

Thermally Activated Gold-Mediated Transition Metal Dichalcogenide Exfoliation and a Unique Gold-Mediated Transfer

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Layered materials like transition metal dichalcogenides (TMDCs) enable exciting new physics in their 2D limit. Combined with successful demonstrations of 2D transistors and devices, the need for high-quality large-scale monolayers increases. In this light, scalable gold-mediated exfoliations attract broad attention to supersede the traditional scotch tape method as a means for high-quality materials. Gold proved to be suitably adhesive for the exfoliation of several 2D materials, including TMDCs. Previously reported methods rely on a simple press and peel mechanism. However, herein, a gold-mediated exfoliation enabled by low-temperature annealing is presented for the first time. This simple modification potentially increases the range of external conditions under which gold-mediated exfoliations operate in a robust manner. The exfoliation achieves scaling with parent crystal areas, rendering it on par with previously reported methods. On top of that, a unique gold-mediated transfer concept is introduced, where gold is repurposed as a metallic (polymer-free) transfer membrane. The transfer allows the deterministic and clean relocation of the exfoliated monolayers onto technologically relevant substrates like SiO₂/Si. The process is benchmarked using MoS₂ as the prototypical TMDC and monolayer areas up to ≈80 mm² are successfully exfoliated and transferred.

by a whole set of outstanding new physics of 2D TMDCs.^[4–7] This started the quest for high-quality and large-scale monolayers, which fostered the development of different techniques ranging from bottom-up approaches like chemical vapor deposition (CVD) and molecular-beam epitaxy (MBE)^[8] to top-down routes via mechanical and liquid exfoliation.^[2,8,9] To date, all routes suffer specific drawbacks. Both CVD and MBE can supply large-area monolayers yet crave optimization for each new TMDC composition and bear challenges in terms of subsequent clean transfer off the growth substrate. Liquid-based exfoliations introduce contaminants, thereby limiting studies of intrinsic material properties. Historically, tape-based mechanical exfoliation has largely carried the advance on 2D material research and the study of their intrinsic properties by supplying high-quality materials in an accessible manner. However, it is easily diagnosed with low yield, limiting its use beyond lab-scale experiments. To overcome these limitations scalable exfoliations

Transition metal dichalcogenides (TMDCs) are layered compounds where layers are held together by weak van der Waals (vdW) interactions and can be cleaved with ease, enabling the exfoliation of a single layer by means of physically thinning down the crystal.^[1,2] This transition from 3D to 2D^[2,3] is accompanied

beyond scotch tape have been investigated.^[10] On this note, gold has been investigated as an exfoliation substrate and provides the needed adhesive forces via strong vdW^[11] or “covalent-like quasi-bonding” (CLQB)^[12] interactions with layered materials. Several TMDCs have already been exfoliated using gold (Table S1,

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Supporting Information),^[11–14] rendering MoS₂ a perfect TMDC prototype for benchmarking gold-assisted exfoliations. Smooth and clean gold surfaces provide the Au/TMDC vdW interactions necessary to overcome the TMDC interlayer interactions, leading to exfoliation of the interfacing layer.^[11] The template-strip method provides these gold surfaces by cleaving a gold film off a smooth template substrate, accessing the uncontaminated part of the former gold template interface.^[15] In this work, template-stripped gold substrates acted as ideal exfoliation substrates to yield large-area and highly continuous MoS₂. An unprecedented thermally activated exfoliation mechanism was observed. The process was complemented by reusing gold as the transfer membrane, thereby implementing a novel polymer-free transfer approach.

The developed TMDC exfoliation process is shown in **Figure 1a** with MoS₂ as the test bed. The metal-stacks can be peeled off the template wafer (template strip), allowing for wafer-scale batches of ultraflat gold exfoliation substrates (see details in Figure S1, Supporting Information). The exfoliation starts with revealing fresh surfaces of MoS₂ and gold, combining them on a hotplate, and finishes by peeling off the MoS₂ parent crystal. This leads to ultra-large MoS₂ layers exfoliated onto gold, as shown in the optical micrograph in Figure 1b. The MoS₂ single-layer areas (1 L) are indicated and measure up to 37 mm² in this example. Some multilayer areas are apparent, but the single-layer coverage outweighs the multilayer fraction by far, supporting the notion of the successful exfoliation of MoS₂ layers in conformal contact with gold. Figure 1c shows a zoom-in of the monolayer region of Figure 1b, revealing the monolayer's continuity over several square millimeters. The layered nature is confirmed using atomic force microscopy (AFM), as shown in Figure 1d,e. The layer's apparent step height of ≈ 0.6 nm is consistent with reported values.^[16] No photoluminescence (PL) was observed for MoS₂ on gold, due to quenching by the metal.^[11,17] Surprisingly, exfoliation did not work without the annealing step at 200 °C. This is distinct

