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Velický, M., Donnelly, G. E., Hendren, W. R., McFarland, S., Scullion, D., DeBenedetti, W. J. I., ... Huang, F. (2018). Mechanism of Gold-Assisted Exfoliation of Centimeter-Sized Transition-Metal Dichalcogenide Monolayers. *ACS Nano*, 12(10), 10463-10472. DOI: 10.1021/acsnano.8b06101

**Published in:**  
ACS Nano

**Document Version:**  
Publisher's PDF, also known as Version of record

**Queen's University Belfast - Research Portal:**  
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# Mechanism of Gold-Assisted Exfoliation of Centimeter-Sized Transition-Metal Dichalcogenide Monolayers

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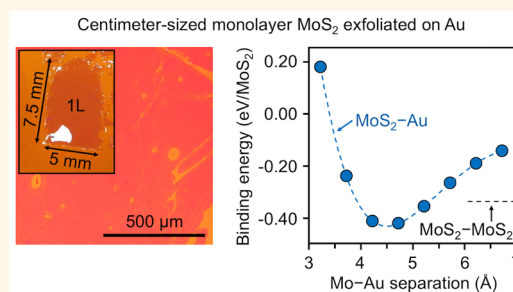
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## Supporting Information

**ABSTRACT:** Exfoliation of large-area monolayers is important for fundamental research and technological implementation of transition-metal dichalcogenides. Various techniques have been explored to increase the exfoliation yield, but little is known about the underlying mechanism at the atomic level. Here, we demonstrate gold-assisted mechanical exfoliation of monolayer molybdenum disulfide, up to a centimeter scale. Detailed spectroscopic, microscopic, and first-principles density functional theory analyses reveal that strong van der Waals (vdW) interaction between Au and the topmost MoS<sub>2</sub> layer facilitates the exfoliation of monolayers. However, the large-area exfoliation promoted by such strong vdW interaction is only achievable

on freshly prepared clean and smooth Au surfaces, while rough surfaces and surfaces exposed to air for more than 15 min result in negligible exfoliation yields. This technique is successfully extended to MoSe<sub>2</sub>, WS<sub>2</sub>, WSe<sub>2</sub>, MoTe<sub>2</sub>, WTe<sub>2</sub>, and GaSe. In addition, electrochemical characterization reveals intriguing interactions between monolayer MoS<sub>2</sub> and Au. A subnanometer-thick MoS<sub>2</sub> monolayer strongly passivates the chemical properties of the underlying Au, and the Au significantly modulates the electronic band structure of the MoS<sub>2</sub>, turning it from semiconducting to metallic. This could find applications in many areas, including electrochemistry, photovoltaics, and photocatalysis.

**KEYWORDS:** transition-metal dichalcogenide, MoS<sub>2</sub>, gold, monolayer, exfoliation, electrochemical, mechanism



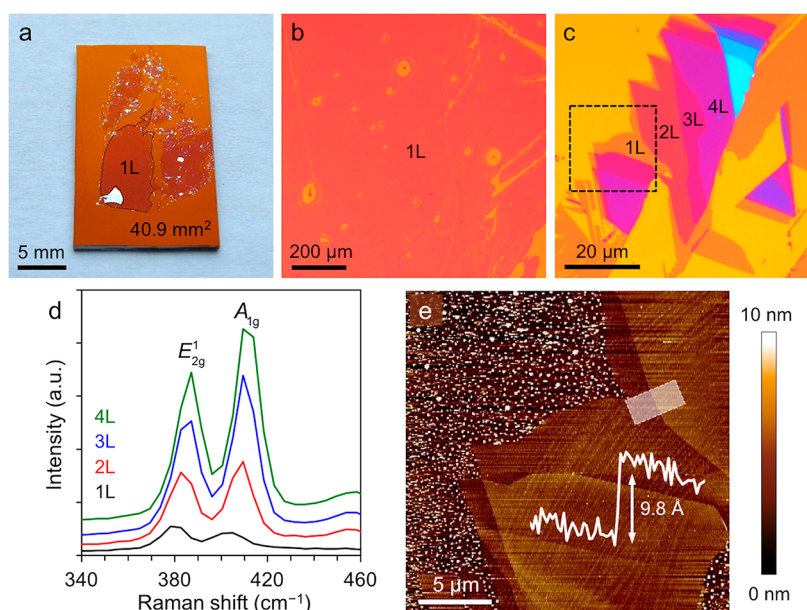
Monolayer transition-metal dichalcogenides (TMDCs) possess a wide range of extraordinary optoelectronic, chemical, and mechanical properties unattainable in their bulk form.<sup>1–3</sup> Many bulk TMDCs are semiconductors with an indirect band gap, which transitions to a direct band gap when in monolayer form, rendering them excellent materials for optoelectronics.<sup>4–6</sup> A major challenge for large-scale application of TMDCs is the competition between material quality and production scalability. For instance, readily scalable liquid-phase exfoliation is tainted by the small size, poor quality, and contamination of the resulting crystals.<sup>7</sup> Chemical vapor deposition yields large-area mono-

layers, but their quality is inferior to those made by mechanical exfoliation (ME), and the method is time-consuming and costly.<sup>8</sup> By contrast, ME generally yields the highest quality monolayer TMDCs, however, their typical lateral dimensions are in the range of tens to hundreds of microns.<sup>9,10</sup> This poses a significant challenge since many characterization techniques, large-scale processing, and applications typically require macroscopic samples. Finding a facile way of producing

Received: August 10, 2018

Accepted: September 28, 2018

Published: September 28, 2018



**Figure 1.** Exfoliation and characterization of MoS<sub>2</sub> on Au substrate. (a) Optical macrograph of a large-area monolayer MoS<sub>2</sub> on a 7.5 nm Au/1 nm Ti/93 nm SiO<sub>2</sub>/Si wafer. (b) Optical micrograph of a large-area monolayer MoS<sub>2</sub>. (c) High-resolution optical micrographs of the mono- and multilayer MoS<sub>2</sub>. (d) Raman spectra (532 nm excitation) of mono- and multilayer MoS<sub>2</sub> in (c), showing the main in-plane ( $E_{2g}^1$ ) and out-of-plane ( $A_{1g}$ ) vibrational modes (spectra are offset for clarity). (e) AFM topography image taken from the area highlighted in (c) by the black square, showing a smooth MoS<sub>2</sub> surface and tape residue on the Au surface. Inset: the corresponding height profile of monolayer–bilayer boundary, taken from the area highlighted by the white rectangle.

large, high-quality monolayer TMDCs is therefore crucial for both fundamental research and technology advancement.

Various techniques have been explored to improve the exfoliation yield. Gold is known to have a strong affinity for sulfur, which has been exploited to enhance the exfoliation of monolayer molybdenum disulfide.<sup>11,12</sup> However, little detail about the underlying mechanism was provided, and the largest MoS<sub>2</sub> size was limited to a few hundreds of microns. A comprehensive understanding of the gold-assisted large-area exfoliation at the atomic level is therefore necessary for devising techniques for the mass production of macroscopic TMDC monolayers, whose small lateral size has previously limited research and technological developments.

