Electronic Supplementary Material (ESI) for Nanoscale Horizons.

Supporting Information

Nanoscale Mapping of Hydrogen Evolution on Metallic and Semiconducting MoS_2 Nanosheets

Tong Sun,[1#] Hanyu Zhang,[2#] Xiang Wang,[1] Jun Liu,[2] Chuanxiao Xiao,[2] Sanjini U. Nanayakkara,[2] Jeffrey L. Blackburn,[2] Michael V. Mirkin,[1*] and Elisa M. Miller[2*]

[1]Department of Chemistry and Biochemistry, Queens College−CUNY, Flushing, NY 11367 and Graduate Center of CUNY, New York, NY 10016, United States

[2]Materials and Chemical Science and Technology Directorate, National Renewable Energy Laboratory, Golden, CO 80401, United States

[#]authors contributed equally to the work

*corresponding authors

1. Experimental Section

Synthesis and Substrate preparation

MoS_2 exfoliation. MoS_2 is synthesized using an improved procedure from our previous study.[1] 500 mg MoS_2 powder (Sigma-Aldrich) is dried at 100 °C under vacuum and mixed with 5 mL n-butyllithium (n-BuLi, 1.6 M) in hexanes in an inert atmosphere for 48 h. After washing excessive n-BuLi by dry hexanes, the intercalated MoS_2 powder is reacted with 100 mL of deionized water (18.2 MΩ) and tip sonicated by a Cole-Parmer 500 W Ultrasonic Homogenizer with a half-inch flat-head tip at ~120 W (20% of full amplitude) for 1 h in an ice bath. To remove all possible salt, the solution goes through a dialysis process against deionized water via MW 12,000 cut-off membranes for 24 h.[2] The solution is then centrifuged twice at 2000 rpm for 60 min to remove all un-exfoliated materials.

Sample preparation. To immobilize the MoS_2 nanosheets onto the indium doped sin oxide (ITO) slides for the SECM experiments, we apply a membrane filtration deposition method.[3] The exfoliated MoS_2 solution is vacuum-filtrated through a 50-nm pore size polycarbonate membrane. The MoS_2 nanosheets are collected on the membrane, while smaller flakes and solution will pass through. The larger MoS_2 nanosheets are transferred onto ITO-coated glass slides (Sigma-Aldrich, 70 – 100 Ω/square) by placing the wet membrane with the MoS_2 side facing the ITO. The membrane/MoS_2 will attach onto ITO firmly via the wet adhesion until dry. Then we dissolve the polycarbonate membrane with chloroform and the MoS_2 nanosheets will adhere to the ITO for further measurements. The MoS_2 samples for the SKPM measurements are prepared via spin-coating dialyzed MoS_2 solution on the silicon wafers at 2000 rpm. To convert 1T MoS_2 to 2H phase, we anneal the MoS_2 on ITO or Si (International Wafer System, Inc. - 0.001 – 0.006 Ω-cm) substrates at 300 °C for 60 min in an inert atmosphere.

Characterization

Materials for SECM. Ferrocenemethanol (Fc, 99%, Sigma-Aldrich) is sublimed before use. KCl (99%), $HClO_4$ (70%) and $NaClO_4$ (99%) are purchased from Sigma-Aldrich and used as received. All aqueous solutions are prepared using deionized water from the Milli-Q Advantage A10 system (Millipore) equipped with Q-Gard T2 Pak, a Quantum TEX cartridge and a VOC Pak with total organic carbon (TOC) ≤ 1 ppb.

Electrodes and Electrochemical Experiments for SECM. Polished disk nanoelectrodes are prepared by pulling 25-μm-diameter annealed Pt wires into borosilicate glass capillaries with a P-2000 laser pipette puller (Sutter Instrument Co.) and polishing under video microscopic control, as described previously.[4] The radius varies from 10 to 100 nm and RG (i.e., the ratio of the insulator radius to that of the Pt disk) varies from 6 to 15. Voltammograms are obtained with a CHI-760E electrochemical workstation (CH Instruments Inc) inside a Faraday cage. The two-electrode setup are used with a 0.25 mm diameter Ag wire coated with AgCl serving as a reference electrode. The feedback mode SECM experiments were also performed in a two-electrode configuration with an unbiased substrate, and the HER experiments are performed in a four-electrode cell using a platinum wire as a counter electrode and an Ag/AgCl reference electrode (Bioanalytical Systems). The nanoelectrodes are characterized by voltammetry and AFM imaging.

