

Anomalous Corrosion of Bulk Transition Metal Diselenides Leading to Stable Monolayers

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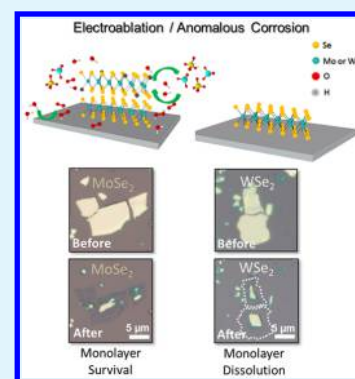
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ABSTRACT: In this paper we provide insight into an anomalous corrosion process, referred to as electroablation (EA), which converts multilayer flakes of transition metal diselenides like MoSe₂ into their corresponding monolayers when micromechanically exfoliated on a conductive electrode and subsequently subjected to a high anodic potential inside a conventional electrochemical cell. Photoluminescence intensity maps and scanning transmission electron microscopy (STEM) images confirmed the single crystalline nature and 2H-hexagonal lattice structure of the remnant monolayer MoSe₂ flakes, indicating the superior corrosion stability of the monolayers compared to that of the bulk counterpart. It is noted that the EA technique is a low-cost alternative for high-yield synthesis of single crystalline monolayer MoSe₂ at room temperature. We also found that the dynamics of such an electro-oxidation-mediated and self-limiting corrosion process differs significantly for MoSe₂ and WSe₂. While we were able to engineer the corrosion conditions for the EA process to obtain monolayers of MoSe₂, our attempts to obtain monolayers of WSe₂ were largely unsuccessful. Finally, we constructed a phenomenological physical chemistry framework to explain such anomalous corrosion processes in transition metal diselenides.

KEYWORDS: electrochemistry, 2D materials, corrosion, transition metal diselenide, monolayers, electro-oxidation



INTRODUCTION

The field of two-dimensional (2D) layered materials is rapidly expanding to a larger variety of atomically thin materials ever since the inspirational discovery of graphene. Within this field, the group of transition metal dichalcogenides (TMDs) has attracted great attention owing to their versatile and intriguing physical and chemical properties, particularly at the monolayer limit.¹ The extraordinary van der Waals (vdW) crystal structure of these compounds accounts for the easy cleavage perpendicular to the crystal *c*-axis down to monolayer. Among various TMDs, molybdenum- (Mo-) and tungsten- (W-)based dichalcogenides offer excellent semiconducting properties which make them appealing for electronic applications such as field effect transistors,^{2–4} radio frequency transistors,^{5,6} low-power transistors,⁷ neuromorphic transistors,⁸ storage devices,^{9,10} and various sensors.^{11,12} Moreover, monolayers of MoS₂, WS₂, MoSe₂, and WSe₂ exhibit a direct bandgap, which allows their application in solar cells,^{13,14}

ultrafast photodetectors,^{15,16} single-photon emitters,^{17,18} light-emitting diodes,^{19,20} gain medium for lasers,²¹ and various other optoelectronic devices.²² While early experimental studies used a top-down micromechanical exfoliation technique in order to obtain monolayers of a wide variety of 2D materials,^{23–26} it has extremely low yield, and the monolayers are often limited in size. In recent years, significant progress has been made in bottom-up synthesis approaches such as chemical vapor deposition (CVD) which can provide large-area monolayers but requires higher processing temperatures and longer processing times.^{27–30} Although the self-limiting electroablation (EA) process does not aim to compete with CVD growth, it is a scientifically intriguing and alternative low-cost synthesis technique for single crystalline monolayer 2D materials with

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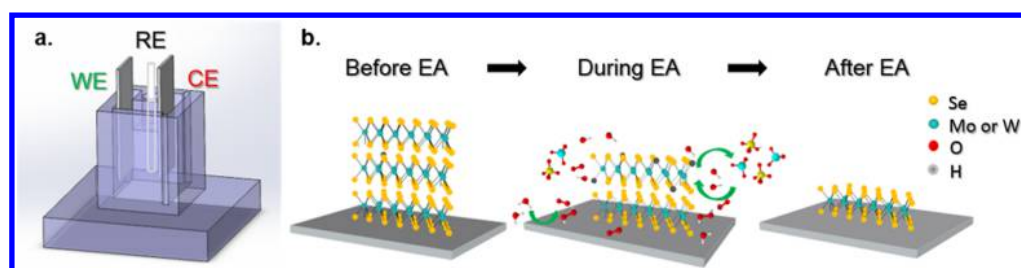


Figure 1. Electroablation (EA) process. (a) Electrochemical cell setup including the working electrode (WE), an Ag/AgCl reference electrode (RE), and a platinum sheet counter electrode (CE). The WE is a conductive TiN/Si substrate with exfoliated flakes. (b) Schematic showing the dynamics of the EA process resulting in monolayer flakes of transition metal disulfides.