Here, we present a facile gold-assisted mechanical exfoliation of extraordinarily large monolayer MoS<sub>2</sub>, up to a centimeter size (Figure 1), and provide detailed investigation on the exfoliation mechanism. Raman spectroscopy, photoluminescence (PL) measurements, X-ray photoelectron spectroscopy (XPS), and scanning transmission electron microscopy (STEM) collectively reveal that the high-yield exfoliation is facilitated by van der Waals (vdW) interaction between the Au surface and the topmost MoS<sub>2</sub> layer. This interaction is stronger than the interlayer vdW interactions in bulk MoS<sub>2</sub>, therefore facilitating the exfoliation of large-area monolayer films. The cleanliness and smoothness of the Au surface are critical for the near-unity yield of monolayer MoS<sub>2</sub>, which can only be achieved on freshly deposited Au films exposed to air for <6 min. The short air exposure prevents the accumulation of airborne organic contaminants on the Au surface, which otherwise weakens the vdW forces between MoS<sub>2</sub> and Au and suppresses the exfoliation. The exfoliation yield also decreases significantly with increasing surface roughness of Au. These findings are confirmed by calculations from the first-principles density functional theory (DFT). The calculated vdW binding energies of several MoS<sub>2</sub>/Au heterostructures, with varied Au–

Mo separations and surface roughness, show excellent agreement with the experiments. We successfully applied this exfoliation technique to a variety of metal chalcogenides, including MoSe<sub>2</sub>, WS<sub>2</sub>, WSe<sub>2</sub>, MoTe<sub>2</sub>, WTe<sub>2</sub>, and GaSe (Supporting Figure S1), and found that the monolayer yield is generally near-unity, limited only by the size of the parent bulk crystal.

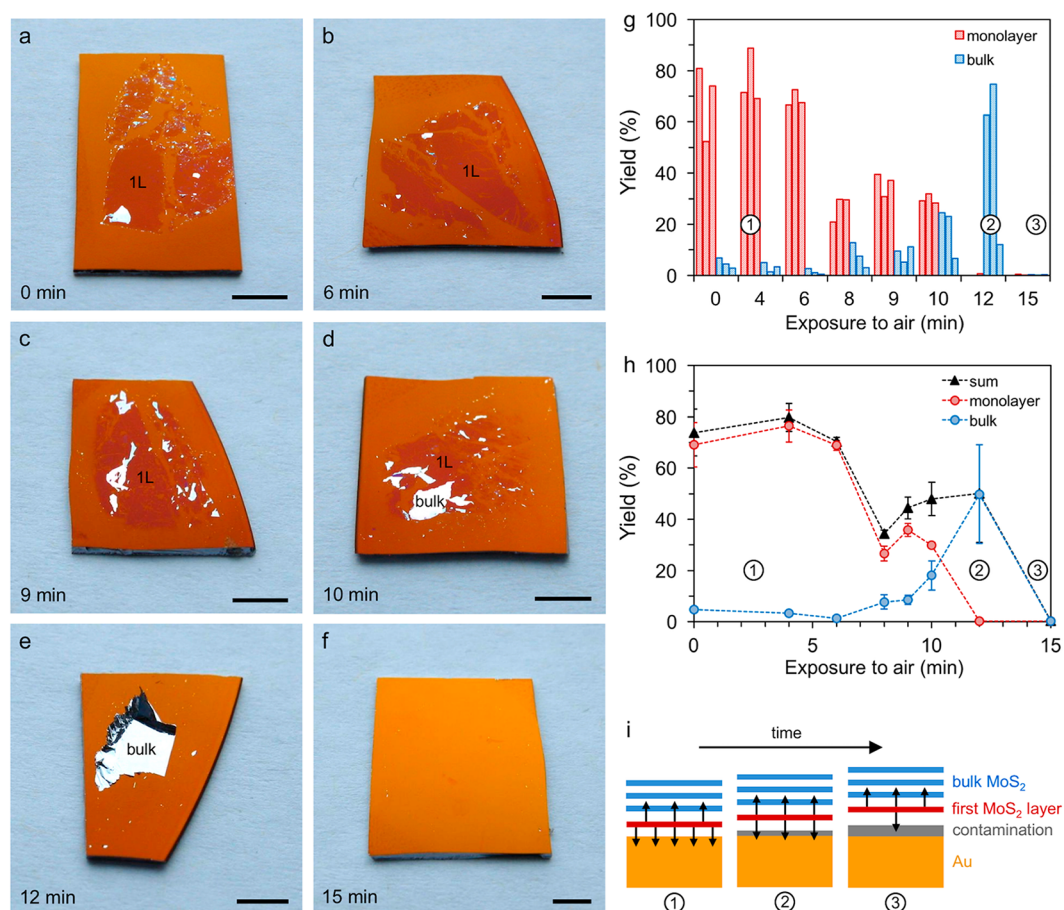
We further discovered intriguing interactions between monolayer MoS<sub>2</sub> and the underlying Au. Electrochemical characterization, using voltammetry and scanning electrochemical microscopy (SECM), reveals that the surface density of electronic states (DOS) of MoS<sub>2</sub> is strongly modulated by the underlying Au and, conversely, that the Au substrate is endowed with the chemical properties of MoS<sub>2</sub>. This is manifested in strong passivation of the Au surface by the physisorbed monolayer MoS<sub>2</sub> for inner-sphere electron transfer, while the outer-sphere electron transfer is almost unaffected due to long-range electron tunneling. These intriguing properties bring opportunities for many applications in areas such as electrode modification and energy storage/conversion.

## RESULTS

### Exfoliation and Characterization of MoS<sub>2</sub> on Au.

Figure 1a shows a macroscopic optical image of MoS<sub>2</sub> exfoliated on a 7.5 nm-thick Au (111) grown by physical vapor deposition (PVD) on a SiO<sub>2</sub>/Si wafer with a 1 nm Ti adhesion layer. MoS<sub>2</sub> monolayers reach lateral dimensions close to 1 cm, limited only by the size and quality of the parent bulk crystal. The microscopic optical image in Figure 1b reveals good crystal uniformity with occasional breaks likely caused by lattice defects, surface contamination, and mechanical stress during exfoliation. The number of MoS<sub>2</sub> layers was unambiguously determined using optical microscopy, Raman spectroscopy, and atomic force microscopy