SECM Setup and Procedures. SECM experiments are carried out using a home-built instrument, which is similar to that described previously.[5] To obtain an approach curve, the tip electrode is first positioned about 100 μm above the substrate surface. To avoid tip crashing, this process is monitored with a long-distance video microscope. Then, the tip is moved closer to the substrate in the automated "surface hunter" mode until the tip current produced by oxidation of

Fc either increased (positive feedback) or decreased (negative feedback) by ~10%. The tip current is collected during the subsequent fine approach or voltammetry. The approach velocity is 20 nm s^{-1}. All experiments are carried out at room temperature inside a Faraday cage. To prevent hydrogen bubble formation either at the tip or substrate electrode, the acid concentration in HER experiments is always less than 40 mM.[6]

In the feedback mode (Figure 1A), a nm-sized SECM probe is brought within a short distance from the MoS_2 nanosheet immobilized on a flat ITO glass surface and covered with electrolyte (Figure S1). The tip is held at a potential (E_T) where Fc oxidation occurs at a rate governed by diffusion. When the tip-substrate separation distance (d) is comparable to the tip radius (a), then the oxidized ferrocene (Fc^+) produced at the tip surface gets reduced at the substrate, and the tip current (i_T) increases with decreasing d (positive feedback; the tip current near the surface is higher than its value in the bulk solution; $i_T > i_{T,\infty}$). If no Fc regeneration occurs at the substrate or the regeneration rate is slow, i_T decreases with decreasing d due to hindered Fc diffusion (negative feedback; $i_T < i_{T,\infty}$). In SG/TC mode (Figure 1B), the tip collects any redox species generated at the substrate surface (e.g., H_2 in Figure 1B). In our experiments, hydrogen is produced at catalytic MoS_2 surfaces, but not at the catalytically inert ITO. Thus, higher tip current is expected above the 1T MoS_2 surface and possibly the nanosheet 2H edges.

In the experiments represented in Figure 2 and Figure 3, the solutions contain 5 mM $HClO_4$, 1 mM Fc, and 0.1 M KCl. For Figure 2, the tip potential, $E_T = 0.45$ V vs. Ag/AgCl. The substrate is either biased at $E_S = -0.75$ V (A) and (C) or at the open circuit potential (B). Also, the tip radius, a, equals 25 nm (A) or 18 nm (B, C) and the separation distance, d, equals 100 nm (A), 20 nm (B), or 80 nm (C). For Figure 3, a equals 60 nm (A, B) or 28 nm (C, D). The substrate is either biased at $E_S = -0.75$ V (C, D) or at the open circuit potential (A,B). The substrate distance, d, equal 60 nm (A, B), 30 nm (C), or 80 nm (D). SECM mapping of HER was a SG/TC mode experiment because the tip/substrate separation distance was significantly larger than the tip radius (e.g., $d \approx 4a$ in Fig. 2C and $d \approx 3a$ in Fig. 3D). Under these conditions, the contribution of the positive feedback was small, and the measured current was mostly due to substrate generation/tip collection process.

XPS. XPS data are obtained on a Physical Electronics 5600 system using Al Kα radiation. Briefly, the XPS setup is calibrated with Au metal, which is cleaned via Ar-ion sputtering. The energy uncertainty for the core level data is +/- 0.05 eV. Thin films are made on Au substrates by depositing solution-exfoliated MoS_2. The mixed phase samples are used as is and the 2H phase is measured after annealing at 300 °C in inert atmosphere. All samples are checked for charging, and X-ray power dependence measurements verify that no samples exhibit charging.