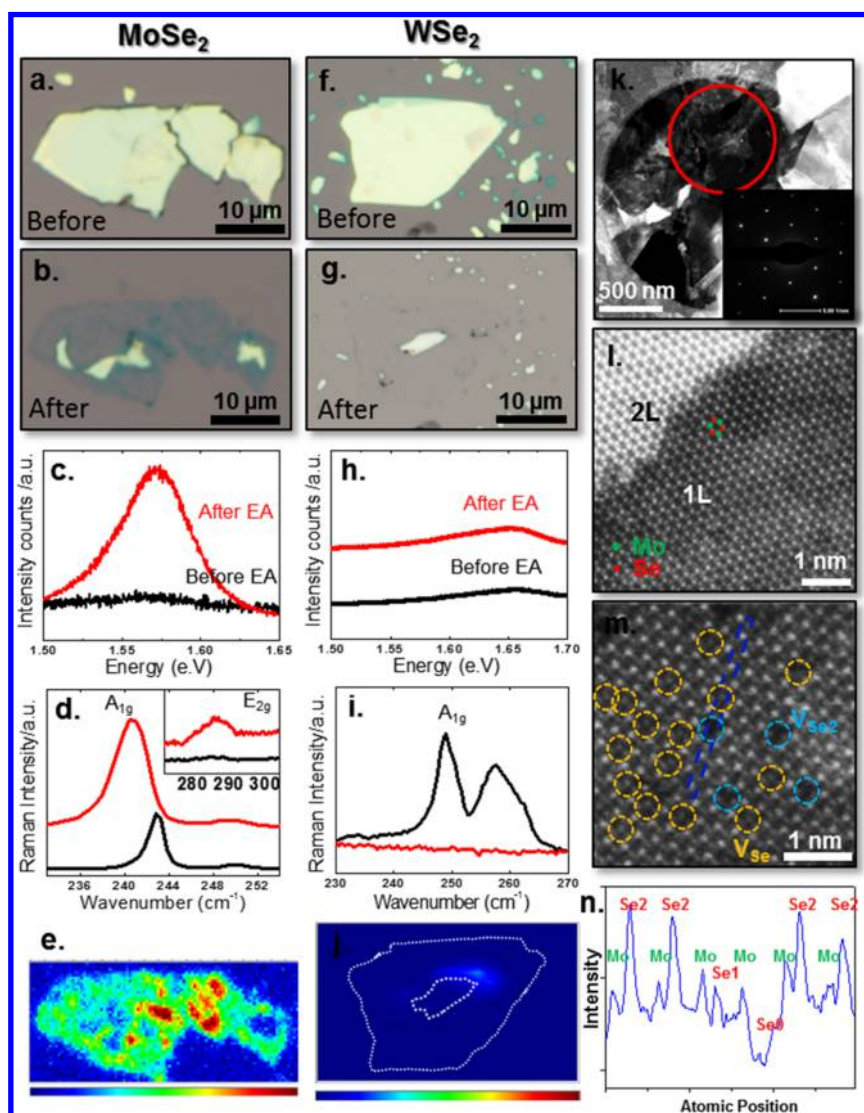


Figure 2. Characterization of electroablated transition metal diselenides. Optical images of a mechanically exfoliated MoSe₂ flake (a) before and (b) after 10 s of EA treatment. (c) Photoluminescence (PL) and (d) Raman spectra taken using a 523 nm laser before and after the EA process for MoSe₂ near the edges of the flake indicate the monolayer remnant. (e) PL map reinforces the evidence of monolayer MoSe₂ after 10 s of EA treatment. Optical images of a WSe₂ flake (f) before and (g) after 10 s of EA treatment. (h) Photoluminescence (PL) and (i) Raman spectra, and (j) PL map for WSe₂ flakes before and after 10 s of EA treatment show complete corrosion of the flake without any monolayer remnant. (k) Low-magnification STEM image of a typical electroablated MoSe₂ flake with single-layer and few-layer regions; inset SAED with hexagonal patterns indicates good crystallinity of 2H-phase MoSe₂. (l) Atomic resolution annular dark field scanning TEM (ADF-STEM) image of the single-layer MoSe₂, Mo (green dots) and Se (red dots) atoms, and sequent layers can be distinguished by the image intensity. (m) ADF-STEM image of the defective single-layer MoSe₂ region; (n) the line intensity of the ADF-STEM image identifies the double and single Se vacancies.

high yield.³¹ In fact, the EA process could be complementary to the CVD processes since it can be used to planarize CVD-grown multilayer TMDs into their corresponding monolayers.

We have already demonstrated that the EA technique can be used to convert multilayer MoS₂ and WS₂ flakes,³¹ exfoliated on a conductive TiN substrate, into their corresponding monolayers by applying a high anodic potential inside a conventional electrochemical cell as shown in Figure 1a. As described in our earlier article, the basal planes of 2D van der Waals (VdW) materials in general and transition metal disulfides in particular are chemically inert, whereas edge sites are energetically active because of the presence of point defects and/or broken bonds. Therefore, under high anodic potentials, oxidizing species generated in the electrolyte solution progressively corrode/etch/ablate the multilayer MoS₂ and WS₂ flakes from their edges toward the center as shown schematically in Figure 1b. However, such edge reactivity is completely inhibited at the monolayer limit through monolayer/substrate covalent interaction, thus making the monolayers virtually incorrodable. As such, monolayer remnants of MoS₂ and WS₂ are left behind after the ablation of the multilayer flakes making the electroablation (EA) process self-limiting.

In this article, we investigate the feasibility of the EA technique for obtaining monolayers of transition metal diselenides like MoSe₂ and WSe₂. MoSe₂ is particularly interesting since it finds application in the catalytic hydrogen evolution reaction,^{32,33} field effect transistors,³⁴ and electrochemical intercalation,³⁵ and it also provides a unique platform to investigate advanced light–matter coupling as it hosts stable and robust excitons with comparably narrow optical resonances.^{36,37} Similarly, WSe₂ offers high carrier mobility, and it is one of the rare 2D materials which offers both electron as well as hole transport that is essential for the development of next-generation complementary logic devices.^{3,38} As we will elucidate in this article, unlike that for sulfides, the dynamics of the EA process is far more intricate for the selenides and requires rigorous optimization of the pH conditions. Further, we will demonstrate that the EA process differs significantly between MoSe₂ and WSe₂ in terms of the final outcome. Although we were successful in obtaining monolayers of MoSe₂ by proper experimental conditioning, our attempts to obtain monolayers of WSe₂ were mostly unsuccessful. We were also able to hypothesize the reaction pathways and kinematics of the reactions involved in the EA process for the selenides to explain our experimental findings. It is noted that our ultimate goal is to develop the EA process as a low-cost and high-yield alternative for obtaining monolayers of a wide variety of two-dimensional (2D) layered materials by understanding the fundamental physical and chemical factors that are involved in the process. This article is one step forward to achieving that objective.

