Mapping Electron Transfer at MoS₂ using Scanning Electrochemical Microscopy

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Abstract

Understanding the role of macroscopic and atomic defects in the interfacial electron transfer properties of layered transition metal dichalcogenides is important in optimizing their performance in energy conversion and electronic devices. Means of determining the heterogeneous electron transfer rate constant, k, have relied on deliberate exposure of specific electrode regions or additional surface characterization to correlate proposed active sites to voltammetric features. Few studies have investigated the electrochemical activity of surface features of layered dichalcogenides under the same experimental conditions. Herein, MoS₂ flakes with well-defined features were mapped using scanning electrochemical microscopy (SECM). At visually flat areas of MoS₂, k of hexacyanoferrate(III) ($[Fe(CN)_6]^{3-}$) and hexacyanoferrate(II) ($[Fe(CN)_6]^{4-}$) was typically smaller and spanned a larger range than that of hexaammineruthenium(III) ($[Ru(NH_3)_6]^{3+}$), congruent with current literature. However, in contrast to previous studies, reduction of $[Fe(CN)_6]^{3-}$ and oxidation of $[Fe(CN)_6]^{4-}$ exhibited similar rate constants, attributed to the dominance of charge transfer through surface states. Comparison of SECM with optical and atomic force microscopy images revealed that while most of the flake was electroactive, edge sites associated with freshly exposed areas that include both macrosteps consisting of several monolayers and recessed areas exhibited the highest reactivity, consistent with reported results.

Introduction

Effective use of layered transition metal dichalcogenides, *e.g.*, MoS₂, WSe₂, and their related heterostructures in energy storage and conversion systems and electronic devices requires understanding charge transfer at the dichalcogenide-electrolyte interface^{1–5} and how transfer rates correlate to the number of layers,^{6,7} atomic defects,^{8,9} and edge sites.^{4,10,11} Similar to sp² carbon materials, dichalcogenides contain covalently bonded atoms in monolayers held together by Van der Waals forces.^{1,2,12} The identity of the active site^{13,14} and the role of edge sites and basal planes in catalysis, where electron transfer occurs in-plane and perpendicular to each layer, respectively, have been of much interest. Similar to sp² carbons, the generally accepted view is that electron transfer is more facile at edge sites than basal planes due to higher electron density and the presence of dangling bonds at edges^{1,5,12,15–19} although non-zero rate constants have been reported at the basal plane.^{11,16,20,21}

Electrochemical methods such as cyclic voltammetry have provided valuable information about the heterogeneous electron transfer rate constant, k, of electrodes. However, in order to investigate spatial differences in the reactivity of layered dichalcogenides, special sample preparation is required to expose specific regions of the electrode,^{10,15,20,22} or an *ex situ* characterization method is needed to correlate the number of proposed active sites to the voltammetric signal.^{6,9,12} The electrode's surface may change upon release of potential control and emersion from electrolyte during such measurements, leading to ambiguous results about the true behavior of the electrode surface.

Electrochemical scanning probe methods and droplet cells have been used to overcome these challenges.²³ Although several studies have spatially probed sp² carbon using electron transfer mediators,^{16,24–26} similar investigations of MoS₂ are fewer.^{7,10,11,22} Recently, a scanning

droplet cell was used to measure *k* at various regions of MoS_2 .^{7,11,20} Scanning electrochemical microscopy (SECM)²⁷ showed that strain enhances the hydrogen evolution reaction (HER) at MoS_2^{28} and that the conductivity of MoS_2 flakes varies widely depending on the nature of the contact.²⁹ Other applications of SECM include measuring the HER kinetics and hydrogen adsorption at amorphous MoS_2 on gold³⁰ and mapping the HER at $MoS_2/graphene$ oxide composites³¹ although spatial differences in the active MoS_2 areas is unclear due to the high probe currents in the SECM images. Likewise, scanning electrochemical cell microscopy (SECCM) demonstrated that the HER at MoS_2 proceeds at the basal planes albeit at much lower rates than edge sites.²¹

Herein, to demonstrate spatial inhomogeneity in the electrochemical behavior of MoS_2 under the same experimental conditions, exfoliated MoS_2 flakes supported on an insulator, *viz.*, Si/SiO₂, were mapped with sub-micrometer resolution SECM. The electron transfer kinetics of three electron transfer mediators, hexaammineruthenium(III) chloride ([Ru(NH₃)₆]³⁺), potassium hexacyanoferrate(III) (ferricyanide, [Fe(CN)₆]³⁻), and potassium hexacyanoferrate(II) (ferrocyanide, [Fe(CN)₆]⁴⁻) were examined. Au electrical contacts served as fiducial marks for comparison of SECM, optical, atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS) images and facilitated positioning the SECM tip probe using the contrast in electrochemical reactivity between Si/SiO₂ and Au.

