Highly Efficient Bulk-Crystal-Sized Exfoliation of 2D Materials under Ultra-High Vacuum

Golam Haider, Bazlul Karim[†], Jan Plšek[†], Michele Gastaldo[†], and Martin Kalbáč*

J. Heyrovský Institute of Physical Chemistry, Czech Academy of Sciences, Dolejškova 2155/3, 182 23 Prague 8, Czech Republic

[†] These authors have equally contributed as second authors to this work.

* Corresponding authors, email: <u>martin.kalbac@jh-inst.cas.cz</u>

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Abstract:

Two-dimensional (2D) materials represent the ultimate limit of miniaturization along the vertical direction, where several fascinating quantum mechanical effects—that are otherwise inaccessible—appear, generating widespread interest in fundamental and applied research. However, the preparation of scalable monolayers is a requirement that is hindered because of the lack of suitable synthesis and manipulation techniques. Here, we report a facile approach for obtaining bulk-crystal-sized 2D monolayers with a yield of almost 100% under ultra-high vacuum (UHV) conditions. We have exfoliated MoS₂ on Au and Ag substrates to demonstrate the exfoliation process, where the spectroscopic measurements suggest a very strong dispersive interaction between the metal substrate and MoS₂, resulting in a high strain field on the topmost layer of the bulk crystal, which is substantially relaxed in the subsequent layer. This vertically inhomogeneous distribution of the strain field reduced the magnitude of interlayer van der Waals interactions, resulting in the high selectivity of monolayer exfoliation. Along with the

scalable exfoliation of monolayers, our method also paves a route to obtain 2D monolayers of materials that are unstable under ambient conditions.

Graphical abstract



Introduction

The groundbreaking discovery of graphene by top-down exfoliation of bulk graphite using Scotch tape led to the foundation of 2D material research.¹ Since then, this technique has been one of the most successful and widely utilized techniques to produce monolayer materials.^{2–4} However, the materials produced by this technique are unpractically small in size and often appear together with a very high ratio of bulk layers. Moreover, the involved viscoelastic stamps in this process release chemical fingerprints on the materials, altering the intrinsic nature of the produced atom-thin layers.^{2,5} The exfoliation of 2D materials under ambient conditions has

been a major shortcoming for direct probing of electronic states, as those measurement techniques require extremely clean materials, which has been achieved by post-preparation cleaning processes.^{6,7} Moreover, because of their high reactivity toward oxygen and water, several key materials, such as high-temperature magnets based on transition metal halides, oxyhalides, and tellurides, could not be exfoliated even inside the controlled atmosphere of a glove box, which greatly hampered the experimental progress of the field.^{8–10}

Several bottom-up techniques to synthesize large-area monolayers have been developed over the last two decades.^{11,12} Great progress has been made in chemical vapor deposition (CVD), attaining large-area synthesis of layers.^{13,14} However, CVD requires rigorous optimization to obtain monolayers of unconventional materials and even more for scalable synthesis. Similar challenges were also encountered by the molecular beam epitaxy (MBE) technique.¹⁵ The materials produced by atomic layer deposition (ALD) are generally amorphous in nature.¹⁶

Mechanical exfoliation of crystals with the assistance of gold tape has provided ultra-large area monolayers.^{17,18} This technique primarily relies on the dispersive interaction between metals and the topmost layer of the bulk crystal, where the interaction potential can be higher than the interlayer interaction potential of the bulk crystals.^{18,19} For the exfoliation, gold was directly deposited on the bulk crystals and cleaved using adhesive tape.²⁰ However, the direct deposition of metals often causes substitution doping of Au atoms in the 2D layers, which could be eventually avoided by Au-film-assisted exfoliation by placing bulk crystals on a pre-deposited metal layer.^{18,19,21} However, taking advantage of the high dispersive interaction potential of this process is challenging because of the aging of the Au films. The fresh Au surface tends to interact with the environment and quickly saturates with chemical impurities, which prevents efficient exfoliation.¹⁹ For other noble metals such as Ag, the interaction with the surrounding impurities is even stronger and hence surface passivation is faster, resulting in no possibility of exfoliation under ambient conditions or in a glove box, where the remnant oxygen and water