EXPERIMENTAL PROCEDURE

The substrates used for this study were Si wafers (resistivity 0.01–0.02 Ω cm) sputtered with 100 nm thick TiN purchased from West Coast Silicon. These substrates were conditioned by heat-treating at 500 °C for 10 min under N₂ ambient using a rapid thermal annealing tool (Allwin21 Heatpulse 610). This annealing step is critical to ensure the chemical stability of our conductive TiN/Si substrates and hence the reproducibility of the electroablation (EA) process. MoSe₂ and WSe₂ crystals were purchased from 2D Semiconductors Inc. and were mechanically exfoliated onto the substrates. The mechanical exfoliation provides pristine-quality crystallites of MoSe₂ and WSe₂ with an

average lateral dimension between 5 and 20 μm and thicknesses ranging from 1 to 100 nm. The electroablation (EA) technique was conducted using a three-electrode electrochemical cell that consisted of the exfoliated substrates as the working electrode (WE), a Ag/AgCl reference (6 mm, BASi) as the reference electrode (RE), and platinum (Pt) sheets as the counter electrode (CE). The electrolyte for the EA technique was prepared with lithium chloride salt (LiCl_(s), VWR) in deionized water and with subsequent addition of 37% hydrochloric acid (HCl, EMD Millipore) to achieve acidic solutions of pH = 1–4. The acidity was measured using a calibrated pH meter (Mettler Toledo SevenMulti). The schematic of the electrochemical cell used for EA is provided in Figure 1a.

The electroablation was carried out in the electrochemical cell via a potentiostat (Solartron Analytical 1287). Linear sweep voltammetry and Potentiodynamic (PD) measurements were used to evaluate the electrochemical dynamics of the exfoliated material by scanning from 0 to 2 V (versus Ag/AgCl) at a scan rate of 10 mV/s. The EA was performed at a constant potential to complete the ablation process of multilayer flakes. The electroablation was characterized using Raman spectroscopy to distinguish between multilayers and monolayers, photoluminescence (PL) mapping to confirm the monolayer transformation, and atomic force microscopy (AFM - Bruker Icon) for thickness investigation. The vibrational modes of mono- and multilayer MoSe₂ and WSe₂ were characterized using high-resolution Raman spectroscopy and PL (Horiba LabRAM HR spectrometer) with a laser excitation wavelength of 532 nm. The as-prepared MoSe₂ was transferred from the TiN substrate to a Quantifoil Au TEM grid by a PMMA-assisted water-transfer method. Transmission electron microscopy, FEI Talos and Titan³ (60–300) at 80 kV at Pennsylvania State University, was used to examine and study the atomic structure of the MoSe₂. The Z-contrast imaging feature of ADF-STEM imaging is used to distinguish the Mo atoms and Se atoms. AFM measurements for thickness evaluation of the electroablation process were made using a Bruker Dimension Icon instrument. Unless otherwise noted, all images were taken after 5 s of EA.

RESULTS AND DISCUSSION

Figure 2a,b shows the optical micrographs of MoSe₂ flakes before and after the EA. It is found that the MoSe₂ flakes became comparatively transparent after the EA, and the edge area is more transparent than the center area, suggesting the formation of an ultrathin MoSe₂ layer. This transformation of multilayer MoSe₂ to monolayer can be seen in the photoluminescence (PL) peak intensity map in Figure 2e. The PL map shows an intense signal from the thinner region and yet a much diminished intensity in the bulky region. PL measurements are routinely used in the literature for unambiguous distinction of monolayer TMDs from their multilayer and bulk counterparts.³⁹ The PL enhancement is a consequence of an indirect to direct bandgap transition that happens only at the monolayer limit. As seen in Figure 2c, the thinner area emits intense PL and exhibits a single prominent maximum at 1.57 eV (792 nm). This emission peak is in excellent agreement with the reported optical bandgap of monolayer MoSe₂ (1.57 eV)⁴⁰ and thus verifies the formation of monolayer MoSe₂ in the EA process. The emission intensity varies across the monolayer area together with a small shift of the luminescence energy. This is related to the Se vacancies already present in the exfoliated material or introduced during the electroablation process.⁴¹ In addition, the Raman spectra in Figure 2d reinforce the evidence of monolayer MoSe₂ formation. The Raman active out-of-plane A_{1g} mode is found at 239 cm⁻¹ for the monolayer MoSe₂.⁴² However, the A_{1g} mode shifts toward higher wavenumbers (243 cm⁻¹) in multilayer MoSe₂ because of the interlayer interaction along the *c*-axis (A_{1g} mode: the Se atoms in all layers oscillate in phase with respect to the corresponding

