Supporting Information

Selective Activation of MoS_2 Grain Boundaries for Enhanced Electrochemical Activity

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S1. Calculation of local electrochemical activity of MoS_2 by gold nanoparticles deposition coverage

The extent of localized electrochemical activity in MoS_2 can be assessed by quantifying the coverage of AuNPs (gold nanoparticles). A greater deposition indicates enhanced electron transfer to that specific site, signifying a more active area.

To compute this coverage, we utilized an Atomic Force Microscope (AFM) image of MoS_2 with deposited AuNPs. The AFM image was transformed into an 8-bit binary format and then subjected to thresholding using ImageJ software [1] (depicted in **Figure S1(b,d)**). To perform this analysis, distinct areas comprising the basal plane and the edges were meticulously separated. The coverage of nanoparticles was determined using the following relationship:

$$Nanoparticles\ coverage = \frac{Area\ of\ Au\ Nanoparticles}{Area\ of\ MoS_2}$$

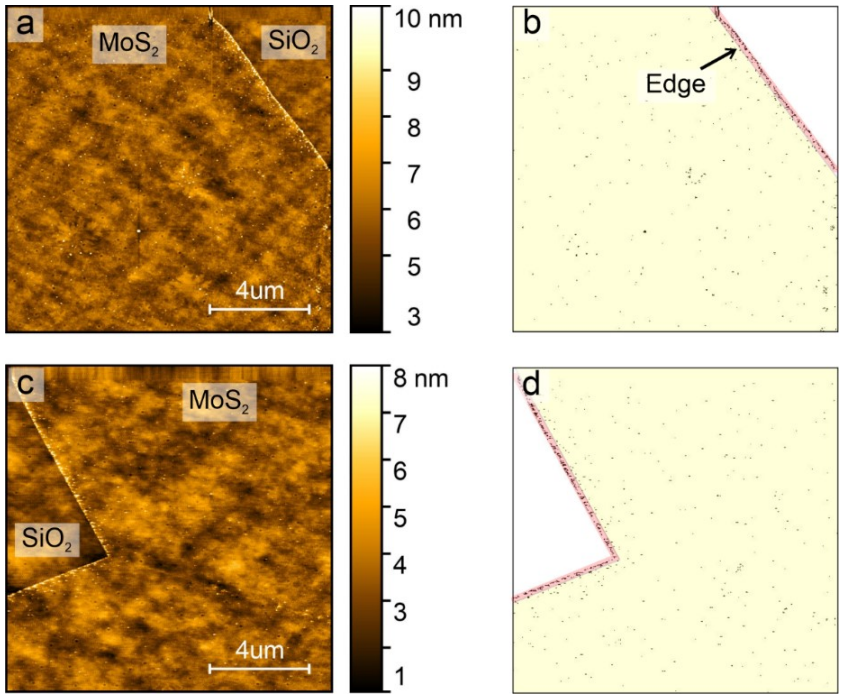

Figure S 1 Nanoparticles coverage analysis: 1(a) AFM Image of MoS_2 with Deposited AuNPs.(b) Threshold Image of the AFM Depicted in (a), After Processing Using ImageJ Software. (c) AFM Image of MoS_2 with Deposited AuNPs (d) Threshold Image of the AFM Depicted in (c)

Au Decorated MoS_2	**Au NPs % Area (Edge)**	**Au NPs %Area (Basal Plane)**	**Ratio (Edge/Basal Plane)**
(b)	17.741	0.229	77.47
(d)	16.611	0.233	71.29

S2. Numerical simulation of catalytic activity

Table 1. Comparison of Nanoparticles Coverage on MoS_2 basal plane and edge Calculated from AFM Images (S1(b) and S1(d) Using ImageJ

Numerical simulations on the total catalytic HER activity were carried out in MATlab®. For this purpose, the film was discretized into 2D elements and each area was assigned a value for electrocatalytic turn-over frequency (TOF) based on experimental results. [2] An increasing coverage from initial nucleation seeds was emulated by sequentially adding elements at the edge of MoS_2 grains. Anisotropic growth was considered by enhancing the attachment in crystallographic direction. Moreover, the initial seed orientation was set to be random, to avoid merging into single-crystalline films. Once these outgrowing edges touched, they were considered grain boundaries and both their TOF value was changed and their growth was stopped. The growth process was continued until the coverage exceeded 99%.