are sufficient to saturate the surface of the fresh Ag film. Ultra-high vacuum (UHV) conditions could substantially extend the lifetime of the fresh metal films. Hence, single and polycrystalline metal films cleaned under UHV conditions have been recently utilized for the exfoliation of 2D materials, and monolayer 2D materials sized in the hundreds of microns have been obtained.^{22,23} However, a thorough cleaning of the surface by plasma etching or ion bombardment is challenging. On the other hand, the metal films prepared directly under UHV conditions offer a chemically unperturbed surface and can lead to better exfoliation results.

The exfoliation yield is related to the interaction between the metal and 2D layers that can be directly probed by Raman spectroscopy.^{24,25} For instance, the MoS₂ monolayer changes its crystalline symmetry from freestanding D_{3h} to C_{3v} group while interfaced with Au.^{26,27} This alters the vibrational selection rules resulting the activation of few forbidden Raman modes, which we probed in our previous study using near-field plasmonic enhancement of samples prepared under ambient conditions.²⁶ We also observed that the obtained intensity varies depending on the number of layers, which is due to partial contamination of the Au surface during the fabrication process.^{19,26} This further limits the exfoliation yield and layer homogeneity.

Scalable synthesis of uniform monolayers thus requires full utilization of the dispersive interaction, which is only possible through the preparation of metal films and exfoliation without exposing the metals to the reactive environment, as we demonstrated here. We probed the layer continuity by optical microscopy imaging. The crystalline quality was obtained by recording macroscopic (~ 1 mm spot) low-energy electron diffraction (LEED) measurement. The interaction between the metal and 2D layer was further supported by X-ray photoelectron spectroscopy (XPS) measurements.

Results and discussion



Figure 1: Optical images of monolayer MoS_2 on exfoliated $\mathbf{a} - \mathbf{c}$) Au/Ti and $\mathbf{d} - \mathbf{f}$) Ag/Ti. The bulk crystals dimension has been marked by continuous lines in \mathbf{a} and \mathbf{d} . The high-resolution microscopic images of the monolayer regions have been presented in $\mathbf{b} - \mathbf{c}$ and $\mathbf{e} - \mathbf{f}$ for the MoS₂ on Au and Ag respectively.

Large-area layers

MoS₂ single layers were exfoliated on ~7 nm/3 nm Au/Ti or Ag/Ti films deposited on SiO₂/Si in our custom-made UHV exfoliation system equipped with *in-situ* e-beam evaporator, where metal deposition and subsequent exfoliation were performed in the same UHV chamber at the base vacuum ~10⁻¹⁰ Torr. A detailed description of the system and the exfoliation technique is provided in the methodology section. Videography of the exfoliation process is presented in the Supplementary Videos 1 (touching) and 2 (retraction), which were recorded using a camera fitted to a viewport of the exfoliation system. The *in-situ* optical images of the exfoliated MoS₂ single layers on Au/Ti and Ag/Ti substrates are presented in **Figures 1** (**a** – **c**) and (**d** – **f**), respectively. The microscopic images were captured by an optical microscope attached to the top viewport of the exfoliation system. A discussion of the exfoliation process is provided in the methodology section. The **Figures 1c** and **f** show the corresponding high-resolution images demonstrating the uniformity of ultra-large single crystalline layers. The dimensions of the exfoliated single layers were determined based on the dimensions of the parent crystal. The

photoluminescence (PL) emission from both monolayers is completely quenched, which is related to the common metal-induced quenching of emission.



Figure 2: Raman spectra of MoS_2 on different substrates. The spectra were recorded under ambient conditions under 532 nm excitation and 1 mW pump fluency.