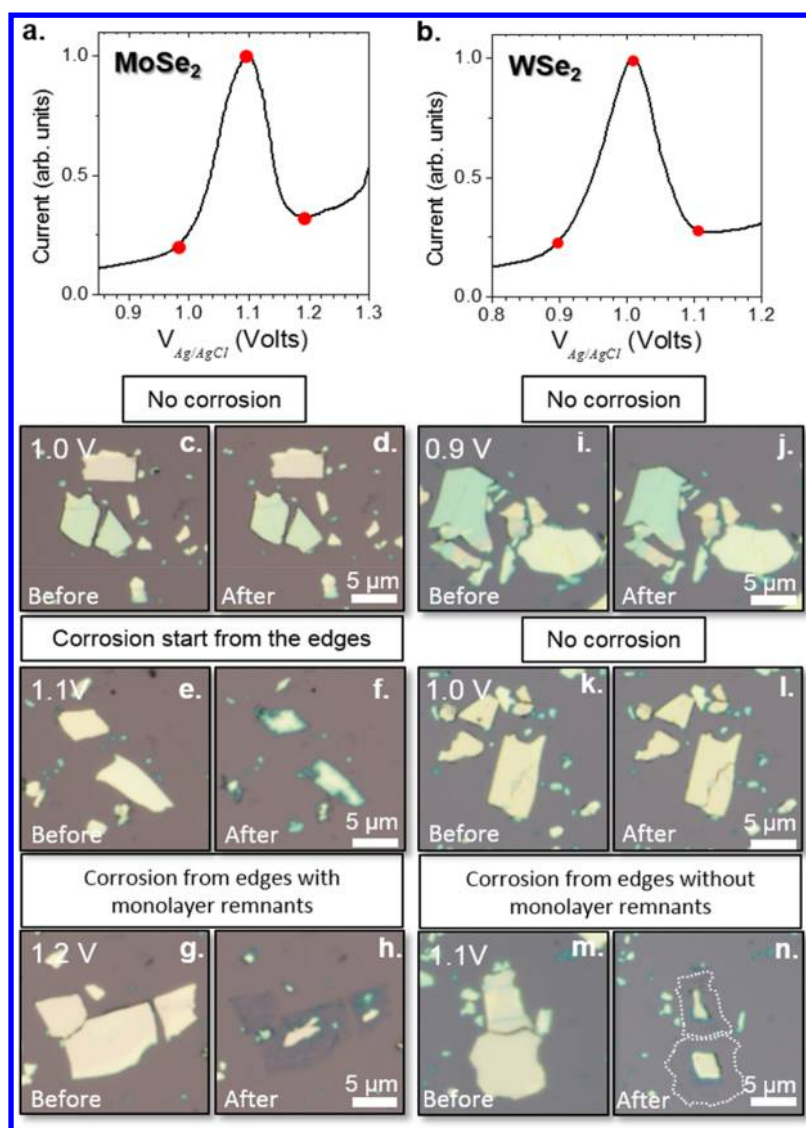


Figure 3. Corrosion and oxidative dissolution of transition metal diselenides. Voltammograms for (a) MoSe₂ and (b) WSe₂ from a range 0.8–1.2 V at pH 3 in 1 M LiCl. (c–h) Optical images of MoSe₂ flakes prior to and after 5 s of EA treatment at 1.0, 1.1, and 1.2 V. (i–n) Optical images of WSe₂ flakes prior to and after 5 s of EA treatment at 0.9, 1.1, and 1.2 V.

center molybdenum atom). The in-plane E_{2g} mode appears at higher wavenumbers, which is found only in the monolayer at 287.2 cm^{-1} because the vibrational mode is weak in multilayers. Several reports have indicated that, for multilayer MoSe₂, the E_{2g} peak is almost invisible at low excitation energies and increases monotonically at excitation energies above 2.54 eV. It was also reported that near the band-to-band transition at ~ 2.5 eV, the Raman intensity of the A_{1g} phonon is enhanced, whereas that of the E_{2g} phonon is not.^{43,44} It is noted that our Raman study uses a laser excitation wavelength of 532 nm (2.3 eV). As such, the Raman peak E_{2g} is not really visible for bulk MoSe₂. The optical images in Figure 2f,g, respectively, present the change of a WSe₂ flake before and after EA treatment. Unlike MoSe₂, the WSe₂ multilayer flake was completely corroded away without any monolayer remnant after the EA. Absence of any detectable signal in the PL measurement (Figure 2h), Raman scan (Figure 2i), and PL mapping (Figure 2j) clearly indicates complete corrosion/ablation of the WSe₂ flake. The scanning transmission electron microscopy (STEM) image of the electroablated MoSe₂ shown in Figure 2k indicates

the monolayer-to-few-layer feature of the flake; the inset corresponding selected area electron diffraction (SAED) pattern reveals the good crystallinity of the as-prepared MoSe₂ with a hexagonal structure. The annular dark field scanning TEM (ADF-STEM) image in Figure 2l displays the atomic structure of the monolayer MoSe₂ flake, and Mo and Se atoms, and sequent layers can be identified by analyzing the intensity profile due to the Z-contrast (atomic number) characteristics of ADF-STEM imaging. Massive single and double selenium vacancies (V_{Se} and V_{Se_2}) can also be distinguished from the Se₂ column in the perfect lattice (Figure 2m,n).