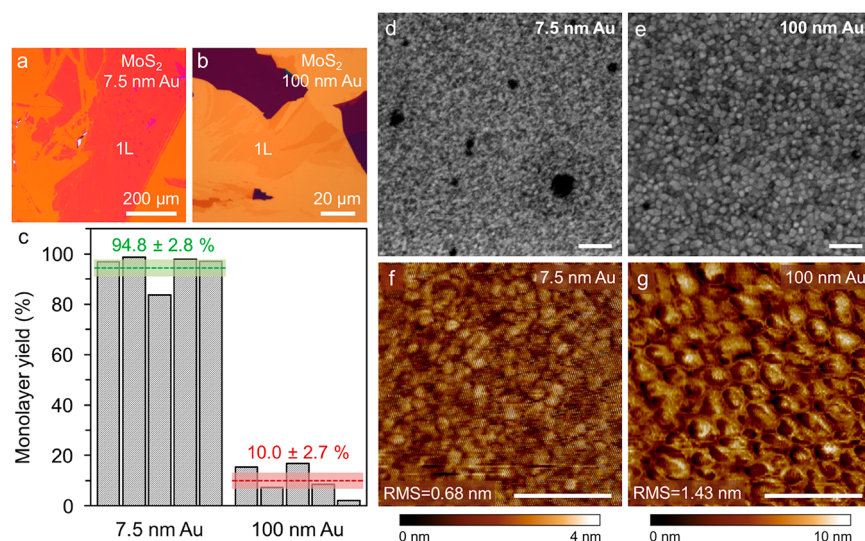
**Figure 2.** Dependence of the MoS<sub>2</sub> exfoliation yield on exposure to air. (a–f) Optical macrographs of MoS<sub>2</sub> exfoliated on 7.5 nm Au at different times after the Au exposure to air. All scale bars correspond to 5 mm. (g) Quantification of the monolayer (red) and bulk (blue) yields at different times (columns are yields at different areas of the sample). (h) Dependence of the average yield with time for monolayer (red circles), bulk (blue circles), and the sum of the two (black triangles). A constant area of 0.25 cm<sup>2</sup> (0.5 × 0.5 cm<sup>2</sup>) was used in all quantifications. (i) Schematic depiction of the evolution of the adhesion forces between different surfaces with the three limiting cases (1–3) assigned in (g–h). Note that the 0 min exfoliation was done immediately (within 10–15 s) after removal of the freshly grown Au from the vacuum chamber load-lock.

(AFM). The high optical contrast of monolayer MoS<sub>2</sub> allows direct counting of the layers (Figure 1c). The Raman spectra in Figure 1d show the two main vibrational modes,  $E_{2g}^1$  (in-plane) and  $A_{1g}$  (out-of-plane), whose intensities increase monotonically with increasing number of MoS<sub>2</sub> layers ( $\leq 4L$ ), as expected.<sup>13</sup> The frequency of both modes blueshifts with the increasing MoS<sub>2</sub> thickness, which is attributed to a stiffening of the vibrations upon layer addition. An anomalous redshift of the  $E_{2g}^1$  mode, due to stacking-induced changes in intralayer bonding, is often observed on insulating substrates.<sup>10,13,14</sup> Here we observe a blueshift of the  $E_{2g}^1$  mode, suggesting a strong interaction between MoS<sub>2</sub> and Au, which leads to an efficient charge transfer and screening of the long-range Coulomb interactions between MoS<sub>2</sub> layers. This is also consistent with the large frequency shifts of 8–10 cm<sup>-1</sup> between the 1L and 4L MoS<sub>2</sub>. AFM topography imaging across a monolayer–bilayer boundary gives a step-height of 9.8 Å (insets in Figure 1e), which is slightly higher than the theoretical thickness of 6.15 Å,<sup>3</sup> but in agreement with the literature.<sup>13,15</sup> No PL was observed in monolayer MoS<sub>2</sub> on Au (Supporting Figure S2) since it is completely quenched due to the conformal contact between MoS<sub>2</sub> and Au, consistent with previous reports.<sup>16</sup> The occasional observation of PL in monolayer MoS<sub>2</sub> on Au<sup>17,18</sup> could be caused by an increased physical separation due to

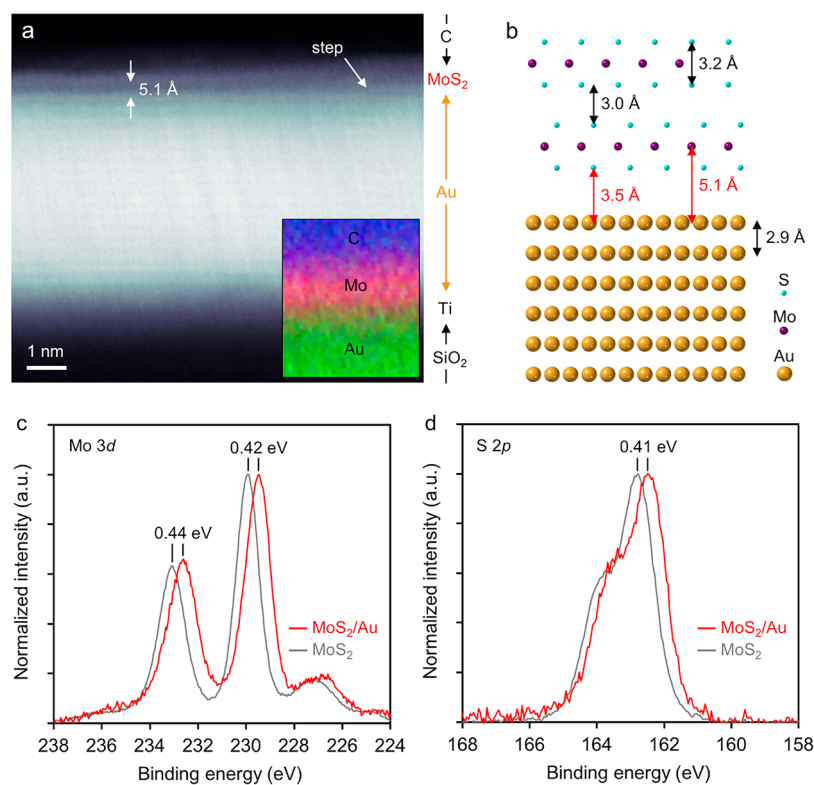
polymer residues and airborne contaminants at the MoS<sub>2</sub>/Au interface.

**Mechanism of the Large-Area Exfoliation.** We found that the exfoliation critically depends on the surface condition of Au, governed specifically by the Au roughness and the aging of the Au surface since its deposition under ultrahigh vacuum. The average area yield of exfoliation, expressed as the percentage of Au surface covered with MoS<sub>2</sub> (see Methods), is large (70–80%, predominantly monolayer) on freshly prepared Au, but gradually decreases with the time of Au exposed to air, with an increasingly larger proportion of bulk MoS<sub>2</sub> (Figure 2). After 15 min, almost no crystals are exfoliated (yield <0.5%). This suggests that the adhesion forces between MoS<sub>2</sub> and Au strongly depend on how long the Au surface has aged in air, which we summarize in the following three stages (Figure 2g–i): Initially (1), the adhesion between Au and the first MoS<sub>2</sub> layer is stronger than the interaction between the first MoS<sub>2</sub> layer and the rest of MoS<sub>2</sub>, resulting in the predominant exfoliation of monolayer MoS<sub>2</sub>. Gradually (2), the MoS<sub>2</sub>–Au adhesion weakens and becomes comparable to the interlayer interactions in bulk MoS<sub>2</sub>, facilitating more efficient exfoliation of thicker MoS<sub>2</sub> (governed by lattice defects), giving rise to a peak in the bulk yield (Figure 2g–h). In the end (3), the MoS<sub>2</sub>–Au adhesion becomes weaker than





