Electrochemical Detection of Isolated Nanoscale Defects in 2D Transition Metal Dichalcogenides

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ABSTRACT: We show that nanometer and sub-nanometer scale defects in two-dimensional transition metal dichalcogenides can be detected electrochemically using scanning electrochemical cell microscopy (SECCM). We detect isolated anomalous electrochemical responses for the hexaaamineruthenium ([Ru(NH₃)₆]³⁺/²⁺) redox couple on mono-, bi-, and trilayer regions of mechanically exfoliated MoS₂. These anomalous sample points display faster electrochemical kinetics, with a diffusion-limited current plateau, compared to the surrounding sample points. The analysis of the electrochemical current suggests that the defects are equivalent to disk-shaped defects with radii of tens of nanometers, or to one-dimensional defects with nanometer to sub-nanometer widths. These results demonstrate that we can effectively isolate and electrochemically amplify the response from individual defects on a sample surface using SECCM, revealing features below the optical diffraction limit that would normally require high-resolution electron microscopy or scanning tunneling microscopy to detect.

INTRODUCTION

Electrochemically active surfaces, including two-dimensional (2D) transition metal dichalcogenides (TMDCs) that we consider here, present a variety of nanoscale morphological features such as vacancies, adatoms, grain boundaries, and impurities. The presence of such morphological features strongly influences the physicochemical properties of the surface and subsequently the electrochemical response. Characterization of the electrochemical response of defects can therefore be helpful to understand electrochemical performance. The collective average responses originating from these features are usually detected via photoemission spectroscopy, Raman spectroscopy, or photoluminescence. However, mapping of individual defects on a surface at the nanoscale requires high-resolution transmission electron microscopy (TEM) or scanning tunneling microscopy (STM).

Electrochemical scanning probe microscopy techniques typically demand complementary microscopy maps such as atomic force microscopy, electron microscopy, or optical microscopy to correlate the morphological features on surfaces with the electrochemical response. This approach was applied to 2D materials in our previous work and other studies of 2D materials. It is somewhat limiting to correlate electrochemical response with complementary microscopy maps as it restricts the assignments to features that only require relatively large spatial resolution to be identified. Atomic-size features still require the use of techniques such as TEM or STM that are challenging to interface with electrochemical methods. However, electrochemistry is unique in that mass transport effects can amplify the size of the spatial region that is affected by a point-like change in the electrode surface. In classical electrochemical methods, this had been demonstrated, e.g., by Amatore et al., when discussing the effect of pin-hole defects on the waveform at SAM-modified electrodes, it is clear that, in electrochemistry, the interplay between the timescale used for potential steps and the size of a diffusion front can be leveraged to increase the characteristic length scale of the observed effects. The recent development of the scanning electrochemical cell microscopy (SECCM) technique offers a unique tool for the study of mass transport-controlled electrochemical processes that allow an analysis of the effect of individual defects, as shown by excellent studies on pinholes in passivating layers or defects in graphene on copper.

In this work, we explore how to detect the presence of individual defects with enhanced electrochemical kinetics in 2D materials using an SECCM approach. We show that it is possible to identify defects with enhanced electrochemical kinetics with a characteristic size ranging from a few angstroms to a few nanometers scale in MoS₂. These defects are too small to be easily mapped via optical or even atomic force microscopy and would normally require TEM or STM approaches for their identification. To the best of our knowledge, we show for the first time the electrochemical detection of isolated nanoscale defects using SECCM.
knowledge, our work is the first to report mapping of defects with enhanced kinetics with high spatial resolution coupled to analysis/modeling of their size and shape based on diffusion-limited currents. Our approach is complementary but highly novel with respect to prior reports by other groups such as Unwin and co-workers,13,24 and Payne and Mauzeroll.20 The small contact area (approx. 1 \( \mu \text{m}^2 \)) offered by SECCM combined with mass transport effects can amplify the characteristic length scale of these defects in the current response. This means that SECCM is thus uniquely sensitive to the presence of otherwise hidden sub-nanometer defects with enhanced kinetics at the material’s surface and reveals nanometer scale defects in 2D TMDCs that otherwise would remain hidden.