Figure 3a,b shows the anodic peaks in the linear sweep voltammetry curves for MoSe₂ and WSe₂. These voltammetry scans were taken by sweeping the anodic potential from 0 to 2 V versus the Ag/AgCl reference and are at a pH of 3.0. The oxidative dissolution of the multilayer MoSe₂ and WSe₂ flakes during the EA process is an irreversible reaction, and thus the anodic peaks can only be seen from the first scan. The optical micrograph pictures in Figure 3c–h and in Figure 3i–n,

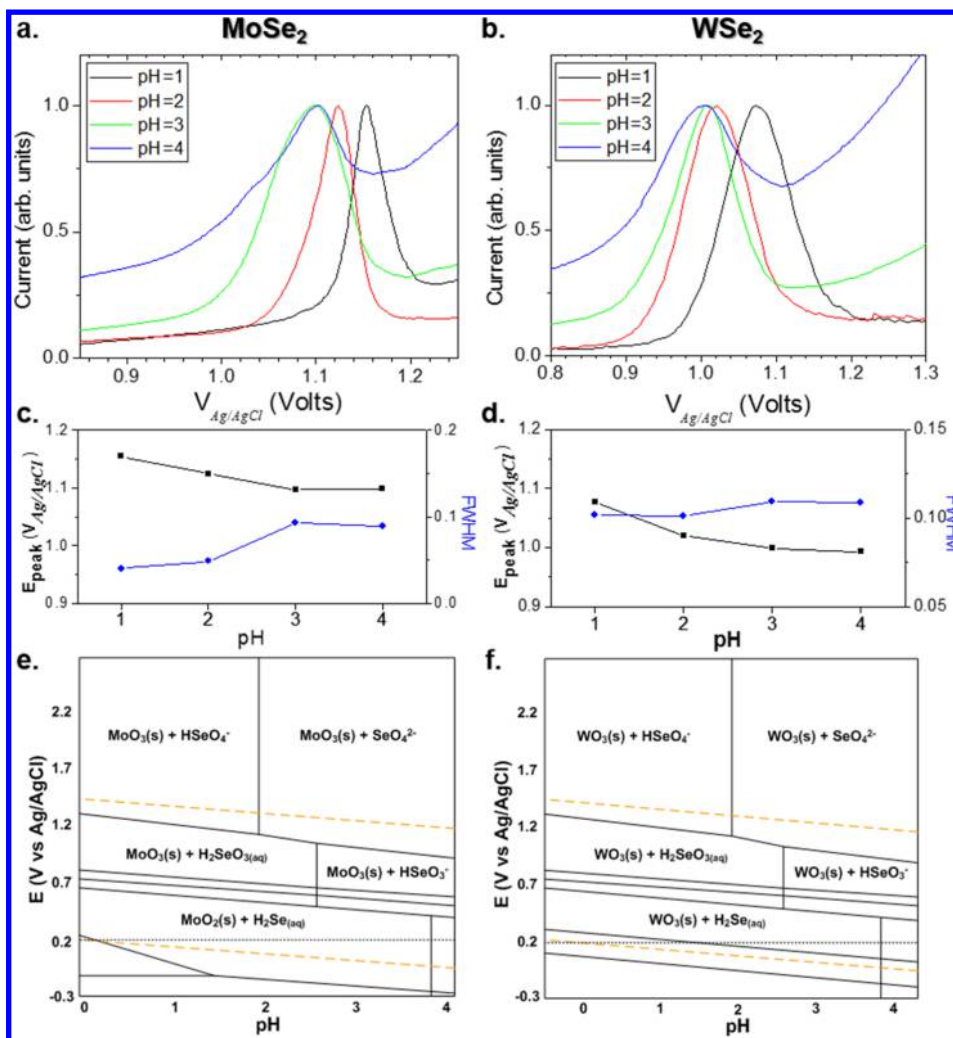


Figure 4. pH dependence of the EA process for transition metal diselenides. Voltammograms of mechanically exfoliated (a) MoSe₂ and (b) WSe₂ flakes on TiN in 1 M LiCl at different acidic solutions of pH = 1–4. The potential was swept from 0 to 2 V vs Ag/AgCl at a rate of 10 mV/s. The current values have been normalized to account for variations in surface flake density. Peak potential and fwhm as a function of pH for (c) MoSe₂ and (d) WSe₂. Pourbaix diagrams at 25 °C, 1 bar for (e) Mo–Se–OH and (f) W–Se–OH systems, generated from The Materials Project database.⁵¹ The potential, $E_{\text{Ag}/\text{AgCl}}$ is in reference to the Ag/AgCl reference electrode (+0.197 V versus the standard hydrogen electrode).

respectively, show the dissolution/corrosion of the multilayer MoSe₂ and WSe₂ flakes after 10 s at the indicated specific applied potentials. For the MoSe₂ flakes, no visible corrosion occurred at potentials below the peak potential (E_{peak}), and limited corrosion started from the outer edges of the flakes at the peak potential of 1.1 V. However, once the applied potential exceeded the peak potential, multilayer flakes were actively corroded away leaving behind monolayer remnants. For the WSe₂ flakes, no visible corrosion occurred even at the peak potential of 1.0 V. However, beyond the peak anodic potential, complete corrosion took place from the WSe₂ flake perimeters without leaving behind any monolayer remnants. For both of these materials it was found that the electroablation process required overpotentials to corrode the multilayers. Also, the corrosion process occurred from the edges to the center of both bulk materials which is similar to our earlier findings on MoS₂ and WS₂. However, while the EA process on MoSe₂ yielded the monolayer, it was unsuccessful for obtaining the WSe₂ monolayer. As we will elucidate in the following sections through more detailed experiments and possible reaction pathways, the monolayer survival is strongly dependent on competing reaction rates between the monolayer and

the bulk layers which in turn are determined by how the transition metal is bound to the chalcogen. As such, the electrochemical properties change as a consequence of altering the transition metal (Mo and W) or the chalcogen component (S and Se).⁴⁵