**Figure 3.** Dependence of monolayer MoS<sub>2</sub> exfoliation yield on Au roughness. (a–b) Optical micrographs of MoS<sub>2</sub> exfoliated on 7.5 and 100 nm Au, respectively. (c) Quantification of the monolayer yield for 7.5 and 100 nm Au. A constant area of 12,100 μm<sup>2</sup> (110 × 110 μm<sup>2</sup>) was used in all quantifications. (d–e) SEM images of 7.5 and 100 nm Au substrates, showing continuous polycrystalline Au coverage with occasional voids and grain sizes varying from 10–20 nm to 40–60 nm for 7.5 to 100 nm-thick Au, respectively. (f–g) AFM images of the same substrates taken immediately after Au deposition, showing indentations within the grains of 100 nm Au and the measured RMS roughness of the surface. Scale bars in (d–g) correspond to 200 nm.

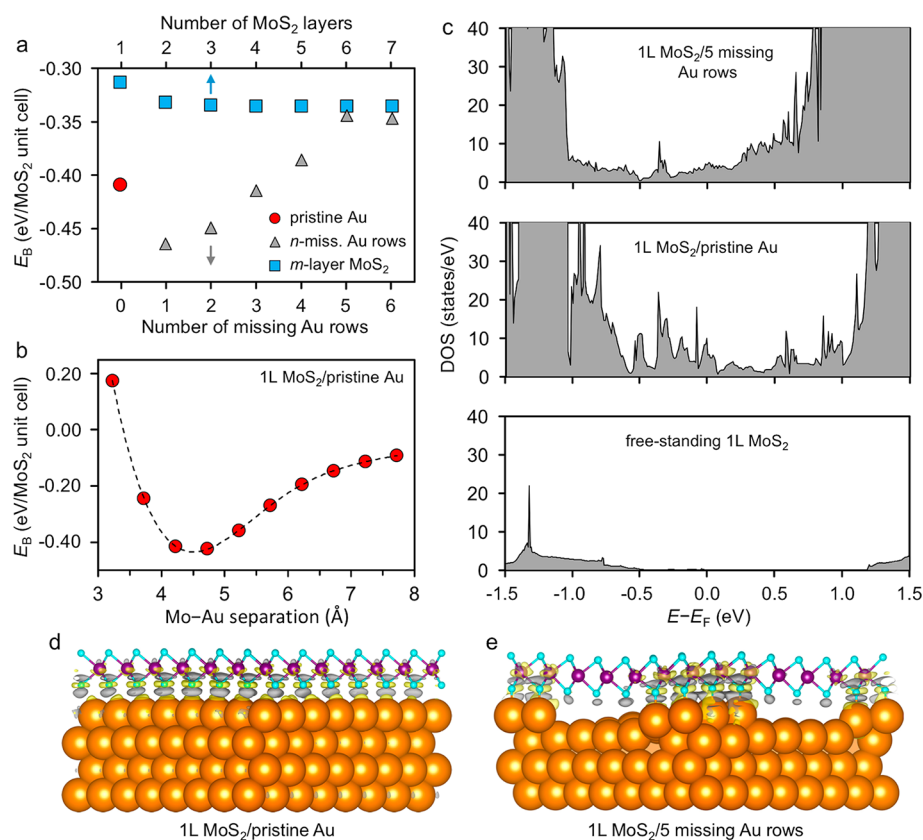


**Figure 4.** STEM and XPS characterization of monolayer MoS<sub>2</sub> on Au. (a) HAADF-STEM image of monolayer MoS<sub>2</sub> on 5 nm Au showing a region of clean MoS<sub>2</sub>/Au interface with an average Mo–Au separation of 5.1 Å. Inset: EELS composite image acquired from the middle region of the image, confirming the presence of Au, Mo, and C. (b) A schematic structure model of the MoS<sub>2</sub>/Au heterostructure. The distances in red are determined from HAADF-STEM, and the distances in black are the lattice parameters of bulk MoS<sub>2</sub> and Au.<sup>3,30</sup> (c–d) High-resolution XPS of Mo 3d and S 2p regions of monolayer MoS<sub>2</sub>/Au (red) and bulk MoS<sub>2</sub> (gray), showing a shift in the binding energy due to charge transfer. The binding energies were obtained from Gaussian fits of the baseline-subtracted Mo 3d and S 2p spectra.

the interlayer interaction in bulk MoS<sub>2</sub>, and the exfoliation yield is negligible.

The above phenomenon is caused by the adsorption of organic airborne contaminants, which transform the freshly

deposited Au surface from hydrophilic to hydrophobic. This was shown by Smith, who confirmed that while a clean Au surface is hydrophilic, exposure to air (but also prolonged dwell time under vacuum) leads to the build-up of a



**Figure 5.** vdW DFT calculations of the MoS<sub>2</sub>–Au interactions. (a) Binding energies determined for several different systems of monolayer MoS<sub>2</sub> on: pristine Au (111), Au (111) with a different number ( $n$ ) of missing Au rows, and  $m$ -layer MoS<sub>2</sub>. (b) Binding energy of monolayer MoS<sub>2</sub> on pristine Au as a function of the separation between Mo and Au atomic planes. The equilibrium separation was determined to be 4.5 Å, in good agreement with the experimental value from HAADF-STEM. (c) DOS for free-standing monolayer MoS<sub>2</sub> (bottom panel), monolayer MoS<sub>2</sub> on pristine Au (middle panel), and monolayer MoS<sub>2</sub> on Au with 5 missing Au rows (top panel). (d–e) Charge density differences calculated for monolayer MoS<sub>2</sub> on: pristine Au (111) (d), 5 missing Au rows (e), plotted as  $\Delta\rho = \rho[\text{Au} + \text{MoS}_2] - \rho[\text{Au}] - \rho[\text{MoS}_2]$ , where the three latter terms are the total charge densities of monolayer MoS<sub>2</sub>/Au, Au slab, and monolayer MoS<sub>2</sub>, respectively.