STEM-EELS. The samples for the STEM-EELS analysis are prepared by dipping the TEM grids into the MoS_2 solution and then dried under atmospheric condition. The STEM-EELS analysis was performed on FEI Tecnai F20 equipped with Gatan Digital Microscopy at an [illegible]

SKPM Imaging. The SKPM apparatus uses a commercial AFM housed in an Ar-filled glovebox. The overall topography and SKPM potential measurements are recorded simultaneously using a single-pass with an external Kelvin Probe Control Unit (Omicron, Kelvin Probe CU) and an external high-frequency lock-in amplifier (Signal Recovery, 7280 DSP) on a Veeco Dimension 5000 AFM and Nanoscope V controller system. Topography is measured using the tapping mode at the first resonance frequency (50 – 70 kHz) of the conductive Pt/Ir coated AFM tip (Nanosensors, PPP-EFM) while an AC bias modulation of 300 − 500 kHz (2nd resonance of the AFM tip) is added to the tip to measure the electrostatic potential. The procedures for AFM/SKPM imaging are reported previously.[7] The mixed-phase MoS_2 nanosheets are solution deposited onto a highly conducting Si substrate. Once the mixed-phase sample is measured by SKPM, it is heated under nitrogen at 300 C for 30 minutes, to ensure complete conversion to the 2H-only phase, which was then subsequently re-measured by SKPM. In all instances, the SKPM measurements and the annealing step, are performed under non-ambient conditions to ensure cleanliness.

2. SI Figures

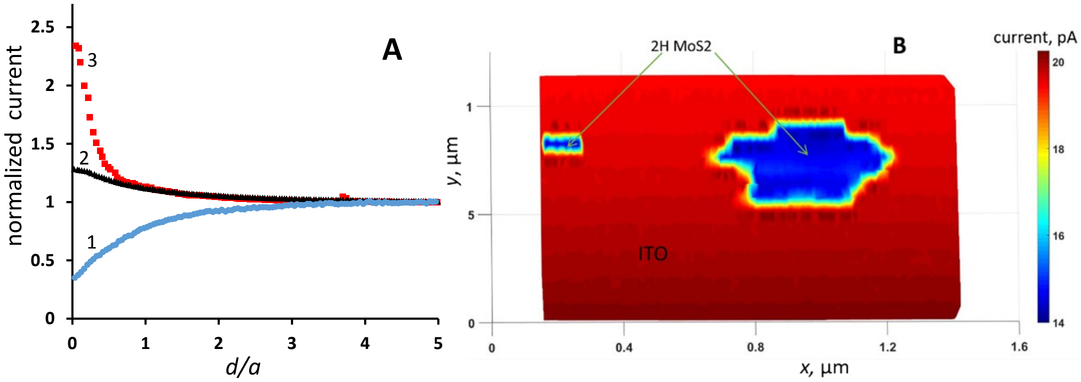

Figure S1. Feedback mode SECM responses are recorded over different phases of MoS_2 and conductive ITO substrate surface in solution containing 1 mM Fc and 0.1 M KCl. (A) SECM approach curves are obtained with a Pt tip approaching 2H MoS_2 (1), ITO (2) and 1T MoS_2 (3) surface. (B) 2D color map of a 2H MoS_2 flake lying flat on the ITO surface. The tip potential was 0.4 V vs. Ag/AgCl and the substrate was unbiased. d = 24 nm (B). a = 20 nm (A) and 58 nm (B).