Experimental Section

Materials. Chemicals were used as received without purification. Sigma-Aldrich (St. Louis, MO) supplied $[Ru(NH_3)_6]^{3+}$ (98 %) and $[Fe(CN)_6]^{4-}$ (ACS Reagent, 95.0 % to 102.0 %). $[Fe(CN)_6]^{3-}$ (ACS grade) was from Mallinckrodt (Paris, KY). Supporting electrolyte was

potassium nitrate (KNO₃, 99.0 % min, Alfa Aesar, Ward Hill, MA) or sodium chloride (NaCl, ACS grade, Mallinckrodt). Electrolyte solutions were passed through filters with 0.3 μ m pore size (Advantec MFS, Pleasanton, CA). Water (18.3 $\Omega \cdot$ cm) from an EASYpure UV system (Barnstead-Thermolyne, Dubuque, IA) was used to clean glassware and prepare solutions. Commercial materials and equipment are identified to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology nor does it imply necessarily that the product is the best available for its purpose.

Au contact fabrication. Au contacts were made to exfoliated MoS₂ flakes using a typical lift-off procedure. Blue cleanroom tape of medium tack was used to cleave flakes from a MoS₂ crystal (Lot 1211005, Structure Probe, West Chester, PA) which were gently pressed onto (1 to 2) cm × (1 to 2) cm pieces of Si(100) wafer (n-doped, 0.05 Ω /cm² to 0.5 Ω /cm², WRS Materials, San Jose, CA) with 300 nm of thermally grown (1150 °C) SiO₂, measured with an ellipsometer (Model M-2000, J. A. Woollam). Wafer pieces were first cleaned in a Model 1020 oxygen plasma cleaner (Fischione Instruments, Export, PA) for 6 min or Piranha solution (4 mL of 18 mol/L H₂SO₄ + 1 mL of 9.8 mol/L (30 % (w/w) H₂O₂) for 1 h and rinsed with H₂O. Caution: Piranha solutions can be explosive if they contact organic materials.

MoS₂ on Si/SiO₂, *i.e.*, the substrate, was rinsed with isopropanol, dried with N₂, and then dried for 5 min on a hotplate at 115 °C before spin coating with LOR 5A resist (MicroChem, Newton, MA) at 370 rad/s (3500 rpm) for 45 s and then baking at 175 °C for 5 min. To avoid silylation of the MoS₂, LOR 5A was used in place of hexamethyldisilazane (HMDS) primer for adhering photoresist to the wafer pieces. AZ5214E image-reversal photoresist (Clarient, Somerville, NJ) was spin coated at 310 rad/s (3000 rpm) for 45 s before prebaking for 1 min at

115 °C. After aligning the chrome photomask (Photo Sciences, Torrance, CA) with the flake in a SussMA6 contact aligner (Suss MicroTech, Garching, Germany), the photoresist was exposed using a dose of 150 mJ/cm² at 405 nm. Postbake was performed for 2 min at 115 °C before a flood exposure with a dose of 200 mJ/cm² at 405 nm. Samples were immersed in AZ300 MIF developer (Clarient, Somerville, NJ) for 2 min and then in H₂O for 1 min before rinsing with H₂O and drying with N₂. Then, 10 nm of Ti and 100 nm of Au were deposited using a Denton Vacuum (Moorestown, NJ) Infinity 22 electron beam evaporator. To remove the photoresist, samples were immersed in Remover 1165 (Rohm and Haas Electronics Materials, Marlborough, MA) for 30 min at 60 °C followed by a second remover bath at 30 min at 60 °C or overnight at room temperature. Finally, samples were rinsed with isopropanol and dried with N₂. Resistance between the two contact pads was determined from the slope of voltage *vs*. current measured using the potentiostat.

Electrochemical measurements. All electrochemical measurements were performed with a CH Instruments (Austin, TX) Model 920D SECM on a marble table inside an aluminum Faraday cage with solid sides to minimize any photochemistry induced from the room lights. At least three separate flakes were used for each measurement. Intervals represent the 95 % confidence level.³² A PTFE electrochemical cell with a volume of 2 mL was used with a Pt or Au wire auxiliary electrode and an Ag|AgCl|1 mol/L KCl (+0.22 V vs. SHE)³³ reference electrode in a salt bridge containing 30 g/L agar (ash 2.5 % to 4.5 %, Sigma-Aldrich) + 0.2 mol/L KNO₃. For mounting the sample in the cell, Cu tape with In contacts to the Au were covered with electroplater's tape (3M, St. Paul, MN) with a hole of area \approx 1 mm × \approx 1 mm to expose the flake to electrolyte. Electrochemical impedance measurements were done in 0.1 mol/L KNO₃ on a cleaved crystal piece contacted to Cu tape with a mass fraction of 75/25 Ga/In eutectic on the back. Electroplater's tape was used to cover the electrode contacts and to expose a crystal area of $\approx 1 \text{ mm} \times \approx 1 \text{ mm}$ to solution.