from the previously reported gold-based exfoliations,^[11–14,18] where no annealing was needed. Following previous reports one would expect room-temperature exfoliation at the smooth template-stripped Au surface (RMS ≈ 0.3 nm, Figure S1, Supporting Information), driven by strong vdW interactions at the interface, as described by Velický et al. for smooth and clean gold (RMS ≈ 0.7 nm)^[11] in conformal contact with TMDCs. However, we were not able to exfoliate at room temperature. Either the interface is already contaminated or the gold growth at the SiO₂ template changes the crystallinity of the resulting gold surface (for nontemplated evaporation mostly Au(111) grains are expected^[11]). Therefore, thermally assisted “self-cleansing” mechanisms^[7] or surface reconstructions^[7] at the gold/MoS₂ interface (effectively a 3D–2D vdW heterostructure) might be possible explanations. The process also worked at lower temperatures down to 150 °C, yet reproducibility and yield decreased. Cleaving the tape off the hot sample, skipping the cooling step, did not change the exfoliation results. The tape was peeled slowly (≈ 0.5 – 1 mm s^{−1}) by hand with an approximate peel angle between 60° and 90°. The details of the (last) peeling step did not show a notable difference in the exfoliation yield. However, the initial peeling of the parent crystal might be more sensitive to such details as ripples and tear-ins could be introduced on the otherwise smooth crystal surface, potentially decreasing exfoliation yield and increasing multilayers exfoliated from teared parent crystal sites. A gentle handling of the parent crystal therefore seems advisable. With 200 °C as the ideal temperature the exfoliation yields highly continuous monolayers, potentially allowing increased reproducibility overall due to the reduced influence of external conditions like carbon contaminants on gold.^[11] Scaling of the exfoliation process was investigated by comparing the parent crystal surface areas in contact with gold with the areas of exfoliated monolayers (**Figure 2a**). Parent MoS₂ with 26 mm² surface area on gold (Figure 2b) revealed 16 mm² 1 L MoS₂ upon

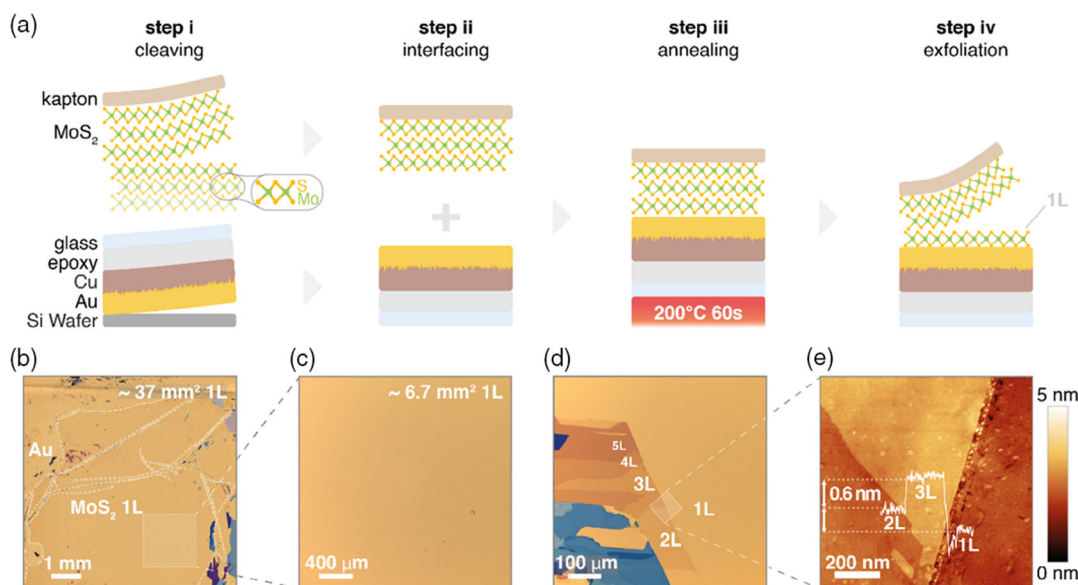


Figure 1. a) The gold-assisted TMDC exfoliation process. b) Optical micrograph of monolayer MoS₂ on gold. The single-layer area (1 L) is outlined and measures 37 mm². c) Zoom-in of the 1 L region. d) Optical micrograph of a multilayer region. The region for the AFM measurement is highlighted. e) AFM height image showing a layer step height of 0.6 nm.