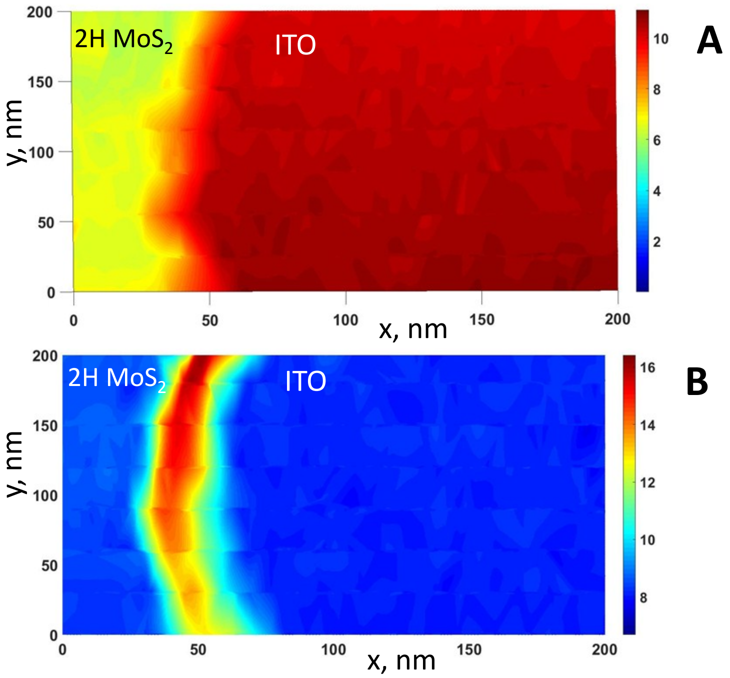

Figure S2. 2D SECM color maps of the topography and reactivity of 2H MoS$_2$ nanoflake edge on the ITO surface. (A) Feedback mode and (B) SG/TC mode images. Solution contained 5 mM HClO$_4$, 1 mM Fc, and 0.1 M KCl. E_T = 0.45 V vs. Ag/AgCl. The substrate was either biased at E_S = -0.75 V (A) or at the open circuit potential (B). *a*, nm = 25 (A,B). *d*, nm = 25(A), 80(B).

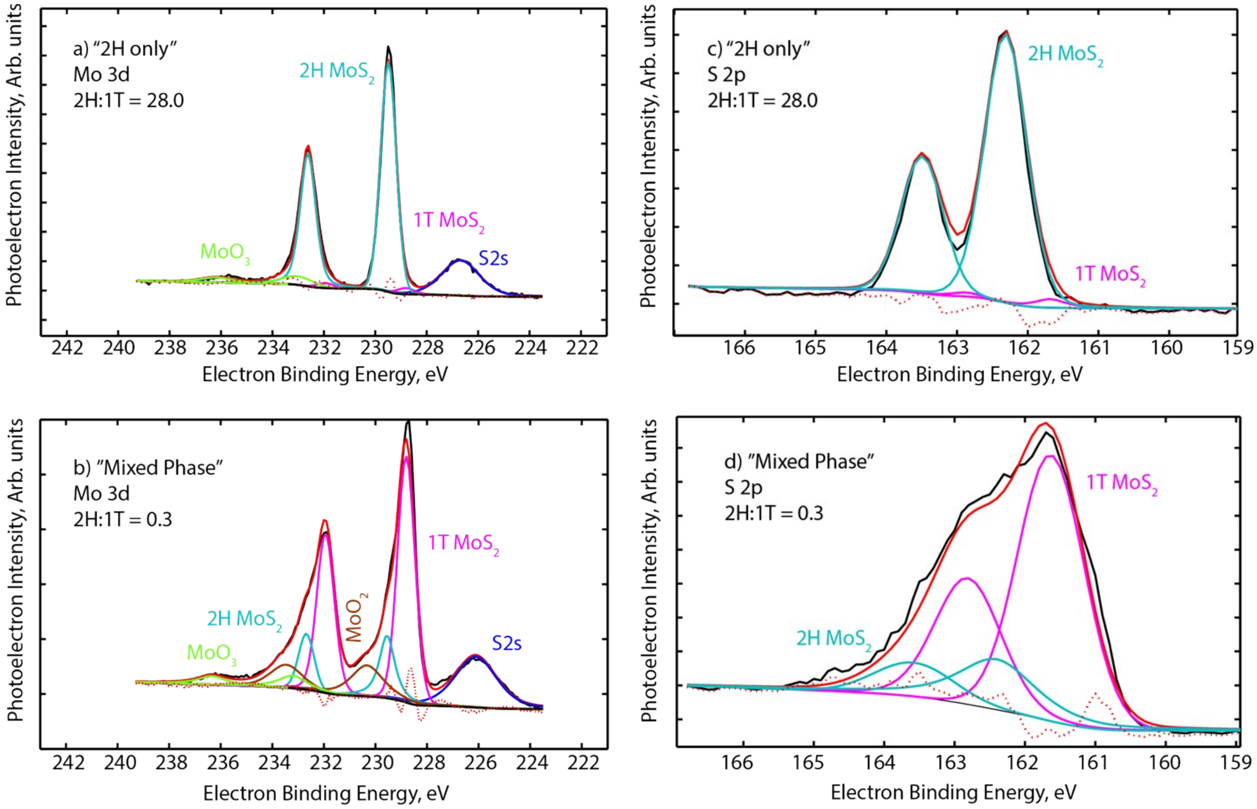

Figure S3. The Mo 3d XPS of a) 2H and b) mixed phase as well as S 2p XPS of c) 2H and d) mixed phase MoS_2 nanosheets, where the black trace is the raw data and the red trace is the fit. The deconvoluted peak fits for the various Mo environments are shown for 1T MoS_2, 2H MoS_2, MoO_2, and MoO_3. Also shown is the S 2s peak fit. To simplify the fits, we only use one peak fit for the S 2s even though it technically should have a peak for both the 1T and 2H phase. The red dotted line is the residual.