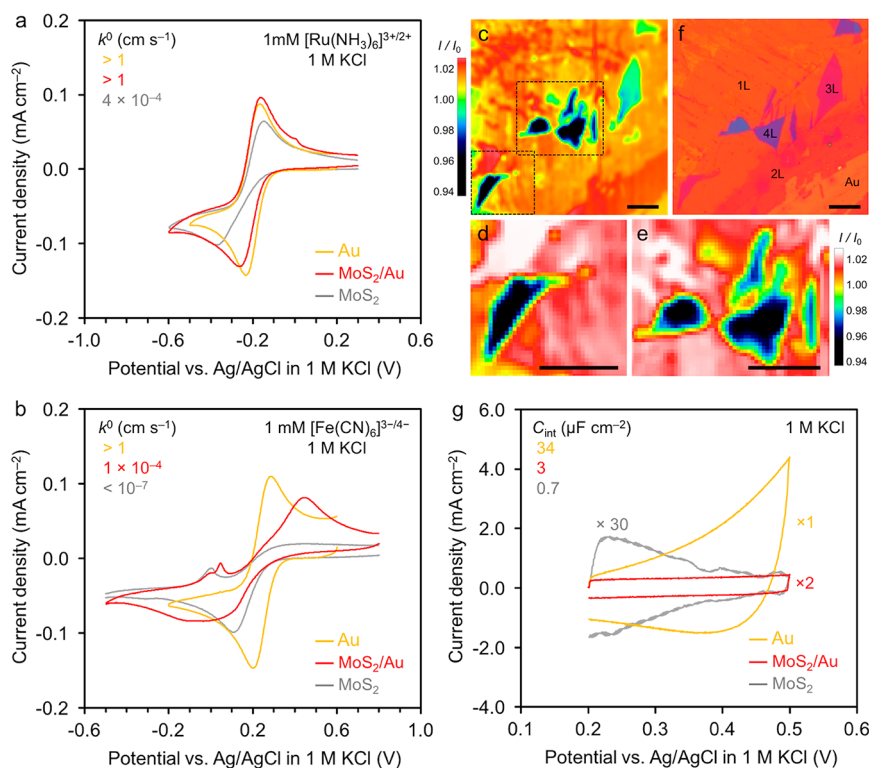
submonolayer of carbonaceous contamination, which quickly turns the Au surface hydrophobic.<sup>19</sup> This was manifested by an abrupt increase of the water contact angle (WCA) on Au by about 30°–40° within 10 min. Indeed, we found that the WCA on Au exposed to air rapidly increases by 15°–30° in the first 15 min (Supporting Figure S3), following the same trend as the exfoliation yield (Figure 2). The contamination layer increases the separation between MoS<sub>2</sub> and Au, weakens the adhesion forces between the two, and consequently reduces the exfoliation yield.

We further found that the yield of monolayer MoS<sub>2</sub> notably decreases with increasing thickness of the Au films, as shown in Figure 3a–c for 7.5 and 100 nm-thick Au. The scanning electron microscopy (SEM) images in Figure 3d–e show that the surface of the 7.5 nm Au is smoother than that of the 100 nm Au, which is further quantified by the AFM topography images in Figure 3f–g. The higher surface roughness of the thicker Au film therefore appears to weaken the vdW interactions between Au and MoS<sub>2</sub>, due to increased physical separation at surface depressions, also supported by theoretical calculations below. The best exfoliation results are achieved on thin Au films of 5–20 nm with root-mean-square (RMS) roughness <1 nm. Despite the polycrystalline nature of the Au films evident from SEM and AFM, the predominant crystal orientation was found to be Au (111) by X-ray diffraction (XRD) measurements (Supporting Figure S4). This is typical

for Au PVD films grown on various substrates, using different deposition conditions,<sup>20–22</sup> and expected from the lowest energy of the Au (111) surface.<sup>23</sup>

**The Nature of MoS<sub>2</sub>–Au Interaction.** The MoS<sub>2</sub> interaction with Au was predicted to be of vdW nature due to weak hybridization.<sup>24,25</sup> However, few have provided direct experimental evidence of the Au–MoS<sub>2</sub> interaction. Here we employed STEM to image the separation between monolayer MoS<sub>2</sub> and Au. The left-hand side of the high-angle annular dark-field (HAADF)-STEM image in Figure 4a shows a region of a clean monolayer MoS<sub>2</sub>/Au interface. The average closest separation between the center of the Mo and Au planes is 5.1 ± 0.3 Å, close to the value of 4.5 Å obtained from theoretical calculations below. This implies a 3.5 Å spacing between the Au and S planes, ~17% larger than the interlayer vdW spacing in bulk MoS<sub>2</sub> (3.0 Å) and ~59% larger than a covalent Au–S bond (2.2 Å),<sup>3,26</sup> confirming that the MoS<sub>2</sub>–Au interaction is strong vdW rather than covalent in nature. Monolayer MoS<sub>2</sub> maintains the spacing due to its conformity with the underlying Au, as seen from the step in the top-right area of Figure 4a. A schematic model of the MoS<sub>2</sub>/Au heterostructure is shown in Figure 4b.

We also employed XPS to further investigate the interaction between MoS<sub>2</sub> and Au. The high-resolution spectra of the Mo 3d and S 2p regions in Figure 4c–d reveal that the binding energies in monolayer MoS<sub>2</sub> decrease by ~0.4 eV in



**Figure 6.** Electrochemical characterization of MoS<sub>2</sub> on Au. (a–b) Cyclic voltammograms of 1 mM [Ru(NH<sub>3</sub>)<sub>6</sub>]<sup>3+/2+</sup> and 1 mM [Fe(CN)<sub>6</sub>]<sup>3-/4-</sup> reduction/oxidation in 1 M KCl at 50 mV s<sup>-1</sup>, respectively. Results for the bare Au surface (gold), monolayer MoS<sub>2</sub>/Au (red), and bulk MoS<sub>2</sub> (gray) are shown. (c) SECM image of different MoS<sub>2</sub> layers on Au, generated in feedback mode using 1 mM [Ru(NH<sub>3</sub>)<sub>6</sub>]<sup>3+/2+</sup> in 0.1 M KCl. (d–e) Magnified SECM images taken from regions highlighted in (c) by the black rectangles. (f) Corresponding optical image of the measured area. All scale bars correspond to 40 μm. (g) Cyclic voltammograms in 1 M KCl at 50 V s<sup>-1</sup> for the determination of the interfacial capacitance. All measurements were carried out under ambient light at room temperature, and argon-deaerated solutions were used in (a–b) and (g).

comparison to bulk MoS<sub>2</sub>. This suggests that there is a significant degree of charge transfer between monolayer MoS<sub>2</sub> and Au, consistent with the observed PL quenching. Almost identical shifts (0.4–0.5 eV) were observed in other MoS<sub>2</sub>–Au systems and explained by the formation of a Schottky barrier at the MoS<sub>2</sub>/Au interface<sup>27</sup> and charge transfer from Au to MoS<sub>2</sub>, leading to an increase of the electron density at the interface.<sup>28,29</sup> Crucially, the lack of changes in the shape and width of the XPS peaks in our work confirms that monolayer MoS<sub>2</sub> maintains its chemical identity upon exfoliation (detailed XPS spectra including the peak fittings are shown in Supporting Figure S5).