Metal substrate-induced phonon softening

The effect of the metal-MoS₂ interaction is evident in the measured Raman spectra of MoS₂/Au and MoS₂/Ag, which were recorded by a confocal Raman microscope under ambient conditions. The Raman modes of the MoS₂/Au, MoS₂/Ag, and SiO₂/Si substrates are shown in **Figure 2**. It should be noted that bulk MoS₂ belongs to the D_{6h} symmetry group and freestanding or monolayer MoS₂ on dielectric substrates belongs to the D_{3h} symmetry group, which is further reduced to $C_{3\nu}$ on metal substrates due to the lack of inversion symmetry.^{26,27} Thus, we used the notation corresponding to the $C_{3\nu}$ group for the MoS₂ monolayer on metals, represented in **Figure 2**. In general, the *E* mode is sensitive to strain and the A_1 is sensitive to both the electrostatic interactions and strain, which are induced by the interaction between the metal and MoS₂. The electrostatic interaction between the metal and MoS₂ caused the layer to be strongly bound to the metal surface, where the lattice mismatch induces the strain and electronic transfer causes doping. Hence, the observed splitting and dramatic phonon softening can be attributed to the high magnitude of the interaction potential.^{25,26} The appearance of the geometrically forbidden E mode around 280 cm⁻¹ and symmetry-forbidden infrared mode A_1 around 450 cm⁻¹ ¹ originates from monolayer MoS₂ on both Au and Ag substrates. The high intensity of these modes and their uniform variation over the layers (Supplementary Figure 1) suggests a much stronger interaction between MoS_2 and the metal layers compared to previous reports ^{19, 26, 28}. Note that the previous observations of the E and A_1 modes were based on a sample prepared under ambient conditions, quickly after the deposition of the Au layers, where the processing time caused partial saturation of the Au layer surface.^{19,26,28} As a result, the magnitude of the MoS₂-metal interaction was reduced from the unperturbed value, and subsequently, the corresponding Raman modes decreased in intensity. Consequently, in our previous study ²⁶, the latter Raman modes were observed only by exploiting the strong nearfield enhancement of tipenhanced Raman measurements. Here, the UHV conditions preserved the reactivity of the fresh metal surface and caused strong binding of the MoS₂ layer to the metal, resulting in an exfoliation process with a yield of nearly 100% (Figures 1a and b). The uniformity of the interaction over the layer was confirmed by the statistical analysis of the obtained Raman spectra from 50×50 μ m² maps performed at different positions of the samples as shown in the

Supplementary Figure 1.

Exfoliation using Ag is uncommon because of the passivation of the silver surface by chemicals present in the environment. Because of the high reactivity of the silver surface, the passivation of the silver film proceeds much faster as compared to the experimental processing time scale. As a result, Ag-assisted exfoliation has not been demonstrated under ambient conditions or even in a glove box, but only under UHV conditions.¹⁸ The higher reactivity of the Ag surface compared to the Au surface is also reflected in the Raman spectra in **Figure 2**, where larger phonon softening was obtained for Raman modes of MoS₂ on a silver substrate.

interaction of MoS_2 and Ag also resulted in a higher exfoliation yield and enhanced layer homogeneity (**Figure 1b**), where only insignificant traces of bulk layers can be found.

However, the contact between the bulk crystal and the substrate is also an important factor that limits layer homogeneity and exfoliated flake size. Even though we flattened the bulk crystals before mounting, there was still a heterogeneous distribution of layer height, which, on a rigid substrate, hindered the complete contact between the bulk crystal and the substrate used for exfoliation. To address this issue, we mounted the crystals on a UHV-compatible elastic spacer between the crystal and the metal sample holder plate. Moreover, the soft spacer also induced a gentler contact and retraction of the bulk crystals, preventing the tearing of the exfoliated monolayers. Note that the Raman spectra of the layers produced without the elastic spacer did not show any substantial difference with respect to the spectra presented in **Figure 2**. Thus, we conclude that the pristine nature of the as-prepared metals under UHV conditions is the key factor that determines the exfoliation yield, where the soft spacer plays a key role in ensuring full contact between the substrate and the parent crystal.



Figure 3: Layer-dependent Raman spectra of MoS_2 on **a**) Au and **b**) Ag obtained under ambient conditions at an excitation of 532 nm and 1 mW pump fluency; 1L, 2L, 3L, and 4L represent mono-, bi-, tri-, and tetra-layer MoS_2 , respectively. The background contrast in the insets is due to the monolayer and deeper contrasts were obtained with more layers. **c**) Schematic illustration of the strain field distribution.