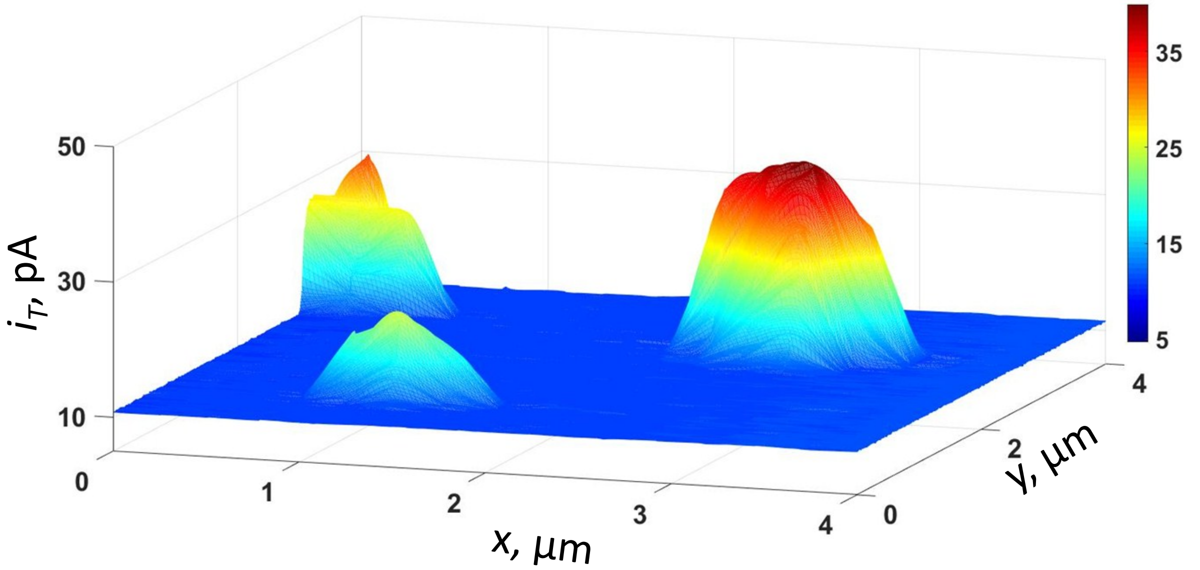

Figure S4. Low-resolution (4 x 4 µm^2) SG/TC map of the HER activity of mixed phase MoS_2 nanosheets. This image seems to show that the entire nanosheet is active toward HER, and the differences between 2H and 1T regions are washed out by diffusional broadening. *a*, nm = 35 nm, *d* = 80 nm. For other parameters, see above.