SECM tip probe fabrication. Pt SECM tips with radius, *a*, of 5 µm were from CH Instruments and polished with 1.0 µm and then 0.3 µm alumina before use. To make submicrometer-sized tips (Figure S1), borosilicate glass capillary tubes (1.0 mm OD, 0.3 mm ID, 7.5 cm long, Sutter Instrument, Novato, CA) and Pt wire ($\phi = 25$ µm tempered wire (99.99 %, Goodfellow, Oakdale, PA) were cleaned by soaking overnight in isopropanol, drying at 120 °C for at least 90 min, and then cooling to room temperature immediately before sealing. A 1.5 cm length of Pt wire was inserted into the tube and then sealed using a three-step pulling procedure^{34,35} (Table S1) in a Model P-2000 pipette puller (Sutter). A 400-14 Two Stage Rotary Vane Vacuum Pump (Vacuum Research, Pittsburgh, PA) was used to evacuate the capillary tubing to <8.0 Pa (60 mtorr) by connecting the ends of the capillary tube and the pump with PTFE tubing.

A Helios NanoLab 660 Dual Beam Scanning Electron Microscope (SEM) and Focused Ion Beam (FIB) (FEI, Hillsboro, OR) system was used to polish the tips³⁴ after final sealing in a MFG-5AP Microforge-Grinding Center (MicroData Instrument, Plainfield, NJ) and coating with 10 nm of Pt using an EM ACE600 Sputter Coater (Leica Microsystems, Buffalo Grove, IL). The ion beam (30 keV, 790 pA) was scanned perpendicular to the end of the tip using a cleaning cross section pattern with 1 ms dwell time. After polishing, back contact was made with Cu wire and a mass fraction of 75/25 Ga/In eutectic. Immediately before use, tips were immersed for 30 s in Piranha solution and then rinsed with H₂O.

Equipment. Optical images were recorded using an Epiphot 300 Metallurgy Inverted Microscope (Nikon, Tokyo, Japan) with a Model OCS-5.0 OptixCam Summit Series CMOS

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Camera (Microscope Store, Roanoke, VA) and then processed using ImageJ (1.49).³⁶ AFM images were obtained using an Asylum Research (Santa Barbara, CA) Cypher instrument in tapping mode with model AC160T-R3 micro-cantilevers (frequency, 300 Hz; force constant, 26 N/m; radius, 7 nm) from Olympus (Center Valley, PA). Processing with Gwyddion (2.49) software³⁷ included performing a plane fit, fixing the minimum height value to zero, and constraining the height scale bar. Raman spectra were obtained using a LabRAM HR800 (Horiba Scientific) microscope and 50X long working distance objective with an excitation wavelength of 532 nm, laser power of 34 mW, and an average of 10 spectra integrated for 2 s.

Following SECM and AFM measurements, XPS was performed using a Kratos AXIS Ultra DLD with a monochromatic Al K α source. The spectrometer was calibrated to Au 4f_{7/2} 84.0 eV, Ag 3d_{5/2} 368.2 eV, and Ag MNN 1128.9 eV signals, and all spectra were collected at a 90° take-off angle. Spectra were fit using Casa XPS software (2.3.15) with the peaks modeled using a Voigt function (70 % Gaussian-30 % Lorentizian) and a Shirley background correction.

Results and Discussion

Characterization of substrate. Lateral dimensions of the flakes (Figure 1) were typically between 30 μ m and 100 μ m with thickness between 80 nm and 250 nm (>100 monolayers).¹²



Figure 1. (a) Optical image of MoS_2 with Au contacts. (b) Raman spectra of MoS_2 flake and bulk crystal.

Resistance between the two Au contacts among the samples varied between 1 k Ω and 30 k Ω . In Raman spectra of the flakes (Figure 1b), E_{2g}^1 and A_{1g} peaks at 380 cm⁻¹ and 404 cm⁻¹, respectively, were similar to the bulk crystal and literature values.³⁸ Electrochemical impedance data of the bulk crystal were plotted (Figure 2) according to the Mott-Schottky equation at 25 °C:

$$\frac{1}{C^2} = \frac{1.41 \, x \, 10^{20}}{\varepsilon N_D} \left[E - E_{FB} - 0.0257 \right] \tag{1}$$

where $C (\mu \text{F/cm}^2)$ is series capacitance, ε is dielectric constant, $N_D (\text{cm}^{-3})$ is dopant concentration, E (V) is applied potential, and $E_{\text{FB}} (\text{V})$ is flatband potential.³⁹ Values of C were calculated from the measured impedance, $Z_{\text{im}} (\Omega)$, at varying frequency, f (Hz):



Figure 2. Mott-Schottky plot of MoS₂ in 0.1 mol/L KNO₃ at varying frequency. Potential step, 0.05 V; amplitude, 0.005 V.