## EXPERIMENTAL SECTION

MoS\(_2\), MoSe\(_2\), and WSe\(_2\) samples were prepared on Au electrode surfaces by mechanical exfoliation from bulk crystals.25 Electrical contact with the sample was established via the underlying Au. Optical and SECCM measurements were made using a Park NX10 instrument (Park Systems, South Korea). The SECCM tips were fabricated from glass capillaries (1.5 mm O.D. and 0.86 mm I.D., BF150-86-7.5, Sutter Instruments, USA) using a P-2000 laser puller (Sutter Instrument, USA) to form a 640 nm radius single-barreled nanopipette. SECCM tips were filled with 1.0 mM [Ru(\(\text{NH}_3\))\(_6\)]\(^3+\) (JMC Corporation, South Korea) in 10 mM KCl (VWR Chemicals, USA). A chloridized Ag wire was used as an Ag/AgCl quasi-reference counter electrode and was inserted into the top end of the nanopipette. SECCM measurements were made at an array of equally spaced points (1.5 \( \mu \text{m} \) apart) in a hopping mode. Upon contact between the nanodroplet at the end of the SECCM tip, a linear sweep voltamogram (LSV) of the one electron reduction of [Ru(\(\text{NH}_3\))\(_6\)]\(^3+\) to [Ru(\(\text{NH}_3\))\(_6\)]\(^2+\) (RuHex\(^2+\)) was conducted at the sample surface with fast sweep rates ranging from 0.2 to 1 V s\(^{-1}\). All potentials are reported vs the Ag/AgCl quasi-reference counter electrode.

## RESULTS AND DISCUSSION

A 640 nm radius single-barreled nanopipette was used to map the one electron reduction of RuHex\(^3+\) to RuHex\(^2+\) on the MoS\(_2\) surface using a hopping mode SECCM, as illustrated in Figure 1A. Optical images of the MoS\(_2\) sample in the region of the SECCM mapping are shown in Figure 1B,C before and after SECCM experiments, respectively. The region of interest contains mono-, bi-, and trilayer MoS\(_2\) immobilized on the underlying Au electrode surface, as determined by optical microscopy displayed in Figure 1B.26 The MoS\(_2\) layers appear to be continuous in the optical images. In our recent publication, we reported voltammetric analysis obtained on MoS\(_2\) and other 2D TMDCs, showing how the electrochemical kinetics of the RuHex\(^2+\) couple depends on the number of 2D TMDC layers and, ultimately, the band gap of the 2D TMDC layer. In this work, we examine the electrochemical responses at individual sample points and identify nanoscale defects at the sample surface.

Figure 2A shows a map of the current obtained at \(-0.25\) V from LSV curves measured at each position/pixel in the probed array; for the \(-0.25\) V bias the drive RuHex\(^2+\) reduction at metallic Au surfaces but insufficient to observe RuHex\(^2+\) reduction at most MoS\(_2\) surfaces, as we reported in our previous publication and is shown in Supporting Information Figure S1. Figure 2A shows certain sample points (shown in orange/red/black) that display current magnitudes that are significantly larger than those observed at the surrounding pixels (shown in yellow/white). Figure 2B shows a map of the applied bias required to observe a current of \(-5\) pA at each pixel, which indicates that the points identified in Figure 2A are also prominent in this constant current map and require lower biases to drive the same current than neighboring pixels. In Section S5, it is detailed why the current threshold of \(-5\) pA was chosen because it provides sufficient contrast for visualizing the defective points. Figure 2B-A identifies positions that yield deviations in current/bias relative to the surrounding sample points; these are highlighted and overlapped with the optical image in Figure 2C. Several of these positions/pixels are aligned along MoS\(_2\) edges, such as those labeled (i) and (ii) in Figure 2C. Therefore, MoS\(_2\) edges appear to be associated with anomalous electrochemical responses, although not all edges show anomalous responses. However, it is not always the case that the anomalous electrochemical responses are associated with MoS\(_2\) edges. For instance, the line of anomalous electrochemical responses labeled (iii) in Figure 2C is not associated with MoS\(_2\) edges.
with a MoS$_2$ edge. The anomalous sample points that are not
associated with a MoS$_2$ edge suggest that other defects, e.g.,
dislocation, grain boundaries, or even physical cracks in MoS$_2$
are at the origin of their responses. Finally, we also observe
sample points with enhanced electrochemical currents that are
isolated and do not belong to a line of anomalous sample
points, such as the point labeled D in Figure 2,BA. These
anomalous sample points suggest that the electrochemical
response is associated with point defects in the MoS$_2$ sample
surface. Additional SECCM maps on MoS$_2$, MoS$_3$, and WSe$_2$
are shown in Figures S8–S11. Anomalous points were
observed on all samples, indicating that defects are commonly
detected on mechanically exfoliated 2D TMDCs.