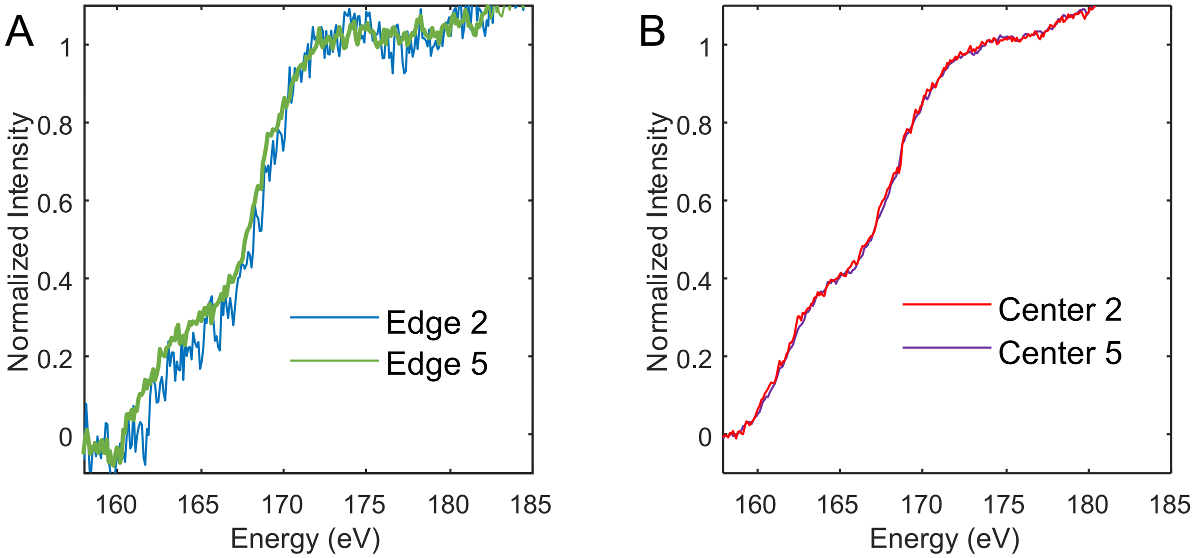

Figure S5. EELS spectra of the S-$L_{2,3}$ edge of a mixed MoS_2 nanosheet at (A) edge and (B) center for various integration times of electron exposures (2 or 5 sec/scan for 50 scans), where the scan areas are shown in Figure 4A. To clearly show the trend, the spectra have been normalized to the signal intensity averages of 170 – 180 eV. We observe that the at the edge of a mixed MoS_2 nanosheet the S-$L_{2,3}$ edge shifts to lower energy with increasing electron beam exposure time; however, the S-$L_{2,3}$ spectra at the center of the MoS_2 nanosheet remains at the same low energy (~160 eV), which is suggestive that MoS_2 mixed phase nanosheet edge is 2H and the center is 1T and is consistent with our SECM data.

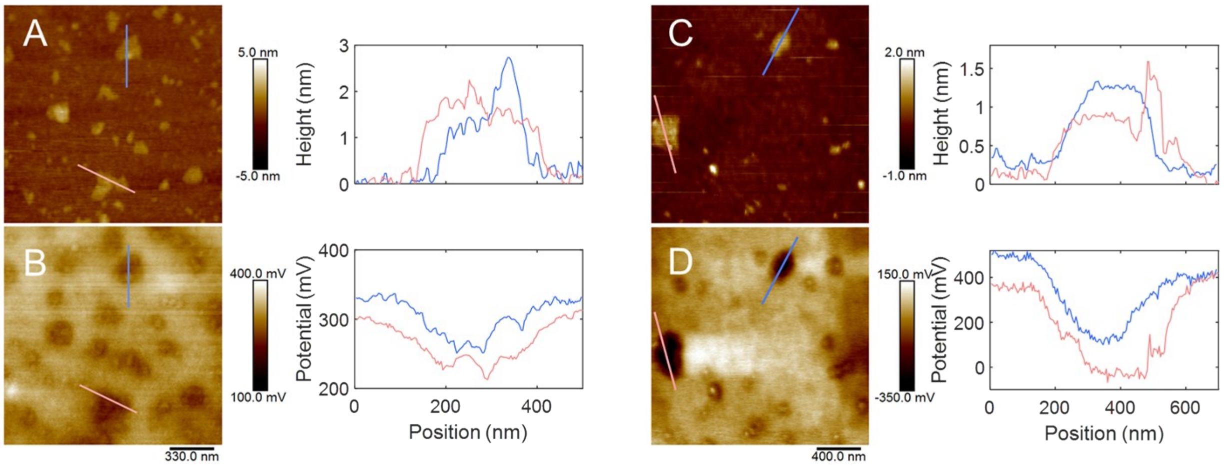

Figure S6. (A) AFM of mixed-phase MoS_2 flakes on Si substrate. The right of the panel shows the height profiles of the flakes marked in the figure. (B) The SKPM mapping of the same area as (A) and the contact potential difference profiles regarding the same flakes in (A). (C) and (D) describe the 2H MoS_2 flakes height profile and voltage mapping, respectively. The changes in the Si contact potentials between the mixed phase and 2H only sample are due to the thermal treatment of the 2H MoS_2 sample, which slightly changes the contact potential of the Si.

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