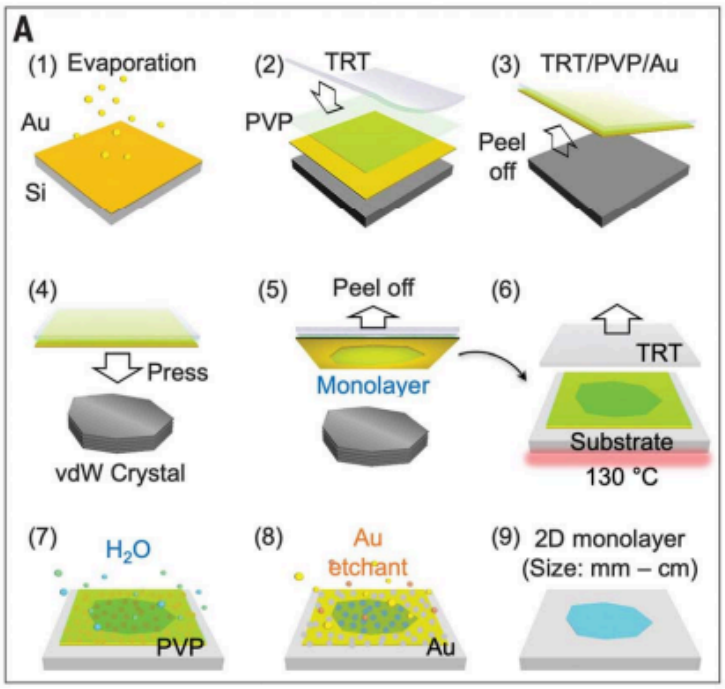
Procedure - Au Exfoliation of TMD

This technique allows us to disassemble 2D materials layer by layer to obtain a monolayer of macroscopic dimension.



The procedure can be split into the following stages:

Preparatory Stage: Ensure the materials and substrates needed for mechanical exfoliation are ready.

- ☐ Deposit 150 nm gold[1] layer on an ultra-flat silicon wafer (NOVA Electronic Materials LLC, p-type doped) via e-beam evaporation (Angstrom Engineering EvoVac Multi-Process thin film deposition system) **CONDUCT IN CLEANROOM**
  - Silicon should be roughly 4 inches; O2 plasma cleaned for 20 minutes
  - The gold is supposed to be an atomically flat gold tape (ultra-flat gold film on a polymer substrate) which is achieved using a template-stripping technique at **10^-7 torr and 0.5 angstroms per second depositing (this guideline does not need to be as stringently followed since it can take a significant amount of time)**
  - **How long can we keep these gold/silicon pieces before they become unusable?**
- ☐ Spin-coat the Au film with a layer of polyvinylpyrrolidone (PVP) (Sigma Aldrich, mw 40000, 10% wt in ethanol/acetonitrile wt 1/1) **https://www.sigmaaldrich.com/US/en/product/sial/pvp40**
  - 3000 rpm, acceleration 1000 rpm/s, 2min
  - Put the silicon with Au and PVP on a hotplate at 150 °C for 5 minutes
  - The point of this PVP layer is to prevent TRT residue from getting on everything
  - 4.5 g ethanol; 4.5 g acetonitrile; 1 g PVP to make the solution

[1] The ultraflat gold tape allows intimate and uniform vdW contact between the gold and the 2D vdW crystal surface, exfoliating a complete monolayer that can be transferred onto the desired substrate. Roughness of gold is not an issue. What other metals aside from Au have been used for this method?

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Exfoliation Stage: Manually exfoliate the monolayer.

- ☐ Pick up PVP and gold using thermal release tape (TRT) (semiconductor corp. Release temperature 90 °C); peel everything off of the silicon
  - Gentle pressing to cover the entire area
- ☐ Press the gold side of this layered TRT/PVP/Au onto the surface of a bulk vdW crystal[2]
  - Use tape to pick up a single crystal and fix it onto IPA cleaned glass slide, cut out the rest of the tape so no residue is picked up
  - Apply gentle pressure
  - We want a reasonably sized bulk crystal — too small of a bulk crystal makes the method harder to implement — use a relatively large crystal cleaved with tape (always use an inner surface of the crystal)
  - At this point, you want to complete the procedure within 12 hours since your monolayer has been exposed
- ☐ Peel off the TRT/PVP/Au from the bulk — now there should be a monolayer on the Au. Transfer this to a silicon substrate.
  - Peel slowly as we don't want cracks or folds on the sample
  - **NO** O2 plasma (UV) cleaning of this new silicon substrate!!! We want the monolayer to stick

Cleaning Stage: Remove the TRT/PVP/Au layers to expose the monolayer.