 $Z_{\rm im} = \frac{1}{2\pi fC} \tag{2}$

The slope of C^{-2} vs. E provides $N_{\rm D}$, and $E_{\rm FB}$ is derived from where the line crosses the potential axis, *i.e.*, the y-intercept, using $E_{\rm FB} = E + 0.0257$. Using $\varepsilon =$ 4.304,⁴⁰ the MoS₂ crystal was *n*-doped with a moderate carrier concentration³⁹ of (4.1 ± 1.0) x 10¹⁶ cm⁻³, about half the reported value for synthetic *n*-type MoS₂ in 0.5 M KNO₃.⁴¹ The $E_{\rm FB}$, \approx +0.1 V, was similar to that of synthetic MoS₂.⁴¹

Characterization of SECM tips. Cyclic voltammetry (Figures S1b, S2a, and S3a) was used to determine the radius, *a*, of the Pt electrode using the equation $i_{T,inf} = 4nFaDC$, where $i_{T,inf}$ is tip current under semi-infinite conditions, *n* is number of electrons, *F* is Faraday's constant (96,485 C/mol e⁻), *D* is the diffusion coefficient, and *C* is the concentration of the mediator.³⁹ Reported values of *D*, 7.2 x 10⁻⁶ cm²/s,^{42,43} 7.2 x 10⁻⁶ cm²/s,^{42,43} 7.6 x 10⁻⁶ cm²/s,³⁹ and 6.5 x 10^{-6} cm²/s,³⁹ for [Ru(NH₃)₆]²⁺, [Ru(NH₃)₆]³⁺, [Fe(CN)₆]³⁻, and [Fe(CN)₆]⁴⁻, respectively, were used. SECM tips were characterized by fitting experimental approach curves, *i.e.*, plot of tip current, i_T , *vs.* tip-substrate separation, *d*, at Si/SiO₂ in *ca.* 4 mmol/L [Ru(NH₃)₆]³⁺ + 0.1 mol/L KNO₃ to theory⁴⁴ to determine the shortest distance between the tip and substrate, d_0 , and the ratio, *RG*, of the radius of the glass sheath to the Pt disk (Figures S2b, S2c, S3b, and S3c). Error in *d* was less than ±1 µm. For SECM mapping, the substrate was first leveled by monitoring i_T of the *a* = 5 µm tip as it was scanned laterally so that the variation in height was less than 1 µm over 1 mm length of the substrate.

Characterization of substrate electron transfer kinetics. Although the exposed Au contact dominates the voltammetry of the composite MoS₂/Au working electrode, electron transfer at MoS₂ could be probed directly using the SECM tip, as shown in Figure 3 for sample MoS₂ 1 listed in Table 1. The tip was poised at a potential, E_T , to collect any species generated at the substrate as the substrate potential, E_S , was changed to modulate its electrochemical reactivity. This configuration is similar to the substrate generation-tip collection (SG-TC) mode of SECM that also involves feedback between the tip and substrate, ^{27,45} as suggested in the inset of Figure 3. The formal potential, E^0 , estimated as $E_{1/2}$ of the substrate, was -0.17 V and + 0.23 V for $[Ru(NH_3)_6]^{3+/2+}$ and $[Fe(CN)_6]^{3-/4-}$, respectively. As expected, i_T increased with increasing substrate overpotential, *i.e.*, the difference between E^0 and E_S .

The electron transfer kinetics of the substrate can be inferred from $i_{\rm T}$,^{27,44} where an increase in $i_{\rm T}$ is due to increasing *k* at the substrate electrode as well as positive feedback between the tip and substrate. Although many studies use the feedback mode to determine *k*, SECM approach curves were shown to be similar for both feedback and SG-TC involving feedback if the ratio of diffusion coefficients of the reduced and oxidized species is near unity.⁴⁵ Table 1 lists the normalized tip current, $I = i_{\rm T}/i_{\rm T,inf}$, at $d = 6 \,\mu$ m for each mediator at separate,



Figure 3. SECM measurements of MoS₂ flake with Au contacts using tip ($a = 5 \mu$ m) as a collector electrode in (blue) 3.6 mmol/L [Ru(NH₃)₆]³⁺, (black) 2.9 mmol/L [Fe(CN)₆]³⁻, and (red) 2.9 mmol/L [Fe(CN)₆]⁴⁻. Supporting electrolyte, 0.1 mol/L KNO₃. $E_T = +0.10$ V, +0.40 V, and -0.10 V for [Ru(NH₃)₆]³⁺, [Fe(CN)₆]³⁻, and [Fe(CN)₆]⁴⁻, respectively. d = 6 μ m; sweep rate, 10 mV/s. Inset is diagram showing collection for [Fe(CN)₆]³⁻. $i_{T,inf} = 4.8$ nA, 3.9 nA, and 3.7 nA for [Ru(NH₃)₆]³⁺, [Fe(CN)₆]³⁻, and [Fe(CN)₆]⁴⁻, respectively.