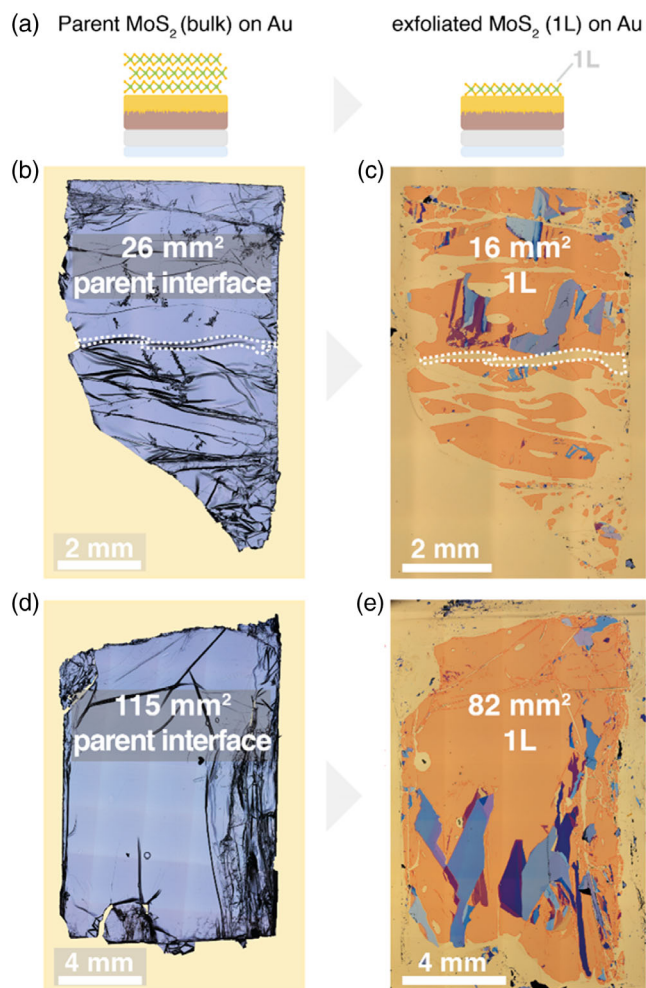


Figure 2. a) Schematic showing the last two steps of exfoliation used to compare the initial parent crystal interface areas on gold with the resulting monolayer areas. b) Parent crystal on gold with 26 mm² interface area. A wrinkle is highlighted (white contour). c) Exfoliated 1 L MoS₂ area with (b) as parent measured 16 mm². d) Parent crystal on gold with 115 mm² interface area. e) Exfoliated 1 L MoS₂ with (d) as parent measured 82 mm². The 1 L areas contributing to the displayed areas are marked in orange.

exfoliation (Figure 2c). The exfoliation coverage clearly reproduced the wrinkled pattern of the parent crystal, following the limits of conformal contact between parent crystal and gold. The highlighted feature (white dotted contour) depicts a fold in the parent crystal, translating to a nonexfoliated area. With the parent crystal as the limiting factor, we realized a scalable method, and using larger (and smoother) crystals led to the anticipated upscaling of the exfoliated monolayer area. Utilizing the largest MoS₂ crystal to our disposal (≈ 115 mm² surface area), 82 mm² of monolayer area was exfoliated (Figure 2d). The herein reported monolayer area presents one of the largest for any gold-mediated exfoliation process to date (see Table S1, Supporting Information), yet the compelling argument is the achieved scaling in a robust and accessible method. A gold-mediated transfer was also implemented utilizing the copper layer. The introduced copper layer can be etched orthogonally to gold using FeCl₃, leaving MoS₂ on a