S3. Electrochemical characterization

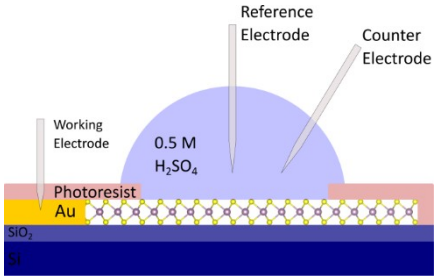

Figure S 2 Schematic of Electrochemical Measurement

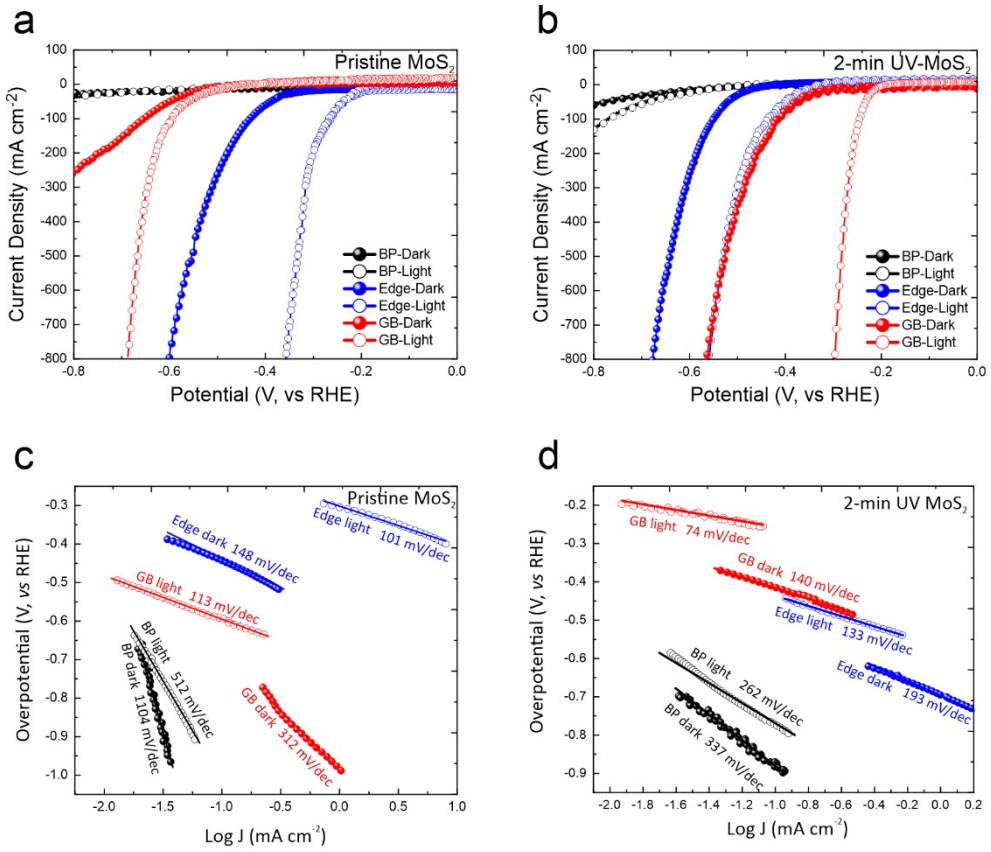

Figure S 3 ***Electrochemical Characterization of MoS_2 under Dark and Light Conditions****. (a) Polarization curve obtained for the pristine MoS_2 samples, under dark condition (filled circles) and light condition (open circles). (b) Polarization curve obtained for the 2 minutes UV-treated MoS_2 samples, under dark condition (filled circles) and light condition (open circles). (c) Tafel slopes corresponding to the measurements of pristine MoS2 samples. (d) Tafel slopes of the UV-treated MoS2 samples.*