visually flat locations on three different MoS₂ flakes and the Au contacts of sample MoS₂1 as well as average values for each flake and all flakes. For MoS₂, the number in parentheses is the range of values. Values of $i_{\rm T}$ were obtained from the steady-state tip current, *i.e.*, where $i_{\rm T}$ is independent of $E_{\rm S}$ (Figures 3 and S4). The slope in the rising tip current as well as the steady-state tip current at Au were higher than those at MoS_2 (Figure 3) due to faster electron transfer that gives rise to greater positive feedback at Au. At Au, the lower I of $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ compared to that of $[Ru(NH_3)_6]^{3+}$ is likely due to the greater sensitivity of $[Fe(CN)_6]^{3-/4-}$ to surface contamination of

Au^{46,47} (*vide infra*). At MoS₂, *I* was typically 0.8 to 1.0 for $[Ru(NH_3)_6]^{3+}$ and 0.5 to 0.9 for $[Fe(CN)_6]^{3-}$, and $[Fe(CN)_6]^{4-}$. Thus, $[Ru(NH_3)_6]^{3+}$ typically exhibited faster kinetics while a wider variation in *k* across samples and within the same sample were observed for $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$, similar to trends observed at defective basal planes on bulk MoS₂ in the literature.^{7,10,11} These observations are attributed to outer- versus inner-sphere interactions of $[Ru(NH_3)_6]^{3+/2+}$ and $[Fe(CN)_6]^{3-/4-}$, respectively, at the substrate^{11,15,39,48} as well as the electronic

Sample	Location	I, [Ru(NH3)6] ³⁺	<i>I</i> , [Fe(CN) ₆] ^{3–}	<i>I</i> , [Fe(CN)6] ^{4–}	
MoS ₂ 1	а	0.92	0.62 0.70		
MoS ₂ 1	b	0.90	0.72	0.68	
MoS ₂ 1	с	0.90	0.77	0.59	
Average of 1		0.90 (0.02)	0.70 (0.15) 0.66 (0.11)		
MoS ₂ 2	a	1.06	0.49 0.46		
$MoS_2 2$	b	0.81	0.59	0.54	
$MoS_2 2$	с	0.77	0.59 0.57		
Average of 2		0.88 (0.29)	0.56 (0.10)	0.52 (0.11)	
$MoS_2 3$	a	1.04	1.05 1.15		
$MoS_2 3$	b	Not measured	0.74 0.66		
$MoS_2 3$	с	Not measured	0.73	0.73 0.68	
$MoS_2 3$	d	1.00	0.89 0.89		
Average of 3		1.02 (0.04)	0.85 (0.33)	0.84 (0.48)	
Average of all		0.92 (0.29)	0.72 (0.56)	0.69 (0.69)	
Au		1.74 ± 0.08	0.87 ± 0.06	0.88 ± 0.01	

Table 1. Normalized tip current, $I = i_T/i_{T,inf}$, for hexaammineruthenium(III) ([Ru(NH₃)₆]³⁺), hexacyanoferrate(III) ([Fe(CN)₆]³⁻), and hexacyanoferrate(II) ([Fe(CN)₆]⁴⁻) at separate locations on three MoS₂ samples and the Au contacts of MoS₂ 1. Number in parentheses for MoS₂ is the range of values. The intervals at Au are reported at the 95 % confidence level.

structure of *n*-MoS₂.^{11,17,49} For $[Ru(NH_3)_6]^{3+/2+}$, $E^{0'}$ is negative of the flat band potential, leading to metallic behavior in contrast to the more positive $E^{0'}$ of $[Fe(CN)_6]^{3-/4-}$, which may decrease the number of available carriers. Accordingly, oxidation of $[Fe(CN)_6]^{4-}$ is expected to be slower than reduction of $[Fe(CN)_6]^{3-}$ based on available states^{17,49} although *I* was not noticeably

different for $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$. However, because $a = 5 \ \mu m$ and the conduction band of MoS₂ is near $E^{0'}$ of $[Fe(CN)_6]^{3-/4-}$, ⁴⁹ i_T likely represents the average reactivity of multiple regions containing local differences in doping concentration⁵⁰ and surface states that may obscure such nuances.

SECM mapping of MoS_2 . The magnitude of i_T was measured as a function of lateral tip position using the SECM tip as a generator (Figure 4a) or collector (Figures 4b and 4c) electrode (Figure 4d) in the electrolyte with $[Ru(NH_3)_6]^{3+}$. When using tips with radii less than 1 μ m, relatively large tip heights, e.g., d was 4.5 times the size of a in Figure 4, were used to avoid damaging the substrate or the delicate end of the SECM tip. SECM and optical images from additional MoS₂ samples are given in Figures S5, S6, and S7. In addition, Figure S8 shows Figures 4a and 4b plotted using a diverging color scheme. Larger $i_{\rm T}$ values correspond to higher reactivity. Only effects from electronic structure or surface contamination that could change the electron tunneling length should be observed in the case of an outer-sphere mediator, *e.g.*, [Ru(NH₃)₆]³⁺.^{15,39,48} Before the SECM images in Figure 4, MoS₂ was mechanically cleaved in the electrolyte and then stored in water overnight (Figure S9). Spatial differences in reactivity were more apparent with the smaller tip (Figure S10), demonstrating the necessity of matching probe size with substrate features. Geometric features in optical (Figures 4e, S5e, and S6f) and AFM (Figures 4f and S11) images corresponded well to variations in i_T . Most of the MoS₂ was electroactive, similar to previous results, 11,16,21 indicated by increasing i_T with increasing substrate overpotential (Figures 4b and 4c, Figures S5c and S5d, Figure S6c, S6d, and S6e). Due to decreased overlap between the tip and MoS_2 at the flake perimeter, i_T was lower in these areas. At macrosteps consisting of several monolayers (region A, Figure 4), i_T was larger, suggesting that electron transfer was more facile at these edges, similar to SECM of graphene^{16,24} as well as