Figure 2D–F shows the LSV responses measured in three
regions, labeled D–F of panel 2A and 2B, respectively; the
LSVs of all 728 sample points are shown in Supporting
Information Figures S2–S7. Figure 2D shows the electro-
chemical response on trilayer MoS$_2$; this position is not part of
a line of anomalous sample points. A significantly enhanced
electrochemical response for RuHex$^{3+}$ reduction is observed at
one point in Figure 2D relative to that of the surrounding
sample points: a current plateau at approximately $-5.5 \, \text{pA}$
between $-0.35$ and $-0.7 \, \text{V}$, while biases below $-0.7 \, \text{V}$ are
insufficient to drive RuHex$^{3+}$ reduction on trilayer MoS$_2$. The
next two sample regions, whose LSVs are shown in Figure
2,FE, lie along the lines of anomalous sample points (iii):
region E is located on trilayer MoS$_2$, while region F is located
on monolayer MoS$_2$. Note that two of the sample points in
Figure 2E show anomalous electrochemical behavior.

The onset biases for RuHex$^{3+}$ reduction that we observe at
the anomalous sample points are identical to those observed
on an Au electrode surface (see Supporting Information Figure
S1). This suggests that the enhanced electrochemical kinetics
for the RuHex$^{3+}/2^+$ redox couple on the anomalous sample
points is equivalent and indistinguishable to that on a metallic
Au surface.$^{27,28}$

We observe a plateau in the reductive current at approximately $-27 \, \text{pA}$ in all the LSVs when applying a bias $-0.8 \, \text{V}$
sufficient to drive the reduction of RuHex$^{3+}$ (< $0.7 \, \text{V}$ on bilayer, $< -0.4 \, \text{V}$ on monolayer, and $< -0.25 \, \text{V}$ on Au, see Supporting Information Figure S1), due
to the diffusion-limited transport of RuHex$^{3+}$ to the MoS$_2$
surface. In an SECCM configuration, the magnitude of the
diffusion-limited current at higher overpotentials depends on
the concentration of RuHex$^{3+}$, the diffusion coefficient, the
contact area between the SECCM nanodroplet, and the sample
surface, as well as the geometry of the SECCM probe.$^{22}$ The
current plateau at the defect points shown in Figure 2,ED is observed at much lower biases (ca. $-0.25 \, \text{V}$), which is consistent with the electrochemical response for RuHex$^{3+}$
reduction on a sufficiently metallic surface. However, the current plateaus are well below the $-27 \, \text{pA}$ observed at higher overpotentials, namely, $-5.5 \, \text{pA}$ for the point in Figure 2D, and $-8.5$ and $-2 \, \text{pA}$ for the points in Figure 2E. In Figure 2F, the anomalous sample point, in black, shows a response at a much higher bias, but does not display a lower current plateau.

In all LSVs (Figure 2D–F) at higher biases the current then obtains the $-27 \, \text{pA}$ diffusion-limited current. This suggests that a small portion of the nanodroplet contact area is exposed to a surface defect with enhanced kinetics. Note that the observation of a current plateau of smaller magnitude than expected based on droplet cell size indicates that the diffusion layer associated with the defect site must be smaller than the one resulting from the total contacted area of the MoS$_2$
surface. Importantly, larger defects will lead to plateau currents that approach the maximum limiting current.