floating gold foil acting as a metal (polymer-free) transfer membrane. The polymer-free transfer process is schematically shown in Figure 3a. The foil on the target substrate is dried in air, annealed to promote conformal contact between the substrate and MoS₂, and then etched using aqueous KI/I₂ to release the MoS₂ monolayer. The KI/I₂ etchant does not exhibit any MoS₂ etching (FeCl₃ is at no point in contact with MoS₂). The transfer process is capable of deterministically transferring the complete monolayer area onto SiO₂, as shown in Figure 3b. The MoS₂ 1L area (82 mm²) is conserved, as well as the relative positions of the MoS₂ features. AFM reveals a SiO₂/MoS₂-1L step height of ≈ 0.9 nm, consistent with previous reports,^[19] and proves the wrinkle-free transfer of the monolayer (Figure 3c). The optical characterization shown in Figure 3d,e features PL emission^[17,20,21] for single-layer MoS₂ and the characteristic E_{12g}^1 and A_{1g}^1 Raman mode frequency, with $A_{1g}^1 - E_{12g}^1$ equating to 18.8 cm⁻¹, as expected for single-layer MoS₂.^[22,23] These results indicate intact monolayers after exfoliation and transfer. The novel polymer-free transfer unlocks the monolayers for use on any substrate. Several polymer-based transfer processes were also tested, which proved to be reliable as well, yet plagued by ubiquitous polymeric residues (Figure S2, Supporting Information). The large monolayer areas achieved here allow to study the electronic structure of MoS₂, in principle on any substrate, using standard photoemission spectroscopy without experiencing issues with sample charging^[17] (details in Figure S4, Supporting Information). The lack of Mo⁶⁺ peaks in the Mo3d core-level region indicates the absence of oxidation,^[24–26] rendering our exfoliation/transfer process a suitable route for high-quality monolayers. Furthermore, the complete etching and removal of gold after transfer were confirmed (Figure S5, Supporting Information). To probe the monolayer quality, ultralarge field-effect transistors (1 mm \times 30 μ m for W \times L) on SiO₂ were fabricated with exfoliated MoS₂ monolayers (Figure S6). The devices showed decent performance (room-temperature mobility $\mu = 8.9$ cm² V⁻¹ s⁻¹, $I_{on}/I_{off} = 1 \times 10^5$), a statement of the intact semiconducting properties and the material quality over a large area. In summary, we present a scalable thermally activated gold-mediated TMDC exfoliation and a novel gold-mediated transfer. Resulting monolayers show high continuity and were proved to maintain the high starting material quality over large areas. The template-strip method paired with silicon wafers allowed us to produce wafer-scale batches of exfoliation substrates. These gold substrates are easily stored and are always just one strip away to initiate ultralarge exfoliations. The herein disclosed process may boost the technological exploitation of 2D TMDC and their heterostructures fuelled by a robust high-throughput exfoliation process with potential for automation. Ultimately, scaling with initial parent crystal areas hints at the importance of large and smooth crystals for scaling up exfoliations into technologically relevant realms.

Experimental Section

Gold Exfoliation Substrates: Polished silicon wafers (Siebert Wafer, $<100>$, 525 μ m thickness) served as ultraflat templates. The wafers were sonicated for 5 min each in acetone, isopropyl alcohol (IPA), and deionized (DI) water and then dried with a nitrogen gun. A 5 min O₂-plasma treatment (Diener Femto PCCE, 0.35 mbar, 500 W, 40 kHz) followed by DI water rinse and 5 min DI water sonication followed. Around 200 nm Au