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Figure 4. SECM images of MoS₂ using the tip ($a = 0.22 \,\mu$ m) as (a) generator and (b,c) collector electrode in 4.4 mmol/L [Ru(NH₃)₆]³⁺ + 0.1 mol/L KNO₃. Current scale bar for (b) and (c) is the same. $E_{\rm T} = (a) -0.45 \,\text{V}$, (b,c) +0.10 V. $E_{\rm S} = (a) +0.10 \,\text{V}$, (b) -0.25 V, (c) -0.35 V. Scan rate, 2.5 μ m/s; step size, 0.5 μ m; $d = 1 \,\mu$ m. (d) Diagram showing feedback between tip and substrate, where Ru(III) and Ru(II) represent [Ru(NH₃)₆]³⁺ and [Ru(NH₃)₆]²⁺, respectively. (e) Optical and (f) AFM images (scan rate, 1 Hz) after electrochemical measurements. Height difference between Au and MoS₂ is 80 nm.

scanning photoluminescence⁵¹ and STM¹⁸ of MoS₂. The lowest reactivity was observed on basal plane areas (region E, Figure 4), particularly those that may not have been disturbed during specimen cleavage (Figure S9). Changes in topography may affect i_T , *e.g.*, a taller feature would increase i_T due to a smaller tip-substrate distance⁵² (region B, Figures 4 and S11d). However, a 2 µm-wide, 1 µm-deep trench (region C, Figures 4 and S11b) was more active than the surrounding region, reflecting a high density of edge sites in the sidewalls. Observed reactivity at the nominally flat region D in Figures 4 and S11b corresponded to an unambiguously freshly cleaved basal surface (Figure S9) although the effect of defects^{8,9,20} smaller than the resolution of the current system must be considered. For comparison, SECM images with [Fe(CN)₆]³⁻ (Figure

S12) were obtained for the same substrate overpotentials, *i.e.*, 80 mV and 180 mV, as with $[Ru(NH_3)_6]^{3+}$ (Figure 3b, 3c). Like $[Ru(NH_3)_6]^{3+}$, most of the MoS₂ was electroactive, and reactivity across the surface became more homogeneous with larger substrate overpotentials.

XPS characterization of substrate after SECM and AFM measurements. The distribution of Au, Mo, S, C, and O on the sample presented in Figures 4, S9, S11, and S12 was mapped using the spherical mirror analyzer for parallel XPS imaging and analysis (Figures 5 and S13). The time delay between SECM and AFM measurements was ≈ 60 days while the specimen was transferred to the XPS immediately after the AFM study. The Au contacts on the SiO₂ surface were clearly revealed in Figure S13a, and the gap between the contacts was filled in the Mo 3d and S 2p maps although the intensity of the latter is much weaker due to the photoelectron sensitivity factors, 0.668 for S 2p versus 3.321 for Mo 3d. The Au contacts were evident in several of the elemental maps due to contribution of strong inelastic scattering from Au 4f and Si 2p and Si 2s. Nevertheless, a color scaled overlay of the respective spectral maps clearly revealed MoS_2 between the Au contact pads in Figure S14. The O 1s map (Figures 5a and S13e) showed negligible oxygen on MoS₂ while the Au contact was extensively covered by oxygencontaining species, making them indistinguishable from the surrounding SiO_2 . Brief Ar^+ sputtering removed this adventitious layer from Au (Figures 5b and S13f). Despite the surface contamination, $[Ru(NH_3)_6]^{3+/2+}$ at Au was still electrochemically reversible (Figure 3). In



Figure 5. O 1s map of the sample in Figure 4 (a) before and (b) after sputtering with 500 eV Ar^+ for 8 minutes. (c) Corresponding optical image.