The current plateaus on the kinetically enhanced defects that we observe in Figure 2D–F can be assessed by calculating the diffusion-limited current at higher overpotentials depending on the size of the equivalent disk-shaped site in the MoS$_2$ surface which would give rise to such a diffusion-limited current. We do not consider the mass transport limitations imposed by the SECCM droplet configuration in our analysis, which is a good approximation.
approximation for defects much smaller than the SECCM droplet. In this case the diffusion-limited current can be described by

\[ i = 4\pi n r D F c \]  

(1)

where \( n \) is the number of electrons transferred in the reaction \((n = 1 \text{ for RuHex}^{3+/2+} \text{ redox couple}), r \) is the equivalent radius of the defect, \( D = 8.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} \) is the diffusion coefficient of RuHex\(^{3+}\), \( F = 96,485 \text{ C mol}^{-1} \) is Faraday's constant, and \( c = 1 \text{ mM} \) is the bulk solution concentration of RuHex\(^{3+}\). Using eq 1, we determine that a diffusion-limited current of \(-5.5 \text{ pA}\) observed in Figure 2D is equivalent to a defect with a radius of 17 nm. Likewise, the diffusion-limited currents of \(-8.5 \text{ and } -2 \text{ pA}\) in Figure 2E correspond to defects with radii of 26 and 6 nm, respectively. The defect in Figure 2F gives a diffusion-limited current plateau that is the same magnitude as RuHex\(^{3+}\) reduction on the entire contacted MoS\(_2\) surface, suggesting that this defect is >83 nm in radius. This simple analysis suggests that the anomalous electrochemical responses that we observe can be generated by nanoscale kinetically enhanced defects in the MoS\(_2\) surface. The percentage of the defect area with respect to the SECCM droplet contact area ranges from 0.01% (6 nm defect) to 0.16% (26 nm defect) and their estimated sizes are well below the diffraction limit and therefore impossible to detect optically.

The relationship between the defect area in the SECCM droplet and the relative diffusion-limited current was simulated by finite element methods, as shown in the scheme of Figure 3A and further details in Supporting Information Section S4. The result of the simulations is displayed in Figure 3B highlighting that defects only need to be present in a small fraction of the surface to give a large and measurable electrochemical response. Similar relationships to the one in Figure 3B are obtained regardless of the absolute droplet area, as shown in Figure S13. However, by changing the pipette aperture (i.e., changing droplet size), a defect of a given size will result in a different limiting current relative to the maximum value expected. Therefore, it is possible to optimize droplet size by modifying the pipette aperture to achieve the best contrast for the detection of differently sized defects. We have included a graph, Figure S14, showing the absolute diffusion limiting current expected for each size of nanoscale defect and pipette aperture used, which can be used to select the size of the droplet needed for optimum detection of differently sized defects.

Figure 3. (A) Simulated axisymmetric two-dimensional concentration profile of RuHex\(^{3+}\) at a disk-shaped defect. (B) Relationship between size of a planar circular defect and the resulting diffusion-limited current, compared to the size and diffusion-limited current of the entire SECCM droplet.