S4. Analysis of spectroscopy following extended exposure to UV-ozone

Raman Analysis

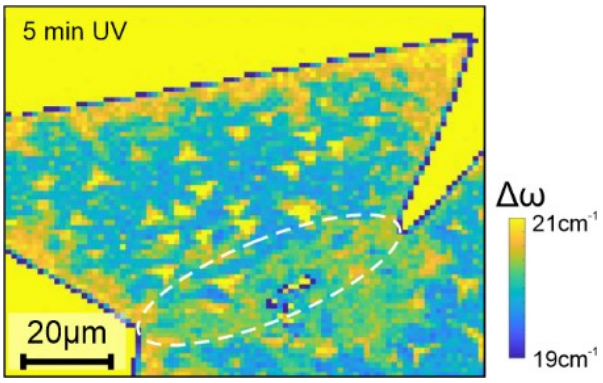

Figure S 4 Spatial distribution of Δω for 5-min UV-treated MoS_2

KPFM Analysis

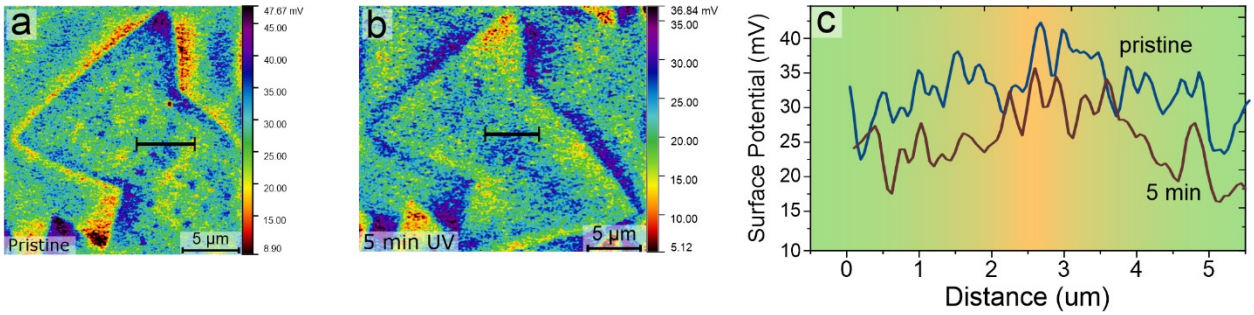

Figure S 5 KPFM surface potential map of (a) pristine (a) 5 min UV-treated MoS2 (c) corresponding cross-sectional plot for pristine and 5 min UV treated MoS_2 at GB

XPS Analysis

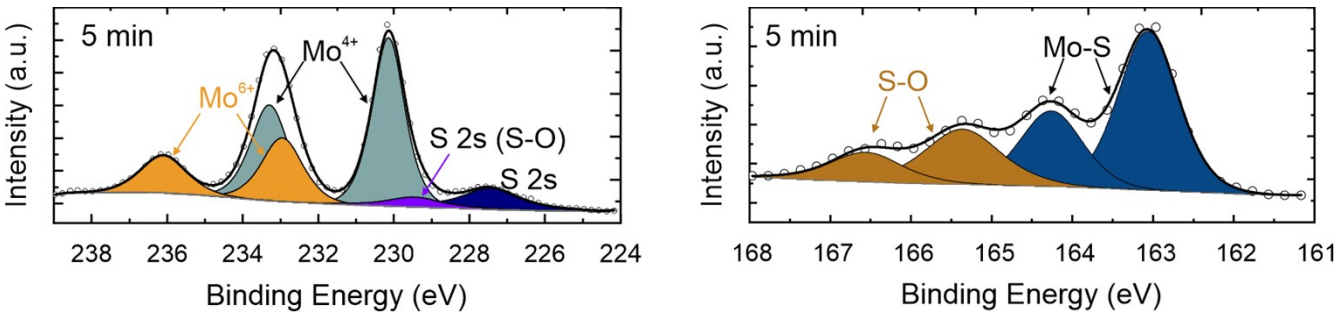

Figure S 6 XPS investigation of MoS_2 subjected to 5-min UV treatment: Mo 3d spectra illustrating increased MoO_3 concentration (f) analysis of S2p region signals

S5. Stability test of the devices and Au photodeposition after 20 cycles of LSV at GB