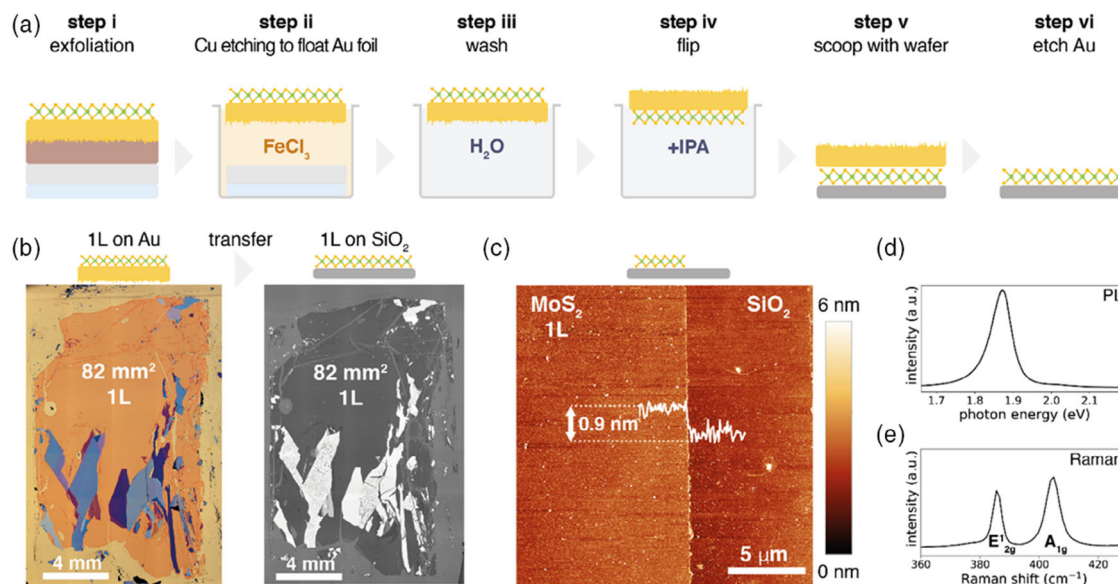


Figure 3. a) The gold-assisted transfer process. b) MoS₂ monolayer on gold and after transfer on SiO₂. Monolayer regions on gold are colored orange to enhance visibility. The red channel of the optical micrograph is used for the image of 1 L on SiO₂. c) AFM height image of MoS₂ monolayer on Si wafer. d) The PL spectrum of MoS₂ monolayer on Si wafer. e) Raman spectra obtained at the same spot.

was deposited via physical vapor deposition ($\approx 1.0 \text{ \AA s}^{-1}$, $\approx 10^{-7}$ mbar) followed by 800 nm copper ($\approx 2.5 \text{ \AA s}^{-1}$). Glass slides ($1.5 \times 1.0 \times 0.7$ mm) were glued onto the metal-coated wafer (Ossila Encapsulation Epoxy S132) and UV cured (254 and 365 nm, 1.5 h).

Gold-Assisted Exfoliation: MoS₂ (2D semiconductors, synthetic MoS₂ crystal) was cleaved with heat-resistant Kapton tape and pressed onto a freshly stripped Au substrate. The stack was annealed on a hotplate in ambient conditions at 200 °C for 60 s and taken from the hotplate to cool down for 10–20 s before peeling the tape.

Gold-Assisted Transfer: Exfoliated MoS₂ on Au was floated on aqueous FeCl₃ (33 wt%). The sample was left in the etchant until the gold foil floating freely on top (≈ 12 h). The foil was fished with a clean wafer piece and transferred into a beaker with DI water to clean off etchant residues. The foil was transferred into a fresh DI water beaker where the surface tension was lowered with IPA to sink and flip the foil. The flipped foil was transferred into a beaker containing the solvent applicable for the target substrate. The substrate was positioned below the foil and the solvent was drained with a pipette, transferring the foil onto the substrate. The sample was dried in air for 1 h before baking on a hotplate (80 °C 1 h, 150 °C 30 min). Au was etched for 30 min with aqueous KI/I₂ etchant (Sigma Aldrich, “Au etchant, standard”) which was deposited on top of the Au foil with a pipette. To wash off Au etchant residues, the substrate was washed with acetone, followed by immersion in acetone and then ethanol. The last solvent in the transfer should wet the target substrate well to allow even spreading of the foil while not exhibiting high vapor pressures at room temperature to avoid blistering of the gold foil during drying.

AFM Measurements: AFM was conducted in ambient conditions with a Bruker Dimension Icon using PeakForce Tapping with a ScanAsyst-Air tip (Bruker).

Raman and PL Measurements: Raman and PL spectroscopy were conducted using a confocal microscope setup (XploRA, Horiba Ltd.) with a 532 nm laser excitation source and 100x objective ($\approx 1 \mu\text{m}$ laser spot size). Laser power was kept below 0.14 mW. All measurements were carried out in ambient conditions.

Photoelectron Spectroscopy: Experiments were conducted at the ENERGIZE end station at Bessy II, using the Mg anode of a Scienta Omicron DAR400 X-ray source (1254.6 eV) and a Focus HIS 13 helium discharge lamp (21.2 eV) for excitation. The kinetic energy of the emitted

electrons was measured by a Scienta Omicron DA30 analyzer and the sample was biased with -10 V when measuring the secondary electron cutoff. Before measurements the sample was annealed at 300 °C in ultra-high vacuum (base pressure $> 10^{-9}$ mbar) for several hours.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

gold exfoliation, monolayer transfer, MoS₂, scalable exfoliation, transition metal dichalcogenides

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