Figure 4. (A) Simulated three-dimensional concentration profile of RuHex\(^{3+}\) at a band electrode with a 1 nm width offset from the center of the 640 nm radius SECCM droplet (with a band electrode length of 798 nm). (B) Simulated LSV responses at a 1 nm wide band electrode transecting the 640 nm radius SECCM droplet with different lengths at a bias of \(-0.5 \text{ V}\). (C) Map of the limiting current at \(-0.5 \text{ V}\) for different widths and lengths of the band electrode in a 640 nm radius SECCM droplet. The contours indicate the combination of the band width and length which give rise to currents of \(-20, -8.5, \text{ and } -5.5 \text{ pA}\), respectively. The lower limit of the electrode length is visible as the curve separating the white area with the rest of the map. This limit is defined as the entire band electrode width at its center point being just contained within the disk of the SECCM droplet.
The anomalous sample points that are arranged in lines (see Figure 2C) might more accurately be described by linear defects in the MoS₂ sample surface (such as dislocations, grain boundaries, or cracks). The electrochemical response of a linear defect that traverses through the SECCM droplet can be approximated by a band electrode with a width \( w \) that traverses the SECCM droplet for a length \( L \). We simulated the time-dependent current response for band electrodes of different widths, which transverse the SECCM droplet during an LSV at 1 V/s, see Supporting Information Section 34 for computational details. A typical simulated concentration profile at a 1 nm wide band electrode, which is offset from the center of the SECCM droplet, is shown in Figure 4A. The simulated response for a 1 nm wide band electrode traversing the SECCM droplet with different offsets from the center and, thus, with correspondingly different electrochemically active lengths, is shown in Figure 4B. The simulations highlight that the length of the band electrode has a large influence on the observed response. Although in the case of our measurements, there is uncertainty on the exact length of the line defect traversing the SECCM droplet, simulating a range of different band electrode sizes allows us to construct a map of all possible width-length combinations that can give rise to a given current plateau, as shown in Figure 4C. A current plateau of \(-8.5\) pA in a linear defect, as observed in Figure 2E, could be obtained only with an electrode band width of less than 20 nm. Likewise, a current plateau of \(-2\) pA would require an electrode band width of less than 1 nm (which is the minimum band width which we simulated). This simple analysis suggests that linear defects would be on the scale of single-nanometer or a few-atoms wide.

The analysis implemented in this work aims to provide an estimate of the electrochemical response of kinetically enhanced defects on 2D TMDCs using an SECCM approach. The conventional diffusion-based voltammetric theory used here has limitations when considering nanoscale electrochemical interfaces, specifically, for electrode radii smaller than 5 nm, the electron transfer kinetics manifested might be different compared to macroscopic electrodes. Still, this diffusion-based theory has been used to describe electrochemical response down to single atoms. Our simulation results highlight that nanoscale defects, which represent a minor portion of the contacted area (\(<0.01\%\)), have a major impact on the electrochemical response. Note that the defect size calculations are based on the diffusion limiting current value, which depend on diffusion properties along the SECCM probe and not the electron transfer kinetics of the defects. Therefore, the special conditions of small wetting areas and mass transport offered by SECCM allow detection of nanoscale electrochemically enhanced domains, which are not easily detectable with other characterization techniques compatible with electrochemical analysis.

**CONCLUSIONS**

SECCM mapping of the electrochemical reduction of \([\text{Ru}^{II} (\text{NH}_3)_6]^{3+}\) on a 2D MoS₂ sample with a 640 nm radius probe has allowed us to identify defects in mono-, bi-, and trilayer MoS₂. These defects give rise to electrochemical responses, which are equivalent to disk-shaped defects with radii of tens of nanometers in size, or to band electrodes of nanometer to sub-nanometer widths. Our results highlight that an SECCM-based approach can isolate and amplify the electrochemical response from surface features orders of magnitude smaller than the SECCM probe, enabling us to detect features electrochemically that are well below the diffraction limit and therefore impossible to detect optically.

Importantly, our results also highlight the impact of nanoscale defects on the overall observed electrochemical response on seemingly defect-free 2D materials. Only a very small defect needs to be present to dominate the electrochemical response of the entire surface area. This suggests that we must be careful in the interpretation of electrocatalysis results on 2D TMDC materials, where the dominant response may not be the intrinsic electrocatalytic response of the material but the electrocatalytic response of the defects present in the material. On the other hand, our results also underline that we only need to introduce a very low density of defects into our sample surface to effectively alter the electrocatalytic properties.

**ASSOCIATED CONTENT**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.2c01656.

Typical RuHex²⁻/³⁺ responses on Au, monolayer, bilayer, and trilayer MoS₂ surfaces, raw data of all LSVs, and simulation details (PDF)

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**Notes**

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