UV-vis spectra of M-1, M-2, M-3 MoS_2 nanosheets and MoS_2 QDs.

Calculation of Turn Over Frequency (TOF)

To calculate the per-site turn over frequency (TOF) for the MoS_2 catalysts, we use the geometry of a MoS_2 surface and the hydrogen evolution current density. The number of surface sites on the flat standard was calculated based on the geometry of MoS_2. Previous experimental measurements of MoS_2 surfaces showed that the sulfur-sulfur bond distance is 3.15 Å. Based on the hexagonal arrangement of sulfur atoms at the MoS_2 surface, this corresponds to an area of 4.296 $Å^2$/S atom, which is used to calculate the surface area occupied by each MoS_2 unit:

$$4.296\frac{Å^2}{S} * \frac{2S}{1\ MoS_2} = 8.593\frac{Å^2}{MoS_2}$$

This can be used to calculate the number of MoS_2 units (the number of surface sites for the flat standard) per cm^2 geometric area:

$$\frac{1\ MoS_2}{8.593Å^2} * \frac{10^{16}Å^2}{cm^2} = 1.164 * 10^{15}\frac{MoS_2}{cm^2}$$

The approximation is reasonable given that the MoS_2 materials have a surface site density close to 10^{15} sites/cm^2.

Turn-over frequencies are calculated from the current densities using the following relation:

$$TOF\ (s^{-1}) = (j, A/cm^2) / [(1.164 \times 10^{15}\ sites/cm^2)\ (1.602 \times 10^{-19}\ C/e^-)\ (2\ e^-/H_2)]$$

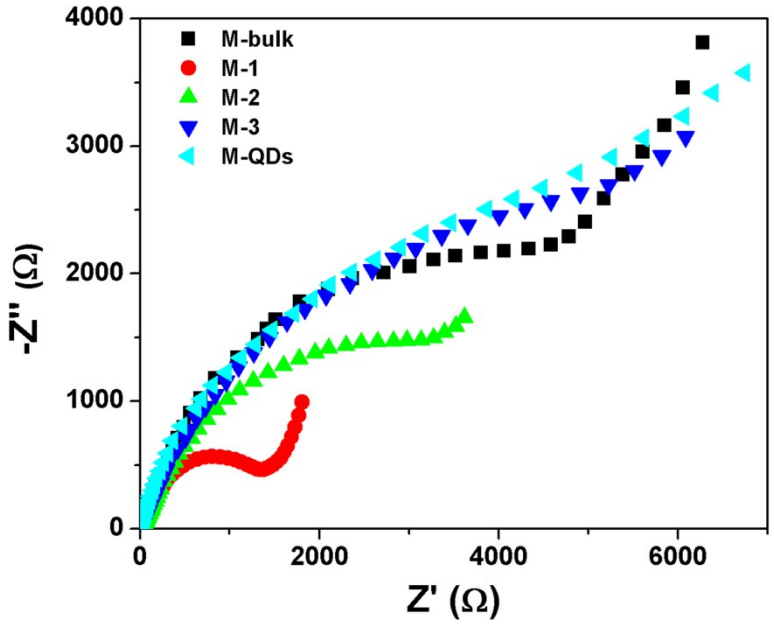

Figure S6. AC impedance spectroscopy study of various MoS_2 catalysts performed in the same configuration from 10^6-0.01 Hz with an AC voltage of 5 mV.