contrast to oxygen, some carbon was evident on the MoS₂ before sputtering. Comparison of MoS₂ before and after cleavage (Figure S9) along with the XPS oxygen and carbon maps (Figure S15) indicated that the freshly exposed surface regions were the most active, namely region D, the recessed trench C, and the macrostep edge A. As evident from Figure S9, the cleanliness of certain areas of the MoS₂ relative to Au may be ascribed to the creation of a fresh MoS₂ surface caused by tip collision with the MoS₂ that resulted in formation of the recessed trench and substantial delamination of the surrounding MoS₂ surface. The state of the most active sections of the MoS₂ surface in Figure 4 is thus analogous to a freshly cleaved surface like that studied by Dryfe and others¹¹ while the Au electrode contact remained covered by an adventitious layer related to extended exposure to laboratory ambient conditions and possibly lithographic processing.^{11,53}

Conclusions

Although our current measurement system is unable to resolve atomic scale features, SECM mapping of MoS₂ flakes with sub-micrometer resolution using electron transfer mediators demonstrated that electrochemical reactivity was highest at visible physical defects and freshly cleaved surfaces, congruent with reported voltammetric measurements. Attention to surface topology is important when interpreting SECM images of MoS₂. Combination of scanning probe functionalities such as AFM-SECM with advances in fabrication of layered materials and related heterostructures with specified defects, *e.g.*, step edges and atomic vacancies, will provide an excellent platform to unravel the connection between charge transfer kinetics and surface structure.

Acknowledgments

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Supporting Information

Sealing parameters for SECM tips. SEM image and cyclic voltammetry of SECM tip. Cyclic voltammetry and approach curves for SECM tips. SECM images of additional MoS₂ flakes in $[Ru(NH_3)_6]^{3+}$. Comparison of SECM images using rainbow and diverging color maps. Optical image of cleaved MoS₂ flake. SECM images with different tip sizes. AFM images of MoS₂ with line profiles. SECM images with $[Fe(CN)_6]^{3-}$. XPS images of substrate. Overlaid, colored XPS images of substrate. Comparison of optical and XPS images of MoS₂. This material is available free of charge via the Internet at http://pubs.acs.org.

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TOC Graphic



Supporting Information

Mapping Electron Transfer at MoS₂ using Scanning Electrochemical Microscopy

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Table

Step	Heat	Filament	Velocity	Delay	Pull	
1. Narrow	700	4	30	220	0	
2. Seal	500	4	30	220	0	
3. Pull	700	4	30	130	150	

Table S1. Parameters for sealing Pt wire in borosilicate glass capillary tubing.

Figures



Figure S1. (a) Scanning electron microscope (SEM) image of SECM tip probe after polishing with focused ion beam (FIB). (b) Cyclic voltammetry of tip in 4.1 mmol/L [Ru(NH₃)₆]³⁺ + 0.1 mol/L KNO₃. $a = 0.07 \,\mu\text{m}$; sweep rate, 50 mV/s.



Figure S2. (a) Cyclic voltammogram, (b) approach curve at Si/SiO₂ adjacent to the MoS₂ on the substrate, and (c) normalized approach curve for (b) compared with theory at an insulator¹ for $a = 0.22 \,\mu\text{m}$ Pt SECM tip in 4.4 mmol/L [Ru(NH₃)₆]³⁺ + 0.1 mol/L KNO₃. $i_{T,inf} = 0.27 \,\text{nA}$; RG = 7; $d_0 = 0.75 \,\mu\text{m}$; step size, 0.033 μm ; step rate, 0.5 $\mu\text{m/s}$.



Figure S3. (a) Cyclic voltammogram, (b) approach curve at Si/SiO₂, and (c) normalized approach curve for (b) compared with theory at an insulator¹ for $a = 4.8 \,\mu\text{m}$ Pt SECM tip in 3.6 mmol/L [Ru(NH₃)₆]³⁺ + 0.1 mol/L KNO₃. $i_{T,inf} = 4.8 \,\text{nA}$; RG = 8; $d_0 = 1.0 \,\mu\text{m}$; step size, 0.067 μ m; step rate, 2 μ m/s.



Figure S4. Tip current for forward sweep of substrate potential at separate locations on (a) MoS₂ 1, (b) MoS₂ 2, and (c) MoS₂ 3 in Table 1. For (a) and (b), 3.6 mmol/L [Ru(NH₃)₆]³⁺, 2.9 mmol/L [Fe(CN)₆]³⁻, and 2.9 mmol/L [Fe(CN)₆]⁴⁻ were used, and $i_{T,inf} = 4.8$ nA, 3.9 nA, and 3.7 nA for [Ru(NH₃)₆]³⁺, [Fe(CN)₆]³⁻, and [Fe(CN)₆]⁴⁻, respectively. For (c), 17 mmol/L

 $[\text{Ru}(\text{NH}_3)_6]^{3+}$, 6.5 mmol/L $[\text{Fe}(\text{CN})_6]^{3-}$, and 4.9 mmol/L $[\text{Fe}(\text{CN})_6]^{4-}$ were used, and $i_{\text{T,inf}} = 23$ nA, 9.5 nA, and 6.2 nA for $[\text{Ru}(\text{NH}_3)_6]^{3+}$, $[\text{Fe}(\text{CN})_6]^{3-}$, and $[\text{Fe}(\text{CN})_6]^{4-}$, respectively. Supporting electrolyte, 0.1 mol/L KNO₃. $E_{\text{T}} = +0.10$ V, +0.40 V, and -0.10 V for $[\text{Ru}(\text{NH}_3)_6]^{3+}$, $[\text{Fe}(\text{CN})_6]^{3-}$, and $[\text{Fe}(\text{CN})_6]^{4-}$, respectively. $a = 5 \ \mu\text{m}$; $d = 6 \ \mu\text{m}$; sweep rate, 10 mV/s.