To further elucidate the interaction between monolayer MoS<sub>2</sub> and Au, we performed first-principles atomistic calculations for a range of systems. Figure 5a shows the binding energy ( $E_B$ , per MoS<sub>2</sub> unit cell) for monolayer MoS<sub>2</sub> on different systems: pristine Au (111) surface, Au surface with  $n$  missing Au rows, and on  $m$ -layer MoS<sub>2</sub>. The calculations suggest  $E_B = -0.41$  eV for monolayer MoS<sub>2</sub> on pristine Au (Figure 5a), which is stronger than the binding between monolayer MoS<sub>2</sub> and bulk MoS<sub>2</sub> ( $E_B = -0.34$  eV for  $m \geq 5$ ), supporting the predominant exfoliation of monolayers, in agreement with our earlier interpretation and other theoretical calculations.<sup>25,31</sup> The binding energy between Au and MoS<sub>2</sub> rapidly decreases with increasing Au–MoS<sub>2</sub> separation (Figure 5b), explaining why a submonolayer contamination significantly inhibits the exfoliation.

Introduction of a small number of surface Au vacancies or adatoms is found to have negligible effects on the binding

energy (–0.42 eV). Conversely, when a large vacancy in the form of  $n$  missing surface rows is introduced to the Au surface, the binding energy changes significantly. As shown in Figure 5a, the  $E_B$  is initially high for  $n = 1$  but decreases to reach a similar magnitude to that of pristine Au for  $n = 3$ . The increased number of active sites with large amount of dangling bonds and charge density at the Au surface initially leads to stronger Au–S interaction, as seen for  $n \leq 3$ . For  $n > 3$ , the comparably poorer conformity of MoS<sub>2</sub> to Au weakens this interaction, which becomes comparable to that of bulk MoS<sub>2</sub> for  $n = 5$  and 6. These calculations are consistent with the observation that the smooth, thin Au can produce large-area exfoliation, while the rougher, thicker Au cannot. This reinforces our conclusion that the surface quality of Au is critical for the success of large-area exfoliation.

The most striking difference occurs in the electronic structure of MoS<sub>2</sub>. The semiconducting character of free-standing MoS<sub>2</sub> changes to metallic in the monolayer MoS<sub>2</sub>/Au heterostructure (Figure 5c). Indeed, the Bader charge analysis indicates a system-dependent electron transfer from Au to the monolayer MoS<sub>2</sub> (Supporting Figure S6). The resulting increase of the DOS at the Fermi level ( $E_F$ ) has a direct impact on the electrochemical behavior discussed below. These states, which originate mainly from S 3s– $p$  orbitals and Mo 4d orbitals, reside at the MoS<sub>2</sub>/Au interface (Figure 5d–e).

**Electrochemical Characterization of the MoS<sub>2</sub>–Au Heterostructure.** The large-area monolayer MoS<sub>2</sub> on Au is an excellent platform for investigations previously limited by



the small lateral crystal size. Figure 6 shows the electrochemical characterization of three macroscopic ( $\sim 0.5 \text{ mm}^2$ ) surfaces: bare Au (gold), monolayer  $\text{MoS}_2/\text{Au}$  (red), and bulk  $\text{MoS}_2$  (gray). The kinetics of the reduction/oxidation of  $[\text{Ru}(\text{NH}_3)_6]^{3+/2+}$  and  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  used as redox mediators, quantified by the heterogeneous electron-transfer rate constant ( $k^0$ ), vary greatly on these surfaces, as illustrated by the voltammograms in Figure 6a–b. Au exhibits the fastest, reversible kinetics for both mediators ( $k^0 > 1 \text{ cm s}^{-1}$ ), expected due to their fast self-exchange rates and the high DOS of Au. The  $k^0$  values on bulk  $\text{MoS}_2$  are  $\sim 4 \times 10^{-4} \text{ cm s}^{-1}$  and  $< 10^{-7} \text{ cm s}^{-1}$  for  $[\text{Ru}(\text{NH}_3)_6]^{3+/2+}$  and  $[\text{Fe}(\text{CN})_6]^{3-/4-}$ , respectively, in agreement with previous work.<sup>32</sup> The kinetics of  $[\text{Ru}(\text{NH}_3)_6]^{3+/2+}$ , which is thought to be an outer-sphere mediator only sensitive to the surface DOS, are reversible on monolayer  $\text{MoS}_2/\text{Au}$  and similar to that of bare Au (Figure 6a), indicating strong electronic coupling and charge transfer between  $\text{MoS}_2$  and Au, in agreement with our results above. The SECM imaging of the  $[\text{Ru}(\text{NH}_3)_6]^{3+/2+}$  redox activity of  $\text{MoS}_2$  on Au (Figure 6c–e) shows a clear correlation with the corresponding optical image (Figure 6f). As the number of  $\text{MoS}_2$  layers decreases, the normalized current ( $I/I_0$ ) increases, indicating a transition from the semiconducting multilayer  $\text{MoS}_2$  to the metallic monolayer  $\text{MoS}_2/\text{Au}$  in agreement with the predicted increase in DOS (Figure 5f), with the highest current observed for the bare Au. In contrast, the kinetics of  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  on monolayer  $\text{MoS}_2/\text{Au}$  slows down by 6 orders of magnitude to  $\sim 1 \times 10^{-4} \text{ cm s}^{-1}$  within the quasi-reversible regime (Figure 6b). The strong suppression of the kinetics of  $[\text{Fe}(\text{CN})_6]^{3-/4-}$ , which is an inner-sphere mediator interacting strongly with the electrode surface, indicates that the Au surface is strongly passivated by the  $\text{MoS}_2$  monolayer. In addition, the open circuit potential in 1 M KCl was found to be the same for monolayer  $\text{MoS}_2/\text{Au}$  and bulk  $\text{MoS}_2$  (0.000 V), but considerably different for Au (0.034 V). No dependence on illumination was observed for monolayer  $\text{MoS}_2/\text{Au}$ , as expected. These results suggest that monolayer  $\text{MoS}_2/\text{Au}$  is chemically similar to  $\text{MoS}_2$  but has an increased DOS acquired from the underlying Au. In other words, monolayer  $\text{MoS}_2/\text{Au}$  is thermodynamically closer to bulk  $\text{MoS}_2$  but kinetically closer to Au. These characteristics could be effectively used to discriminate between the outer- and inner-sphere electron-transfer mechanisms. A similar concept of electronic modulation was recently demonstrated for graphene on Au.<sup>33</sup>