The voltammetry plots for different pH values are shown in Figure 4a,b for MoSe₂ and WSe₂, respectively. For both MoSe₂ and WSe₂, the peak potential (E_{peak}) decreases with increasing pH between acidities of 1 to 4, which can be explained on the basis of the Nernst equation.⁴⁶ E_{peak} versus pH for MoSe₂ and WSe₂ is shown in Figure 4c,d, respectively. The slope of the E_{peak} versus pH curve for MoSe₂ was found to be ~30 mV/pH, between pH = 1 and 2, which indicates a one-proton–two-electron transfer mechanism corresponding to oxidation of Mo-based dichalcogenides from Mo⁴⁺ to Mo⁶⁺ consistent with previous reports.^{47,48} It is noted that the redox potential of a reaction involving m protons and n electrons shifts $(m/n) \times 59$ mV per 10-fold change in proton activity (which, in the case of water, is per pH unit). The larger slope of the E_{peak} versus pH curve for WSe₂ (~55 mV/pH) suggests a different reaction mechanism (possibly one-proton–one-electron transfer mechanism) and hence can be related to the dissolution of

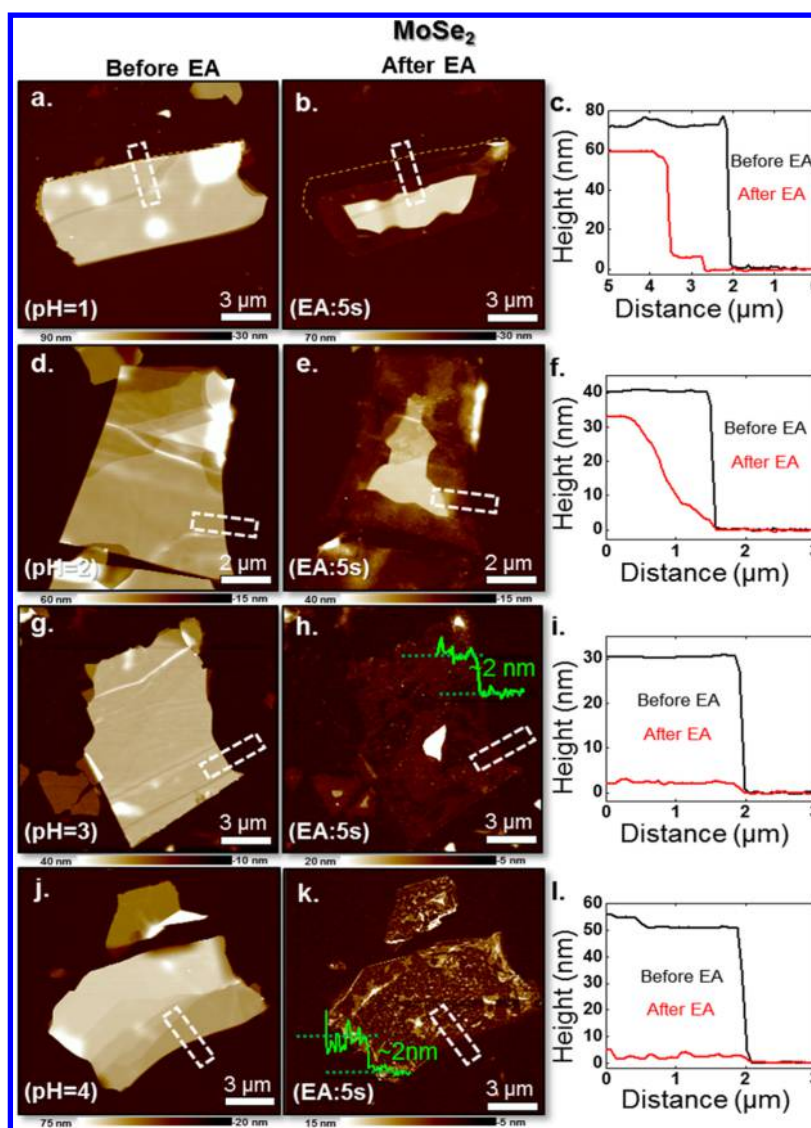
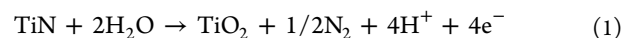


Figure 5. AFM images and height profiles for multilayer MoSe₂ flakes before and after 5 s of EA process in (a–c) pH = 1, (d–f) pH = 2, (g–i) pH = 3, and (j–l) pH = 4 solution.

monolayer WSe₂ unlike the survival of monolayer MoSe₂, under similar reaction conditions.⁴⁵ It is also noticeable that the peak shape varies from sharp (at pH 1) to broader (at pH 4) with increasing pH value for both MoSe₂ and WSe₂. When the value of the fwhm is larger, it is easier to activate the ions in the electrochemical reaction.^{49,50} The peak broadening at higher pH values, therefore, suggests that more reactive species are involved in the corrosion process for MoSe₂ and WSe₂.

The oxidative dissolution kinetics of MoSe₂ and WSe₂ are complicated and involve the electro-activities of their edge planes, the formation of oxides, and their solubility. We propose two types of oxidative species that participate in and/or catalyze the corrosion of multilayer MoSe₂ and WSe₂: (1) the hydroxide ions (OH⁻) which are present in the electrolyte solution and (2) oxidizing agents such as O₂, H₂O₂, etc., which are generated at the interface of TiN and the electrolyte as a result of the applied high anodic potentials.⁵² These oxidizing agents gradually passivate the TiN substrate through the formation of TiO₂ following the reaction given by eq 1.⁵³ However, the passivation of TiN does not obscure the

corrosion of MoSe₂ and WSe₂ since the passivation kinetics is significantly slower than the EA process.