- ☐ Place substrate with monolayer onto hotplate at 130 degrees Celsius
- ☐ Place substrate face up in deionized (DI) water to dissolve PVP for 2 hours
- ☐ The sample on the substrate covered by Au is rinsed with acetone (to dry it use gentle N2 or let the fume hood dry it) and cleaned by O2 plasma for a little less than 3 minutes (not any longer) to remove any remaining polymer residues.
- ☐ Place substrate face up in etchant solution(I2/I-) for 10 minutes to dissolve Au
  - KI/I2 gold etchant solution (2.5g I2 and 10g KI in 100ml DI water. Iodine, 99.99%, Alfa Aesar; potassium iodide, 99.9%, Alfa Aesar) as mentioned in [1]
  - We do not know if this solution will impact the optical properties of the sample so it is best to not keep the substrate in the etchant longer than 10 minutes
- ☐ Now we should have a monolayer! Rinse it with DI water and isopropanol, and dry it with N2.
  - Place sample face up in DI water for 1 hour
  - Quickly rinse in IPA and dry with N2

[2] Pick up hBN with a different metal. If attempting to use graphene, deposit gold directly onto bulk graphene and pick up the graphene in that way.

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Inventory of Supplies

Gold Deposition:

- gold crucible
- UV-cleaned silicon wafer (whole)

Mechanical Exfoliation:

- PVP solution — 4.5 g ethanol (in fume hood; waste container TBD) 4.5 g acetonitrile (need waste container) 1 g pvp powder (chemical bench cabinet 1)
- as of now, there is an existing pvp solution in the fume hood
- thermal release tape (exfoliation drawer)

Cleaning:

- deionized water (cabinet under fume hood)
- acetone, IPA, N2 gun
- etchant solution — iodine (TBD- need waste container) , potassium iodide (cabinet under fume hood)

A similar procedure for gold-tape exfoliation of TMD from [2]:

- "We first deposit a 150 nm gold film on Si wafer by e-beam evaporation (0.05 nm/s), then spin-coat the gold film by polyvinylpyrrolidone (PVP) solution (Sigma Aldrich, mw 40000, 10% wt in ethanol/acetonitrile wt 1/1) at 1500 rpm for 2 min, with the acceleration of 500 rpm/s, and anneal at 150 °C for 2 min. A single-sided heat release tape is cut into small pieces (~1 × 1 cm2 square) and stuck onto the PVP/ gold surface to peel off the gold film from the Si wafer to form a gold tape, which is then gently pressed onto a TMD single crystal (purchased from HQ Graphene) to exfoliate a monolayer. The TMD monolayer on the gold tape is then transferred onto a desired substrate. We then heat the substrate with everything on top using a hot plate at 135 °C for 3 min to remove the heat release tape, followed by water soaking for 4 h to remove the PVP layer on gold. Finally, the gold layer is removed by gold etchant (2.5 g I2 and 10 g KI in 100 mL deionized water), and the TMD monolayer on substrate is washed by water and isopropanol, then dried by a nitrogen gun."

Sources

[1] Liu F, Wu W, Bai Y, Chae SH, Li Q, Wang J, Hone J, Zhu XY. Disassembling 2D van der Waals crystals into macroscopic monolayers and reassembling into artificial lattices. Science. 2020 Feb 21;367(6480):903-906. doi: 10.1126/science.aba1416. PMID: 32079769. https://par.nsf.gov/servlets/purl/10155494

[2] Li, Q., Alfrey, A., Hu, J. *et al.* Macroscopic transition metal dichalcogenides monolayers with uniformly high optical quality. *Nat Commun* 14, 1837 (2023). https://doi.org/10.1038/s41467-023-37500-1

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