

## Monolayer MoS<sub>2</sub> quantum dots as catalysts for efficient hydrogen evolution

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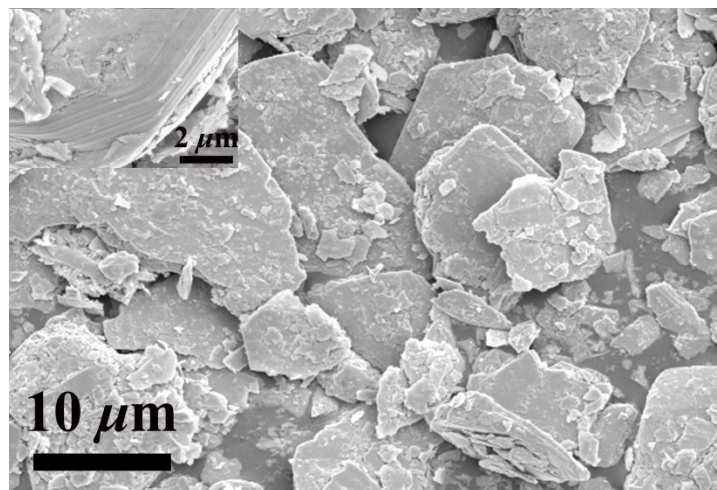


Figure S1. SEM image of bulk MoS<sub>2</sub>.

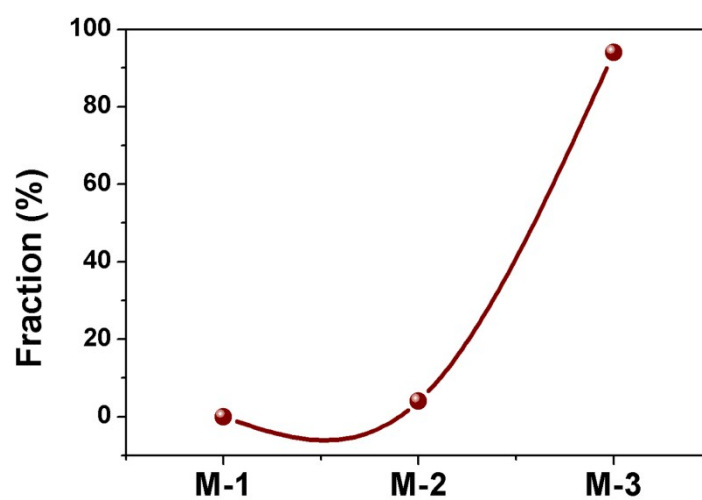


Figure S2. The content of MoS<sub>2</sub> nanosheets that less than 10 nm in lateral size varies with the exfoliation numbers.

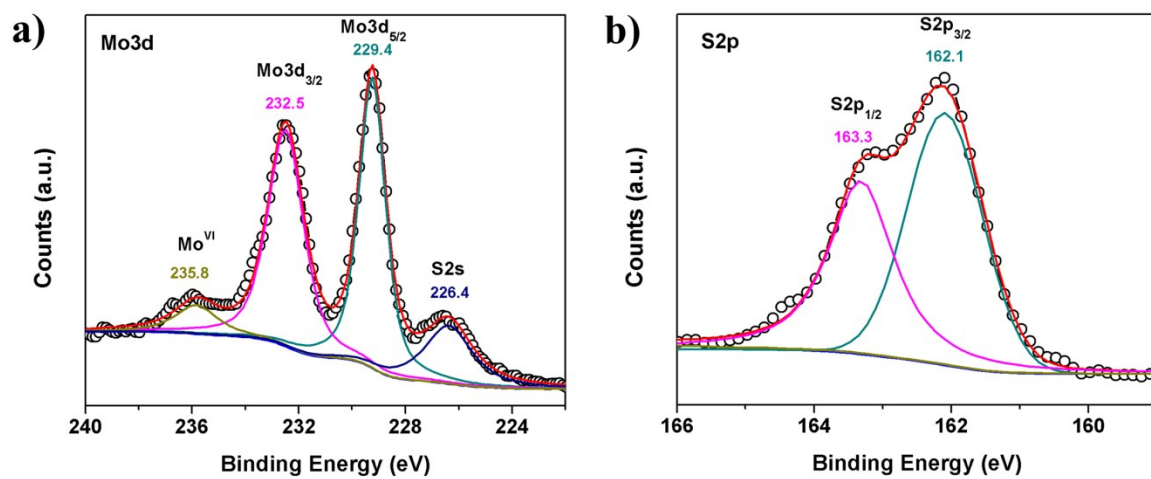


Figure S3. X-ray photoelectron spectra of the Mo 3d a) and S 2p b) regions of the MoS<sub>2</sub> QDs.