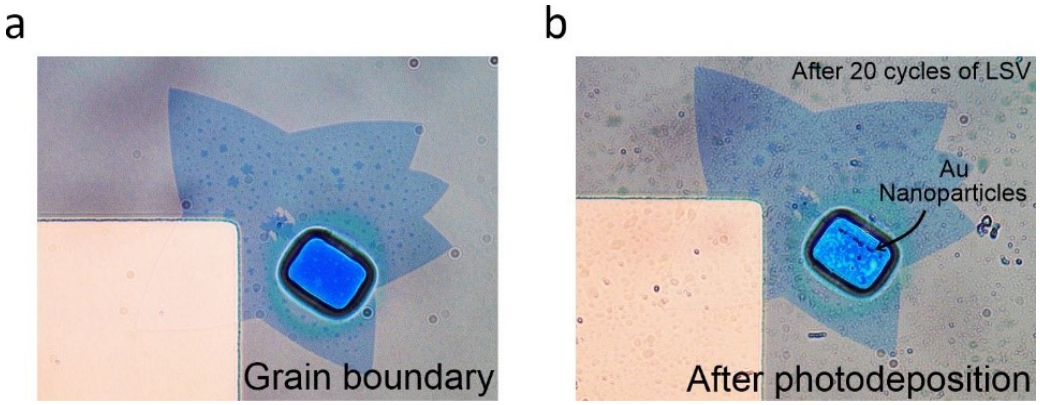

Figure S 7 Stability test of the MoS_2 flakes containing grain boundaries. (a) Micrograph of the device featuring an exposed window at the grain boundary. (b) Micrograph illustrating the selectively deposited Au nanoparticles at the grain boundary after 20 cycles of Linear Sweep Voltammetry (LSV) measurements. The Au nanoparticles were photo-deposited following 20 cycles of LSV.

S6. Gibbs free energy of hydrogen adsorption in various configuration:

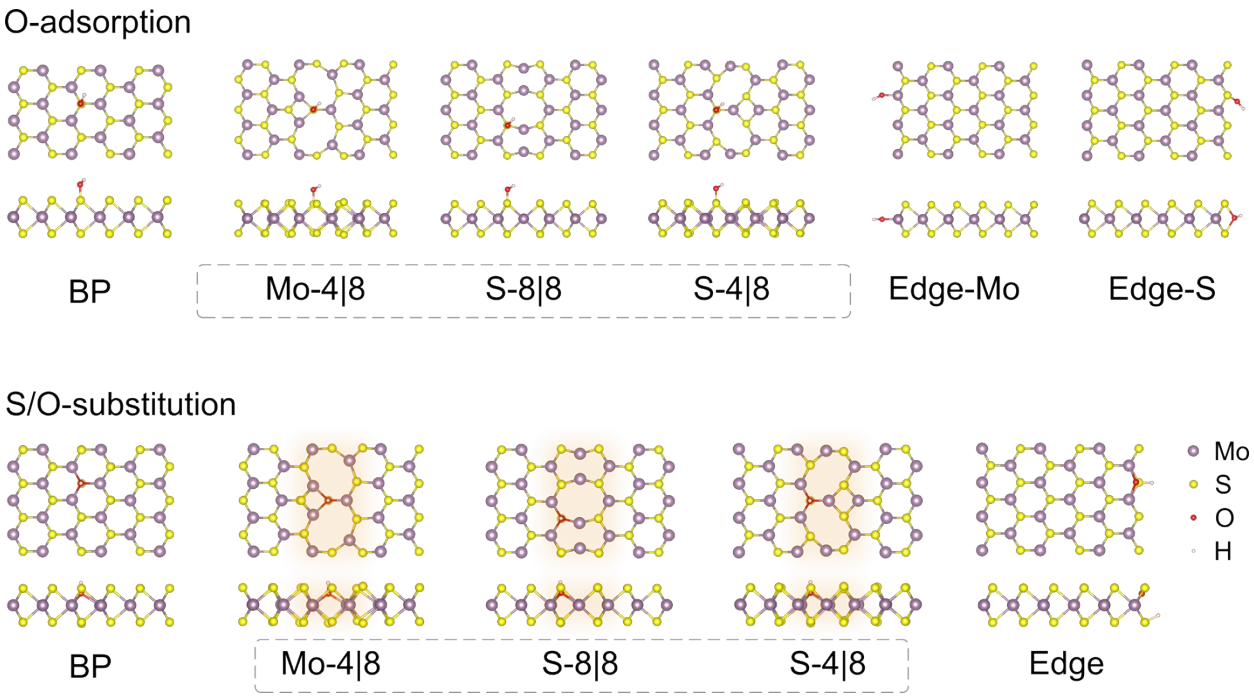

Figure S 8 Hydrogen adsorption configuration for the (a) O-adsorbed and (b) S/O substituted MoS_2 system

References

(1) Schneider, C. A.; Rasband, W. S.; Eliceiri, K. W. NIH Image to ImageJ: 25 years of image analysis. *Nature methods* **2012**, *9* (7), 671-675.

(2) Li, G.; Zhang, D.; Qiao, Q.; Yu, Y.; Peterson, D.; Zafar, A.; Kumar, R.; Curtarolo, S.; Hunte, F.; Shannon, S. All the catalytic active sites of MoS2 for hydrogen evolution. *Journal of the American Chemical Society* **2016**, *138* (51), 16632-16638.