To explain the corrosion dynamics of MoSe₂, we postulate that oxygen, initially, gets chemisorbed at the edge planes of MoSe₂ to form O–Se bonds. DFT calculations show that the formation energy of oxygen adsorption from the O–Se bond (–0.284 eV) has a relatively lower stability compared to the energy of oxygen replacement Mo–O bond (–2.504 eV).^{54,55} As such, the chemisorption is followed by desorption of oxygen with a possible “kick-out” of O–Se species. This leaves behind unsaturated bonds for the transition metal, which then is readily available to form Mo–O bonds in the presence of oxygen. Moreover, Se vacancies present at the edge planes further facilitate Mo–O bond formation. From viewing the Mo–O–Se Pourbaix diagram in Figure 4e, it is apparent that the most likely reaction products at different pH and potential ranges are MoO₃, HSeO₄⁻, or SeO₄²⁻ as given by eq 2.^{56,57} As for WSe₂, the O–Se (–0.132 eV) bond is even more unstable compared to the replacement of W–O bonds (–2.184 eV). For WSe₂, the

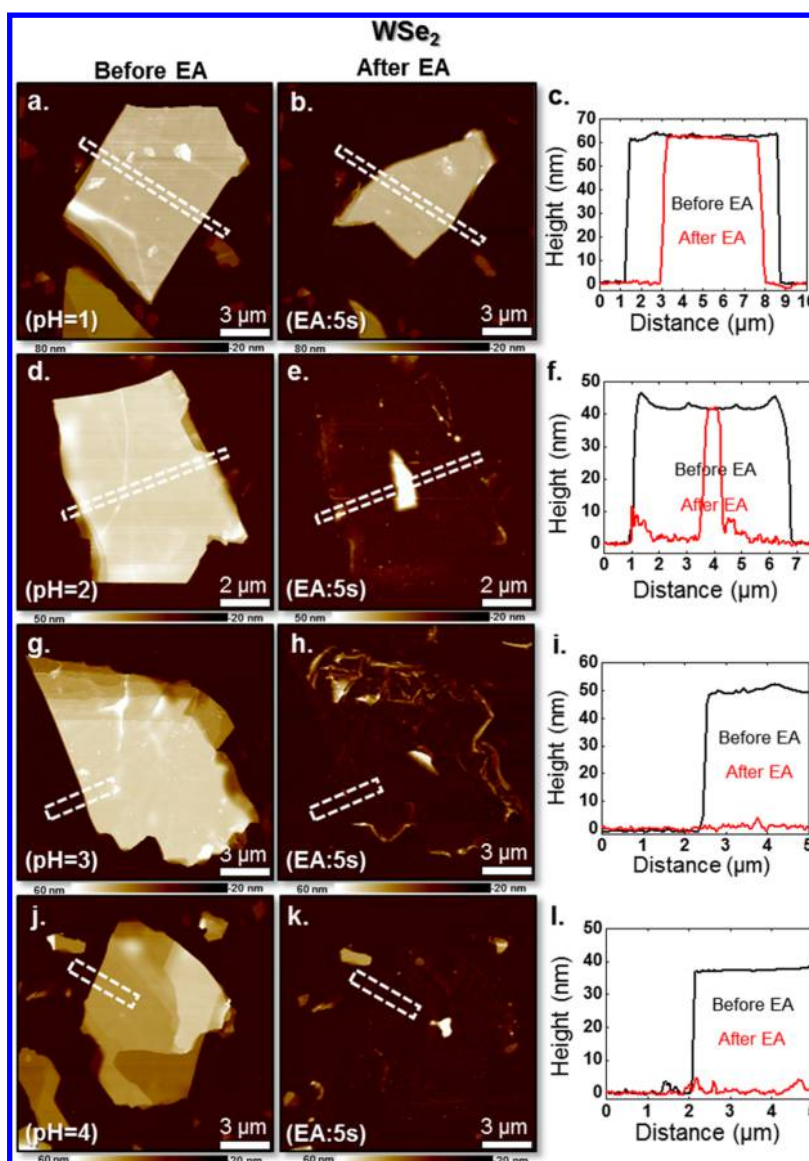
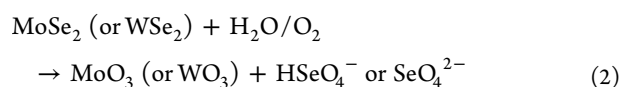
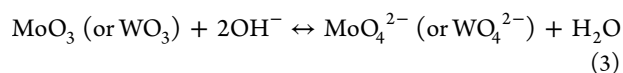


Figure 6. AFM images and height profiles for multilayer WSe_2 flakes before and after 5 s of EA process in (a–c) pH = 1, (d–f) pH = 2, (g–i) pH = 3, and (j–l) pH = 4 solution.

Pourbaix diagram in Figure 4f shows that the probable products are WO_3 , HSeO_4^- , and SeO_4^{2-} .



MoO_3 and WO_3 are known to be thermodynamically unstable and readily hydrolyzed into molybdate and tungstate following eq 3, which results in the dissolution of the oxide and hence completion of the corrosion process for the bulk layers.^{58,59}



Other studies also show that elemental species such as MoO_4^{2-} and SeO_4^{2-} could be generated at anodic potentials above 1.0 V.⁶⁰

To explain the survival or dissolution of the monolayer after the EA treatment, we invoke a hypothesis which assumes a competing rate of corrosion for the layer in contact with the TiN substrate and the rest of the bulk layers. If the corrosion

rate for the monolayer is much slower compared to the corrosion rate for the rest of the bulk layers, the monolayer will survive, as in the case of MoSe_2 . However, if the corrosion rates are similar, the entire flake will dissolve without a monolayer remnant, as in the case of WSe_2 . This suggests that, for MoSe_2 , the covalent-type interaction between the monolayer edges and the TiN substrate is much stronger than that in the case of WSe_2 . It is noted that this finding for the transition metal selenides is significantly different from that for the transition metal sulfides, where both MoS_2 and WS_2 monolayers survived after the EA treatment indicating much stronger monolayer/substrate interaction for the sulfides.

