Anomalous Corrosion of Bulk Transition Metal Diselenides Leading to Stable Monolayers

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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,2–5 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

Received: August 30, 2017
Accepted: October 13, 2017
Published: October 13, 2017

DOI: 10.1021/acsami.7b13107
ACS Appl. Mater. Interfaces 2017, 9, 39059–39068
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.
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 MoS$_2$ and WS$_2$ flakes, 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 MoS$_2$ and WS$_2$ 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 MoS$_2$ and WS$_2$ 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 MoSe$_2$ and WSe$_2$. MoSe$_2$ is particularly interesting since it finds application in the catalytic hydrogen evolution reaction, field effect transistors, and electrochemical intercalation, 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. Similarly, WSe$_2$ 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. 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 MoSe$_2$ and WSe$_2$ in terms of the final outcome. Although we were successful in obtaining monolayers of MoSe$_2$ by proper experimental conditioning, our attempts to obtain monolayers of WSe$_2$ 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.

### RESULTS AND DISCUSSION

Figure 2a,b shows the optical micrographs of MoSe$_2$ flakes before and after the EA. It is found that the MoSe$_2$ flakes became comparatively transparent after the EA, and the edge area is more transparent than the center area, suggesting the formation of an ultrathin MoSe$_2$ layer. This transformation of multilayer MoSe$_2$ 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 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. 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 at a prominent maximum at 1.57 eV (792 nm). This emission peak is in excellent agreement with the reported optical bandgap of monolayer MoSe$_2$ (1.57 eV) and thus verifies the formation of monolayer MoSe$_2$ 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. In addition, the Raman spectra in Figure 2d reinforce the evidence of monolayer MoSe$_2$ formation. The Raman active out-of-plane $A_g$ mode is found at 239 cm$^{-1}$ for the monolayer MoSe$_2$. However, the $A_g$ mode shifts toward higher wavenumbers (243 cm$^{-1}$) in multilayer MoSe$_2$ because of the interlayer interaction along the c-axis ($A_{1g}$ mode: the Se atoms become comparatively transparent after the EA, and the edge area is more transparent than the center area, suggesting the formation of an ultrathin MoSe$_2$ layer. This transformation of multilayer MoSe$_2$ 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 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. 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 at a prominent maximum at 1.57 eV (792 nm). This emission peak is in excellent agreement with the reported optical bandgap of monolayer MoSe$_2$ (1.57 eV) and thus verifies the formation of monolayer MoSe$_2$ 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. In addition, the Raman spectra in Figure 2d reinforce the evidence of monolayer MoSe$_2$ formation. The Raman active out-of-plane $A_g$ mode is found at 239 cm$^{-1}$ for the monolayer MoSe$_2$. However, the $A_g$ mode shifts toward higher wavenumbers (243 cm$^{-1}$) in multilayer MoSe$_2$ because of the interlayer interaction along the c-axis ($A_{1g}$ mode: the Se atoms
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 MoSe$_2$, 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 $\sim$2.5 eV, the Raman intensity of the $A_{1g}$ phonon is enhanced, whereas that of the $E_{2g}$ phonon is not. 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 MoSe$_2$. The optical images in Figure 2f, respectively, present the change of a WSe$_2$ flake before and after EA treatment. Unlike MoSe$_2$, the WSe$_2$ 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 WSe$_2$ flake. The scanning transmission electron microscopy (STEM) image of the electroablated MoSe$_2$ 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 MoSe$_2$ with a hexagonal structure. The annular dark field scanning TEM (ADF-STEM) image in Figure 2l displays the atomic structure of the monolayer MoSe$_2$ 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$_{Se2}$) can be distinguished from the Se$_2$ column in the perfect lattice (Figure 2m,n).

Figure 3a,b shows the anodic peaks in the linear sweep voltammetry curves for MoSe$_2$ and WSe$_2$. 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 MoSe$_2$ and WSe$_2$ 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,
respectively, show the dissolution/corrosion of the multilayer MoSe$_2$ and WSe$_2$ flakes after 10 s at the indicated specific applied potentials. For the MoSe$_2$ flakes, no visible corrosion occurred at potentials below the peak potential ($E_{\text{peak}}$), 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 WSe$_2$ 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 WSe$_2$ 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 MoS$_2$ and WS$_2$. However, while the EA process on MoSe$_2$ yielded the monolayer, it was unsuccessful for obtaining the WSe$_2$ 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).

The voltammetry plots for different pH values are shown in Figure 4a,b for MoSe$_2$ and WSe$_2$, respectively. For both MoSe$_2$ and WSe$_2$, the peak potential ($E_{\text{peak}}$) decreases with increasing pH between acidities of 1 to 4, which can be explained on the basis of the Nernst equation. $E_{\text{peak}}$ versus pH for MoSe$_2$ and WSe$_2$ is shown in Figure 4c,d, respectively. The slope of the $E_{\text{peak}}$ versus pH curve for MoSe$_2$ was found to be $\sim$30 mV/pH, between pH = 1 and 2, which indicates a one-proton−two-electron transfer mechanism corresponding to oxidation of Mo-based dichalcogenides from Mo$^{4+}$ to Mo$^{6+}$ consistent with previous reports. 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 $E_{\text{peak}}$ versus pH curve for WSe$_2$ ($\sim$55 mV/pH) suggests a different reaction mechanism (possibly one-proton−one-electron transfer mechanism) and hence can be related to the dissolution of
monolayer WSe₂ unlike the survival of monolayer MoSe₂ under similar reaction conditions. 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. 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. These oxidizing agents gradually passivate the TiN substrate through the formation of TiO₂ following the reaction given by eq 1.

$$\text{TiN} + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 1/2\text{N}_2 + 4\text{H}^+ + 4e^-$$  

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). 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. 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 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.
Pourbaix diagram in Figure 4f shows that the probable products are $\text{WO}_3$, $\text{HSeO}_4^-$, and $\text{SeO}_4^{2-}$.

$$\text{MoSe}_2 \text{ or WSe}_2 + \text{H}_2\text{O}/\text{O}_2 \rightarrow \text{MoO}_3 \text{ or WO}_3 + \text{HSeO}_4^- \text{ or SeO}_4^{2-}$$  \hspace{1cm} (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.$^{58,59}$

$$\text{MoO}_3 \text{ or WO}_3 + 2\text{OH}^- \leftrightarrow \text{MoO}_4^{2-} \text{ or WO}_4^{2-} + \text{H}_2\text{O}$$ \hspace{1cm} (3)

Other studies also show that elemental species such as $\text{MoO}_4^{2-}$ and $\text{SeO}_4^{2-}$ 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 process in (a–c) pH = 1, (d–f) pH = 2, (g–i) pH = 3, and (j–l) pH = 4 solution.

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.
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−l, 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 ≪ 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 ≈ 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 ≫ 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

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

The work of A.D., A.S., D.S.S., and S.D. was partially supported through Grant ECCS-1640020 from National Science Foundation (NSF) and Contract 2016-NE-2699 from Semiconductor Research Corporation. The work of Y.T.H. was supported by HKU exchange program, pilot scheme, and the General Research Fund from the Research Grants Council of Hong Kong Special Administrative Region, China, under Award 17202314 and 17204516 (S.-P.F.). The authors would also like to acknowledge useful discussion and critical insight from Dr. Mark W Horn.

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DOI: 10.1021/acsami.7b11107

ACS Appl. Mater. Interfaces 2017, 9, 39059−39068

**NOTE ADDED AFTER ASAP PUBLICATION**
This paper published ASAP on 10/26/2017. The affiliations were modified and the corrected version was reposted on 10/27/2017.