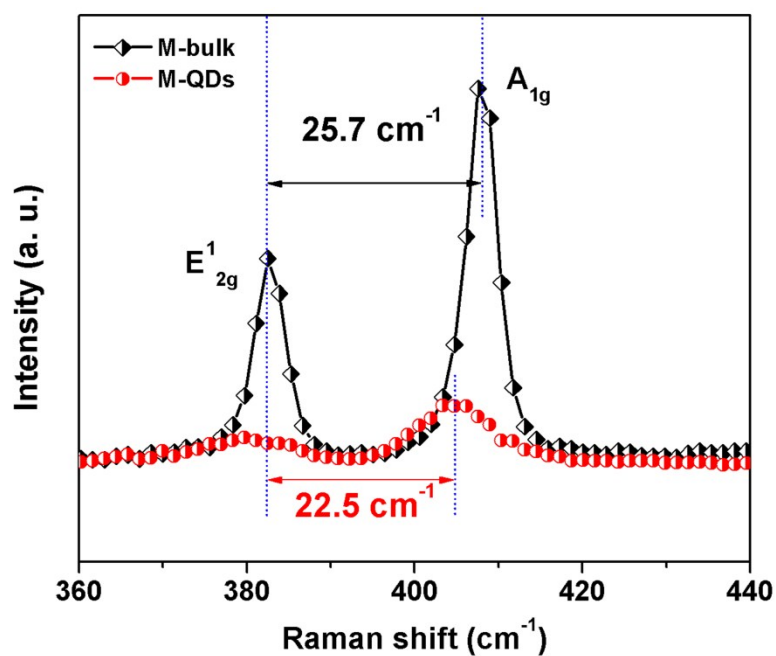


Figure S4. Raman spectra recorded using a 532 nm laser for bulk MoS<sub>2</sub> and MoS<sub>2</sub> QDs.

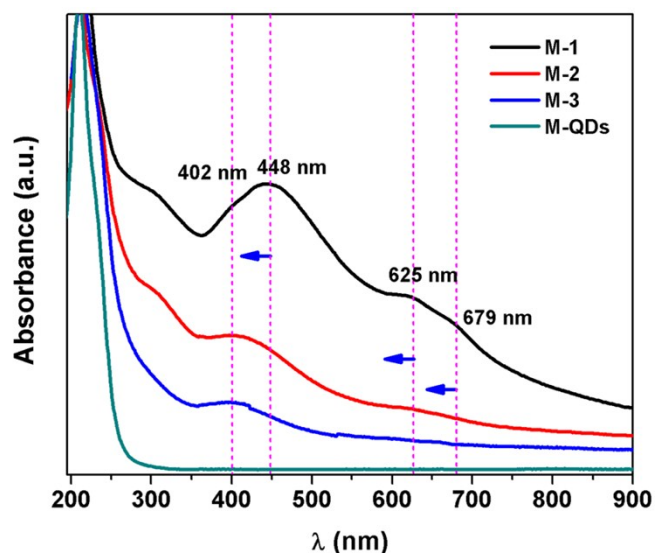


Figure S5. UV-vis spectra of M-1, M-2, M-3 MoS<sub>2</sub> nanosheets and MoS<sub>2</sub> QDs.

### Calculation of Turn Over Frequency (TOF)

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

$$4.296 \frac{\text{Å}^2}{\text{S}} * \frac{2\text{S}}{1 \text{ MoS}_2} = 8.593 \frac{\text{Å}^2}{\text{MoS}_2}$$

This can be used to calculate the number of MoS<sub>2</sub> units (the number of surface sites for the flat standard) per cm<sup>2</sup> geometric area:

$$\frac{1 \text{ MoS}_2}{8.593 \text{Å}^2} * \frac{10^{16} \text{Å}^2}{\text{cm}^2} = 1.164 * 10^{15} \frac{\text{MoS}_2}{\text{cm}^2}$$

The approximation is reasonable given that the MoS<sub>2</sub> materials have a surface site density close to 10<sup>15</sup> sites/cm<sup>2</sup>.

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

$$\text{TOF (s}^{-1}\text{)} = (j, \text{A/cm}^2) / [(1.164 \times 10^{15} \text{ sites/cm}^2) (1.602 \times 10^{-19} \text{ C/e}^-) (2 \text{ e}^-/\text{H}_2)]$$

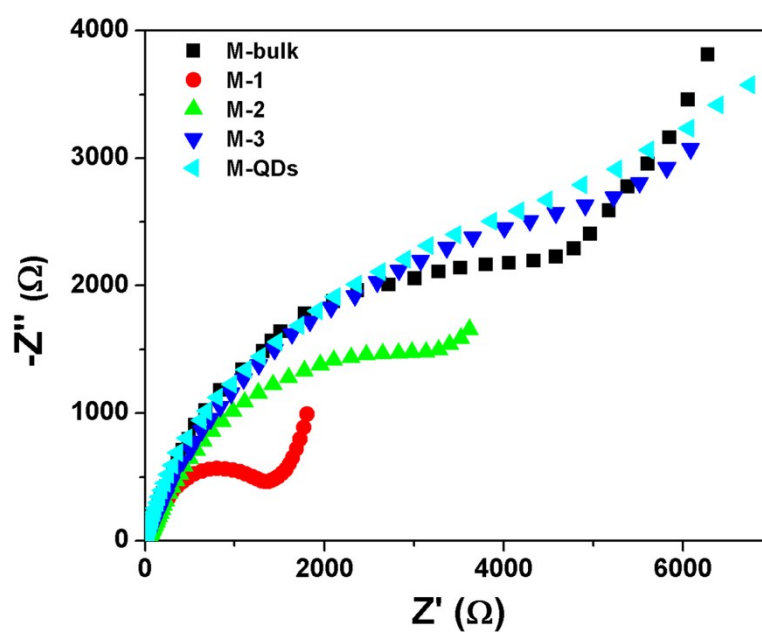


Figure S6. AC impedance spectroscopy study of various MoS<sub>2</sub> catalysts performed in the same configuration from 10<sup>6</sup>-0.01 Hz with an AC voltage of 5 mV.