The changes in the phonon modes observed for the monolayer MoS_2 on metal, are attenuated in the bilayer/multilayer MoS_2 (**Figure 3**). The observed broadening of the *E* mode in the bilayer can be interpreted as the combined emissions from the altered phonons in the strained layer attached to the metal and the natural phonons in the second layer.^{26,28} Similarly, the modified A_1 phonons are only visible as a shoulder peak in the bilayer, suggesting a nearly complete restoration of the phonon mode frequencies in the second layer. The modifications of the Raman peaks can be barely traced in the case of tri-layer samples.

On the other hand, the layer-dependent Raman spectra on the Ag substrate exhibit a different trend, particularly for the E (i.e., E_{2u}) mode (Figure 3b). As also seen in Figure 2, the softening of the phonon energies is more dramatic here. As the difference in lattice parameter between Ag and Au crystals is negligible in comparison to the difference between MoS₂ and metals, this additional phonon softening is related to the higher affinity of Ag-S with respect to Au-S.²⁹ As a result, significant intensity of the shoulder peak is visible for up to three layers. However, the electrostatic interaction-induced change in the A_1 (A_{1g}) mode is impeded by the first layer of MoS_2 , resulting in a nearly complete recovery of the A_1 phonon modes in bilayer MoS_2 . This corroborates with the splitting of E mode (~ 380 cm^{-1}) peaks in bilayer, where the lower energy peak is the contribution from the bottom strained monolayer attached to metal and the high energy mode is the restored phonon modes from the second layer. The Raman modes in tri and tetra-layer flakes exhibit greater suppression of the phonon softening, however, the most dramatic changes were observed between mono and bilayer. This inhomogeneous distribution of strain field perpendicular to the layer plane as shown in Figure 3c leads to a substantial softening of the interlayer van der Waals (vdW) interactions between the layer attached with metal and the subsequent layers, which provide very high selectivity of only monolayer exfoliation, as can be seen in Figure 1.



Figure 4: High-resolution XPS spectra of MoS_2 on different substrates for **a**) S 2p and **b**) Mo 3d lines.

The nature of bonding

We performed XPS measurements to better understand the influence of the MoS₂-metal surface interaction on the Mo–S binding energy. The high-resolution XPS spectra of Mo 3d and S 2p of MoS₂ on different substrates are shown in **Figures 4a** and **b**, respectively. The MoS₂ layer on the Au and Ag substrate exhibits a systematic broadening of the Mo 3d and S 2p peaks, which is strikingly different from previous results, where only an overall shift of Mo and S emission lines was observed.¹⁹ The peak fitting procedure reveal a new peak at a lower binding energy for both Mo 3d and S 2p line, which is due to the robust interaction of MoS₂ with metals enabled by the UHV conditions. The lower energy lines (LEs) are more prominent on MoS₂/Ag compared to MoS₂/Au. The obtained S/Mo atomic ratio (shown in **Supplementary Table 1**) reveals a higher fraction of interacting sulfur atoms in the case of MoS₂ exfoliated on Ag compared to MoS₂ exfoliated on Au. This can be explained by the stronger affinity of S to Ag compared to Au. This observation also agrees with the greater softening of phonon modes and explains the greater exfoliation yield obtained when using an Ag substrate compared to an Au substrate. The stronger affinity of Ag and MoS₂ compared to Au and MoS₂.²⁹ Nevertheless, no clear evidence of S–Au or S–Ag covalent bonding was found in the XPS spectra, which indicates that the interaction between the metal and sulfur is non-covalent.

Crystalline quality



Figure 5: Macroscopic LEED measurement. LEED patterns of the exfoliated flakes on **a**) Au and **b**) Ag substrates.