Figure S5. SECM images of MoS_2 using the tip ($a = 5 \mu m$) as (a,b) generator and (c,d) collector electrode in 3.9 mmol/L [Ru(NH₃)₆]³⁺ + 0.1 mol/L KNO₃. $E_T = (a,b) -0.45$ V, (c,d) +0.10 V. $E_S = (a)$ open circuit, (b) 0.00 V, (c) -0.25 V, (d) -0.35 V. Scan rate, 50 µm/s; step size, 5 µm; d = 7 µm. (e) Optical image of MoS₂.



Figure S6. SECM images of MoS₂ using the tip ($a = 5 \mu m$) as (a,b) generator and (c,d,e) collector electrode in 4.1 mmol/L [Ru(NH₃)₆]³⁺ + 0.1 mol/L KNO₃. $E_T = (a,b) -0.45$ V, (c,d,e) +0.10 V. $E_S = (a)$ open circuit, (b) +0.10 V, (c) -0.20 V, (d) -0.25 V, (e) -0.35 V. Scan rate, 50 µm/s; step size, 5 µm; $d = 7 \mu m$. (f) Optical image of MoS₂.



Figure S7. (a) SECM images of MoS₂ using the tip ($a = 0.7 \,\mu\text{m}$) as a collector electrode in 4.1 mmol/L [Ru(NH₃)₆]³⁺ + 0.1 mol/L KNO₃. $E_{\rm T} = +0.1$ V; $E_{\rm S} = -0.45$ V; scan rate, 100 μ m/s; step size, 2 μ m; $d = 1 \,\mu$ m. (b) Optical image of MoS₂.



Figure S8. Comparison of SECM images plotted using matplotlib² with the (a,b) Jet (*i.e.*, rainbow) and (c,d) Coolwarm (*i.e.*, diverging) color maps of MoS₂ in 4.4 mmol/L $[Ru(NH_3)_6]^{3+} + 0.1 \text{ mol/L KNO}_3$. $E_T = (a,c) + 0.1 \text{ V}$ and (b,d) -0.25 V. Experimental details are given in Figure 4 of the main text.



Figure S9. Optical images of MoS_2 flake (a) before and (b) after mechanically cleaving using the SECM tip.



Figure S10. Comparison of MoS₂ SECM images using the tip as a collector in 4.4 mmol/L $[\text{Ru}(\text{NH}_3)_6]^{3+} + 0.1 \text{ mol/L KNO}_3$ with $a = (a) 0.22 \text{ }\mu\text{m}$, (b) 5 μm . $E_T = +0.10 \text{ V}$; $E_S = -0.25 \text{ V}$; scan rate, (a) 2.5 $\mu\text{m/s}$, (b) 10 $\mu\text{m/s}$; step size, (a) 0.5 μm , (b) 2 μm ; $d = (a) 1 \mu\text{m}$, (b) 7 μm .



Figure S11. (a,c) AFM images of MoS_2 flake with (b,d) corresponding line profiles. Experimental details are given in Figure 4 of the main text. Note that the y-axis is different in (b) and (d). Scan rate, 1 Hz.



Figure S12. SECM images of MoS₂ flake (optical image in Figures 4e and S9b) in 3.5 mmol/L [Fe(CN)₆]^{3–} + 0.1 mol/L NaCl with a = (a,b,c) 5 µm and (d) 0.22 µm Pt tip as collector electrode. d = (a,b,c) 7 µm and (d) 1 µm; $E_T = +0.40$ V; $E_S = (a) +0.15$ V, (b) +0.10 V, (c) +0.05 V, and (d) 0.00 V; scan rate, 10 µm/s; step size, 2 µm.



Figure S13. XPS maps of the specimen following the AFM experiments shown in Figure 4 and S11. (a) Au 4f, (b) Mo 3d, (c) S 2p, (d) C 1s, (e) O 1s, and (f) O 1s after Ar^+ sputtering with 500 eV Ar^+ for 8 minutes.



Figure S14. Colorized overlaid maps of (a) Au 4f, Mo 3d, O 1s, (b) Au 4f, Mo 3d, S 2p, and (c) C 1s and O1s collected after the AFM experiments shown in Figure 4 and S11.



Figure S15. Comparison of (a) optical, (b) colorized O 1s (green) and C 1s (red) XPS maps, and (c) O 1s XPS map of MoS₂ flake.

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