Capacitance measurements in 1 M KCl also reveal significant differences between the three surfaces (Figure 6g). The interfacial (measured) capacitance  $C_{\text{int}}$  is a sum of two capacitances in series:  $C_{\text{int}}^{-1} = C_{\text{SC}}^{-1} + C_{\text{EDL}}^{-1}$ , where  $C_{\text{SC}}$  and  $C_{\text{EDL}}$  are the space charge and electrical double-layer capacitances at the electrode/liquid interface.<sup>34</sup>  $C_{\text{int}} = 34 \mu\text{F cm}^{-2}$  for bare Au and is equal to  $C_{\text{EDL}}$  due to the efficient Thomas-Fermi screening in metals ( $C_{\text{SC}} \gg C_{\text{EDL}}$ ).  $C_{\text{int}} = 0.7 \mu\text{F cm}^{-2}$  in bulk  $\text{MoS}_2$  and is equal to  $C_{\text{SC}}$ , since in semiconductors  $C_{\text{SC}} \ll C_{\text{EDL}}$ . An intermediate  $C_{\text{int}} = 3 \mu\text{F cm}^{-2}$  in monolayer  $\text{MoS}_2/\text{Au}$  is mostly dominated by  $C_{\text{SC}}$  ( $C_{\text{int}} \approx 0.9 C_{\text{SC}}$ , calculated using the  $C_{\text{EDL}}$  determined for Au). The shapes of the voltammograms in Figure 6g reflect the differing electronic band structures of the three different surfaces. The metallic Au behaves as a typical pseudocapacitor with a redox (faradaic) activity superimposed over the double-layer charging at high potentials. The response of bulk  $\text{MoS}_2$  is typical for an n-type semiconductor, with the higher currents at low potentials corresponding to the charge carrier accumu-

lation regime. Surprisingly, monolayer  $\text{MoS}_2/\text{Au}$  exhibits a rectangular-shaped voltammogram, indicating a purely capacitive (nonfaradaic) response, which originates solely from the double-layer charging. Such potential-independent capacitance response, which is typical of an electrochemical supercapacitor,<sup>35,36</sup> is significantly different from the responses of bulk  $\text{MoS}_2$  and bare Au. This suggests that monolayer  $\text{MoS}_2/\text{Au}$  system (and potentially many other TMDCs/Au) could provide an interesting platform for the design of supercapacitors and other devices for electrochemistry, photocatalysis, and energy storage/conversion.

## CONCLUSIONS

We present a facile gold-assisted mechanical exfoliation of extraordinarily large monolayer  $\text{MoS}_2$ , up to a centimeter-scale, limited mainly by the parent bulk crystal size. We carried out detailed spectroscopic and microscopic characterizations together with first-principles DFT calculations to provide an atomic-level understanding of the exfoliation mechanism. The large-area exfoliation is found to be facilitated by strong vdW interaction between Au and the topmost layer of  $\text{MoS}_2$ , which critically depends on the cleanliness and smoothness of the Au surface. Near-unity yield of monolayer  $\text{MoS}_2$  is achieved on freshly grown thin Au films (5–20 nm) with RMS roughness  $< 1 \text{ nm}$  and exposure to air for  $< 6 \text{ min}$ . The yield becomes negligible after 15 min of exposure due to the accumulation of airborne contamination on Au. Such previously unknown stringent experimental conditions have important consequences for the development of large-area exfoliation and growth techniques. We have successfully extended the technique to  $\text{MoSe}_2$ ,  $\text{WS}_2$ ,  $\text{WSe}_2$ ,  $\text{MoTe}_2$ ,  $\text{WTe}_2$ , and  $\text{GaSe}$ . Electrochemical characterization reveals that the surface DOS of monolayer  $\text{MoS}_2$  is strongly modulated by the underlying Au, turning it from semiconducting to metallic. Conversely, the subnanometer-thick monolayer  $\text{MoS}_2$  strongly passivates the chemistry of the underlying Au electrode, but does not prevent charge transfer from solution to Au. Our work sheds light on the mechanism of gold-assisted exfoliation, provides important guidance for the production of macroscopic TMDC monolayers, and has important implications for many research areas, such as electrode modification, photovoltaics, and photocatalysis.

## METHODS

**Materials Preparation.** PVD films were prepared with a DC magnetron sputtering system (Kurt J. Lesker CMS-A) using targets ( $> 99.99\%$ ) from Testbourne Ltd. (Ti) and Birmingham Metal Ltd. (Au). The  $\text{SiO}_2/\text{Si}$  wafers (IDB Technologies Ltd.) were cleaned in acetone and isopropanol and blow-dried before placing in a load-lock, evacuated to  $\sim 10^{-7}$  Torr by a turbomolecular pump (Shimadzu TMP-303LM) backed by a mechanical pump (Adixen ACP 15). They were then transferred to the deposition chamber, evacuated to  $\sim 10^{-9}$  Torr using a cryopump (Brooks CTI-Cryogenics 10F). All the pumps were oil-free, and the residual gas environment was continuously monitored by mass spectrometry prior to the sputtering. Depositions were done at room temperature under a 5 SCCM Ar flow at partial pressure of  $10^{-3}$  Torr. A Ti adhesion layer was deposited at  $15^\circ$  incidence at a rate of  $0.5 \text{ \AA s}^{-1}$  before the Au deposition. The Au layer was deposited at a  $33^\circ$  incidence at a rate of  $1.5 \text{ \AA s}^{-1}$ . Both targets were presputtered prior to the deposition. All metal chalcogenides were exfoliated from bulk crystals (Manchester Nanomaterials Ltd.) directly onto the Au substrates using the “scotch-tape” method reported elsewhere,<sup>37</sup> applying a downward pressure, rather than lateral rubbing. The crystals were exfoliated, and therefore exposed to air, immediately prior to the contact with Au ( $< 5 \text{ s}$ ) in order to

minimize the airborne contamination of their surface. Bulk crystals were either natural (molybdenite) or synthesized by chemical vapor transport (MoSe<sub>2</sub>, MoTe<sub>2</sub>, WS<sub>2</sub>, WSe<sub>2</sub>, WTe<sub>2</sub>, and GaSe). The exfoliation and subsequent characterization (except the vacuum techniques) were performed at 20–23 °C and 50–70% relative humidity.

**Microscopy, Spectroscopy, Reflectivity, and Diffraction Characterization.** Macroscopic optical images were taken using a Canon PowerShot A720 IS digital camera. Microscopic optical images were taken using a BX51 microscope (Olympus Corp) with an Infinity2-2 CCD camera and Infinity Capture 6.2 software (Lumenera Corp). The exfoliation yield should ideally be calculated as the ratio between the area of the exfoliated film and the contact surface area of parent MoS<sub>2</sub> crystals. However, as the size of the parent crystals and their surface defect and impurity densities vary for different exfoliations, such approach is impractical. To circumvent this uncertainty, we used a constant sampling area (rather than the actual parent crystal size) for each yield comparison. For Figure 2, identical square areas of 0.5 × 0.5 cm<sup>2</sup> were chosen at three different locations on each of the sample using Fiji/ImageJ software (v.2.0) to maximize the area of exfoliated MoS<sub>2</sub> films inside the square boxes. The exfoliation yield (*Y*) was then calculated as  $Y (\%) = A_M/A_S \times 100\%$ , where *A<sub>M</sub>* is the area of exfoliated MoS<sub>2</sub> inside each of the square box and *A<sub>S</sub>* is the sampled area. The results are shown in Figure 2g. Similarly, a sampling area of 110 × 100 μm<sup>2</sup> was used to calculate the roughness-dependent exfoliation yields in Figure 3. Such a method allows meaningful quantitative comparison of the yield dependence on the surface condition of Au and provides a quantitative assessment of the capability of the technique. 532 or 633 nm lasers of 1 mW power focused through a 100× MPlan N objective (Olympus Corp) to ~1 μm<sup>2</sup> spot size were used for Raman spectroscopy and PL measurements, collected by a Jobin Yvon HR640 Raman spectrometer and Andor MCD 2.6 software. AFM measurements were performed with a Digital Instruments Veeco Dimension 300 AFM with 30 nm Si-SPM tips (Nanosensors) in tapping mode. The contact angle measurements were carried out using a Dino-Lite Edge AM7115MZTL Digital microscope and in-house rotating-state goniometer. A field emission JEOL JSM-6500F SEM at an accelerating voltage of 5–10 kV was used for SEM imaging. The X-ray reflectivity and XRD, taken using a D8 Discover diffractometer (Bruker Inc.), were used to determine the thickness and crystallographic orientation of Au, respectively. XPS was performed using a nonmonochromatic Mg K<sub>α</sub> source, collecting the photoelectrons at glancing incidence from the surface normal, from an area of ~0.8 cm<sup>2</sup>. The spectrometer energy analyzer work function was calibrated using an Ag standard. Tougaard baseline subtraction and normalization to the maximum intensity were applied to all spectra. STEM samples were prepared in a FEI Strata 400 focused ion beam using a standard cross-section fabrication procedure.<sup>38</sup> STEM and electron energy loss spectroscopy (EELS) imaging were performed using a NION UltraSTEM operated at 100 keV.