To demonstrate the high quality of the exfoliated monolayers, we performed macroscopic (beam spot size ~ 1 mm) LEED measurements of the samples exfoliated on Au and Ag surfaces. The results are shown in **Figures 5a** and **b**, respectively. On both Ag and Au metal surfaces, we obtained prominent hexagonal patterns, demonstrating the high crystalline quality of the exfoliated layers. For MoS_2 on the Au substrate, we observed a pronounced broadening of the diffraction spots. At the same time, no diffraction pattern from the Au or Ag film could be observed on the produced samples, demonstrating the high polycrystallinity of the metal layers. Thus, the broadening of the diffraction spot on Au can be associated with the lack of crystallinity in the Au film and the lattice mismatch-induced strain in MoS_2 . The absence of such broadening in the samples exfoliated on Ag could be due to the different interaction mechanisms of MoS_2 with Ag with respect to Au. Hence, more advanced studies on the nature of the interaction between 2D layers and metals are needed.

Exfoliation mechanism

Based on the results of the spectroscopic studies, we can describe the exfoliation mechanism as follows. The strong dispersive interaction between the metal substrate and the 2D layer resulted in very strong adhesion between the metal substrate and the constituent elements of the layer, reducing the Mo-S binding energy. This strong adhesion and lattice mismatch at the interface produced a uniform biaxial strain field in the topmost layer of the bulk crystal as suggested by the softening of phonons, particularly the E mode around 380 cm⁻¹. However, the strain remained relaxed in the adjacent layer (i.e., the second layer) during the "contact period" of the exfoliation process, which was confirmed by the dominant appearance of unchanged E-mode phonons in the bilayer. This large difference of strain between adjacent layers reduces the magnitude of interlayer vdW forces. The dispersive interaction is hindered by the topmost layer due to the sandwich S–Mo–S geometry, as evidenced by the complete restoration of A₁ phonons around 400 cm⁻¹ in the bilayer. This synergistic influence of the generated strain and the adhesive force between the metal layer and the topmost MoS₂ layer exceeds the interlayer vdW force between the first MoS₂ layer on metal and the adjacent one during cleaving/retraction. This in turn enables the selectivity of the exfoliation of only monolayer MoS₂. Furthermore, the UHV conditions prevent surface passivation, which cause uniform adhesion of the MoS₂ layer with the substrate. The soft support of the crystal on the manipulator enables full contact between the substrate and the parent MoS₂ crystal, resulting in an extremely large area of exfoliation.

Conclusion and outlook

We developed a facile technique to exfoliate centimeter-scale pristine monolayer 2D materials with near-100% exfoliation yield. The area of the exfoliated 2D single layers (MoS_2 in the present case) is only limited by the dimensions of the parent bulk crystals and the size of the target substrates. The extremely high yield of the exfoliation process is possible due to the robust and uniform interaction of the metal layer with the topmost layer of the parent bulk

crystal. We attribute this success to the UHV conditions, which prevent passivation of the metal surface and thus boost the strong interaction between the metal and the topmost layer of the bulk crystal. This argument was supported by the activation of forbidden phonon modes as well as softened phonon energies in the Raman spectra of monolayer MoS₂ on Ag and Au metal substrates. Likewise, the Mo–S binding energy on metal substrates was reduced. A more prominent softening of phonon energies and higher intensities of the Raman forbidden modes were observed for MoS₂/Ag compared to MoS₂/Au, suggesting a stronger interaction of the MoS₂ layers with Ag, which also resulted in more efficient exfoliation, reaching the limit of the bulk crystal size. We concluded that this strong interaction between the metal and the metal substrate is non-covalent in nature.

When thinned to their monolayer limit, layered materials often reveal entirely new properties compared to their bulk counterparts. Seamless integration of such diverse properties originating from different layers in a heterostructure is highly beneficial for artificial quantum matter design. However, the prospects of this field depend on the creation, manipulation, and probing of scalable single layers and their heterostructures, where state-of-the-art techniques struggle to meet the demand. Our work in this regard provides a technological breakthrough, which will open a new route to obtain large-area monolayers of MoS_2 and beyond but also provide access to other fundamental properties and unique functionalities.