The mechanism of the oxidative dissolution for MoSe_2 was also studied by altering the OH^- concentration from 10^{-13} (pH = 1) to 10^{-10} (pH = 4) on a flake with similar lateral dimensions and thicknesses. Figure 5 shows the AFM height profiles for multilayer MoSe_2 flakes before and after 5 s of EA for different pH values. The EA process was conducted under a constant overpotential of 1.2 V for MoSe_2 and 1.1 V for WSe_2 . It was found that the pH value plays an important role in the

survival of monolayer MoSe₂ and also in the corrosion profile. For pH = 1, as shown in Figure 5a–c, the entire flake is slowly corroded from the edges into a smaller island without leaving any monolayer remnant. For pH = 2, as shown in Figure 5d–f, the flake is corroded from the edges into a pyramidal structure with some monolayer remnant. For pH = 3, as shown in Figure 5g–i, the flake is uniformly corroded from the edges into a much smaller island leaving a clean monolayer remnant. Finally, for pH = 4, as shown in Figure 5j–l, the flake is completely corroded away leaving a monolayer remnant. However, in the last instance, the monolayer remnant shows some nonuniformity. The pH-dependent monolayer survival can be explained with the help of differing corrosion rates for the bulk layers compared to that for the monolayer. It is reasonable to assume that the bulk layers have a much higher corrosion rate constant (k_B) owing to a weak van der Waals (VdW) interlayer interaction, whereas the corrosion rate constant for the monolayers (k_M 's) are much smaller because of their strong covalent interaction with the substrate, i.e., $k_M \ll k_B$. However, the ultimate corrosion rate is determined not only by the corrosion rate constants but also by the available concentration of the oxidizing species ($[C_{OX}]$) that creates the Mo or W oxides and the hydroxide ions ($[OH^-]$) that are necessary for the dissolution of such oxides in the solution to complete the corrosion process. The reaction rate can be written as $r_{B,M} = k_{B,M}[C_{OX}][OH^-]$. At pH = 1, the concentration, $[C_{OX}]$, is likely to be limited by both a higher interfacial potential barrier at the electrolyte/electrode interface (i.e., smaller value for fwhm as discussed in the context of peak broadening in the voltammetry measurements in Figure 4a,b for the generation of oxidizing species) as well as diffusion of those species across the bulk layers. As such, the corrosion rate for the bulk layers (r_B) is comparable with the corrosion rate for the monolayers (r_M), i.e., $r_B \approx r_M$ and both have a low magnitude resulting in slow corrosion of the entire flake without any monolayer remnant. At pH = 2, the concentration, $[C_{OX}]$, increases slightly because of the lowering of the interfacial potential barrier at the electrolyte/electrode interface (i.e., larger value for fwhm); however, the $[OH^-]$ concentration is increased by an order of magnitude enhancing the bulk corrosion rate. The pyramidal shape of the corrosion profile can be explained from the Boltzmann–Poisson distribution of the OH⁻ ions across the bulk layers of the flake since the OH⁻ ions need to diffuse from the bulk solution toward the interface against the drift field that is present due to the positive potential applied to the TiN substrate. This would result in higher $[OH^-]$ concentration and hence a higher corrosion rate at the top of the flake which is furthest from the TiN interface. However, the bulk corrosion rate close to the interface can still be diffusion-limited which explains sporadic monolayer survival at pH = 2. At pH = 3, the $[OH^-]$ concentration becomes so large throughout the entire thickness of the flake that $r_B \gg r_M$. As such, the entire flake is rapidly corroded away to a tinier island leaving behind a clean monolayer remnant. For pH = 4 and above, the $[OH^-]$ concentration becomes extremely large such that even the monolayer corrosion becomes significant resulting in corrosion of the monolayer. Figure 6 shows the AFM height profiles for multilayer WSe₂ flakes before and after 5 s of EA for pH = 1, 2, 3, and 4. Unlike MoSe₂, there were no monolayer remnants for WSe₂ at any given pH value, indicating a much higher corrosion rate for WSe₂ monolayers. However, similar to MoSe₂, the bulk corrosion rate for WSe₂ was found to be much faster at higher pH.

CONCLUSION

The dynamics of the anomalous corrosion process, referred to as electroablation (EA), was investigated, and experimental outcomes were explained from a fundamental physical chemistry framework for the transition metal diselenides. We can engineer the EA process conditions and obtain monolayers of MoSe₂. However, the attempts to obtain monolayers of WSe₂ were unsuccessful because of its significantly higher corrosion rate. We proposed that the bulk layers have a much higher reaction rate constant owing to a weak van der Waals (VdW) interlayer interaction compared to that of their monolayer counterparts since the monolayers benefit from strong covalent interaction with the substrate. The rate constants also depend on the bond strength of the transition metal and the chalcogen atoms. As such, the corrosion properties differ when either the transition metal (Mo and W) or the chalcogen component (S and Se) is altered. The monolayer survival is, ultimately, determined by the competing corrosion dynamics between the bulk and the monolayer.

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Author Contributions

Y.T.H. and S.D. conceived the experiments and analyzed the data. Y.T.H., A.D., A.S., and D.B. performed all the experiments related to electrochemistry and did the monolayer characterization. D.S.S. assisted the experiments and analysis of materials. F.Z. performed the TEM experiments. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

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