**Computational Methods.** First-principles *ab initio* calculations were carried out with the Vienna *ab initio* simulation package.<sup>39</sup> The generalized gradient approximation along with the Tkatchenko–Scheffler method were used to correct the energy due to dispersion interactions.<sup>40,41</sup> This was used along with a 345 eV plane-wave cutoff. The projector augmented wave pseudopotentials were utilized to model the bonding environment between atoms.<sup>42,43</sup> Energy convergence for the electronic and ionic minimizations was set at 1 × 10<sup>-5</sup> and 1 × 10<sup>-4</sup> eV, respectively. Au (111) and monolayer MoS<sub>2</sub> unit cells were relaxed with a 12 × 12 × 6 and 12 × 12 × 1 Γ-centered k-grid, respectively. From this an 8 × 8 × 4 Au surface was created as well as a 7 × 7 × 1 MoS<sub>2</sub> supercell. This resulted in ~1.0% lattice mismatch, which was applied to the Au surface to avoid spurious variation on the strain sensitive MoS<sub>2</sub> energetics. The bottom two Au layers were fixed as bulk, while the top two Au layers, representing the surface, were allowed to relax. After the introduction of defects, the Au surface was allowed to relax further. The MoS<sub>2</sub> supercell was then placed on top of the Au surface, and the MoS<sub>2</sub>/Au heterostructure was allowed to relax once again. Binding energies of 1L MoS<sub>2</sub> on *m*-

layer MoS<sub>2</sub> were calculated as  $E_B = E_{(m+1)L} - E_{mL} - E_{1L}$ , where  $E_{(m+1)L}$ ,  $E_{mL}$ , and  $E_{1L}$  are the total energies of (*m* + 1)-, *m*-, and 1-layer MoS<sub>2</sub>, respectively. Binding energies of 1L MoS<sub>2</sub> on Au systems were calculated as  $E_B = E_{1L+Au} - E_{Au} - E_{1L}$ , where  $E_{1L+Au}$  and  $E_{Au}$  are the total energies of 1L MoS<sub>2</sub> on Au and the Au slab, respectively.

**Electrochemical Measurements.** All electrochemical measurements were performed using a CHI920D potentiostat (CH Instruments, Inc.). The electrochemical setup is schematically shown in Supporting Figure S7. The *k*<sup>0</sup> values were estimated from the peak-to-peak separation in the voltammograms (10–400 mV s<sup>-1</sup>). This was done using the Nicholson method and the Klingler–Kochi method in the reversible-quasireversible and irreversible regime, respectively, following the methodology reported elsewhere (eqs (1) and (2) in ref 44, respectively). Diffusion coefficients of 7.4 (5.3) × 10<sup>-6</sup> cm<sup>2</sup> s<sup>-1</sup> and 7.7 (6.2) × 10<sup>-6</sup> cm<sup>2</sup> s<sup>-1</sup> for the oxidized (reduced) forms of [Ru(NH<sub>3</sub>)<sub>6</sub>]<sup>3+/2+</sup> and [Fe(CN)<sub>6</sub>]<sup>3-/4-</sup>, respectively, were determined from voltammetry at polished 2 mm diameter Pt disk using the Randles–Ševčík equation.<sup>35</sup> The interfacial capacitance (*C<sub>int</sub>*) was calculated by integrating the current over the potential range as described elsewhere and averaged for scan rates between 10–50 V s<sup>-1</sup>.<sup>45</sup> The reference potential used here (Ag/AgCl in 1 M KCl) is +0.232 V on the standard hydrogen electrode scale, taking the activity coefficient of Cl<sup>-</sup> into account.<sup>46</sup> SECM was obtained using a 1 μm diameter Pt ultramicroelectrode probe with a glass radius of ~25 μm (Heka), operated in feedback mode at a working distance of *ca.* 1 μm. The probe potential was set to reduce/oxidize [Ru(NH<sub>3</sub>)<sub>6</sub>]<sup>3+/2+</sup> under diffusion control, while the substrate was unbiased. The probe current (*I*) measured near the surface was normalized to the current in bulk solution (*I*<sub>0</sub>).

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.8b06101.

Optical micrographs of various metal chalcogenide monolayers exfoliated on Au substrate; PL measurement of MoS<sub>2</sub> on Au; water contact angle measurement on Au as a function of its exposure to air; XRD measurement of the Au films; detailed XPS spectra including peak fittings; Bader charge-transfer analysis of MoS<sub>2</sub>/Au heterostructures; schematic of electrochemical setup (PDF)

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### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This project has received funding from the UK EPSRC (grant no. EP/N025938/1), the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement no. 746685, and the UK National Measurement System (Department of Business, Energy & Industrial Strategy) and was supported by Seagate Technology (Ireland) under SOW no. 00077300.0 and the

Royal Academy of Engineering under the Research Chairs and Senior Research Fellowships Scheme, CCMR (NSF-DMR-1719875), PARADIM (NSF-DMR-1539918), DOE CSGF (DE-FG02-97ER25308), NSF-CHE-1708025, and the Alfred P. Sloan Foundation. E.J.G.S. acknowledges the use of computational resources from the UK national high-performance computing service (ARCHER) for which access was obtained *via* the UKCP consortium (EPSRC grant ref EP/K013564/1), the UK Materials and Molecular Modelling Hub for access to THOMAS supercluster, which is partially funded by EPSRC (EP/P020194/1). The Queen's Fellow Award (M8407MPH), the Enabling Fund (A5047TSL), and the Department for the Economy (USI 097) are also acknowledged.

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