Materials and methods

Bulk MoS₂ crystal

The large-area bulk natural MoS_2 crystal was purchased from Manchester Nanomaterials Ltd. Prior to mounting it to the sample plate, we shaped the crystal to nearly 1 cm² so that it fitted with the holders. The crystal surface was cleaved using Scotch tape before insertion into the UHV chamber. We also flattened the crystal by pressing it between two clean SiO₂/Si wafers.

UHV exfoliation of MoS₂ on Au and Ag

Our custom-made UHV exfoliation system is composed of a 4-axis multicentered micromanipulator (µM1) as a crystal-holding stamp, another 2-axis multicentered micro-manipulator (µM2) as the substrate-holding stage, and several wobble-sticks for transfer of the samples. For obtaining 2D layers in the desired orientations, µM2 also serves as a goniometer and a heating stage (Figure 6a). Prior to exfoliation, the bulk 2D crystal was shaped, flattened, and attached to a SiO₂/Si wafer using a vacuum-compatible epoxy (Torr Seal epoxy), which was fixed on a custom-made flag-style sample plate with tantalum clips. At the same time, the substrates were fixed on flat flag-style sample plates by tantalum clips. Prior to the exfoliation, the substrates were chemically cleaned and annealed at 200 °C, followed by deposition of a very thin metal (Au and Ag) layer with an adhesive (Ti) layer by *in-situ* e-beam evaporation of metals inside the UHV exfoliation chamber. To obtain a fresh interface of the 2D layer, a pre-exfoliation of the bulk crystal attached at µM1 was performed under UHV conditions by bringing it into contact with an adhesive tape (double-sided Kapton tape) attached to another sample plate on µM2. For the exfoliation of monolayers on the desired substrates, the metal-coated substrates were fixed at µM2, and the Kapton-cleaved bulk crystal at µM1 was slowly brought into contact with the substrate. Afterward, the bulk crystal was detached slowly. The process released a very large-area monolayer on the metal-coated substrate, which was examined using an optical and Raman microscope attached to the top viewport, as schematically shown in Figure 6a. An optical image of the manipulators during the contact period of exfoliation is presented in the inset of Figure 6a. The complete process was carefully monitored through viewports on the chamber. The video recording of the exfoliation process is provided in Supplementary Movie 1 and 2. A photograph of the complete exfoliation system showing different components is provided in Figure 1b. For exfoliation, we used MoS₂ crystals, which were shaped according to the allowed dimension of our holder design. As the assisting metal layers, we used Au and

Ag of 5–10 nm thickness. To obtain smooth metal layers, the metals were deposited at a rate of ~ 0.1 Å/s.



Figure 6: The exfoliation system. **a**) Schematic representation of the positions of μ M1, μ M2, and the microscope for *in-situ* probing of the layers. The inset is the photograph of the manipulators holding the substrate and bulk crystal for exfoliation. **b**) Photograph of the complete system.

Optical imaging and spectroscopy

The *in-situ* optical images were recorded using a custom-made optical microscope fitted with a Mitutoyo 10X long-distance objective. The *ex-situ* optical images were recorded using a standard Olympus optical microscope under ambient conditions. PL and Raman spectra were

recorded using a WITec alpha300 R confocal Raman spectrometer under the 1 mW excitation power of a 532 nm laser.

Surface-sensitive spectroscopic measurements, XPS, and LEED

For surface-sensitive spectroscopy, the samples were carried to our XPS-STM cluster in a UHV transfer vacuum suitcase attached to a load-lock, which allowed transferring them without breaking the UHV conditions. The XPS measurements were performed in a Phoibos 150 Specs spectrometer with a base pressure lower than 10^{-10} torr. A monochromatised Al K α small radiation source with a spot size of 1 mm² was used for the excitation of the electrons. The pass energy of the electron energy analyser was set at 20 eV. The take-off angle between the analysed photoelectrons and the substrate surface was 90°. The overlapping spectral features were resolved into individual components using the damped non-linear least squares method after subtraction of Shirley background using Gaussian-Lorentzian line shape. The surface atomic content was accomplished assuming a homogenous distribution of atoms and Scofield photoionization cross-section.

The LEED images were acquired on the as-prepared sample surfaces after UHV transfer. An electron energy of 70 eV was used on both surfaces.

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