Synthesis of Graphene

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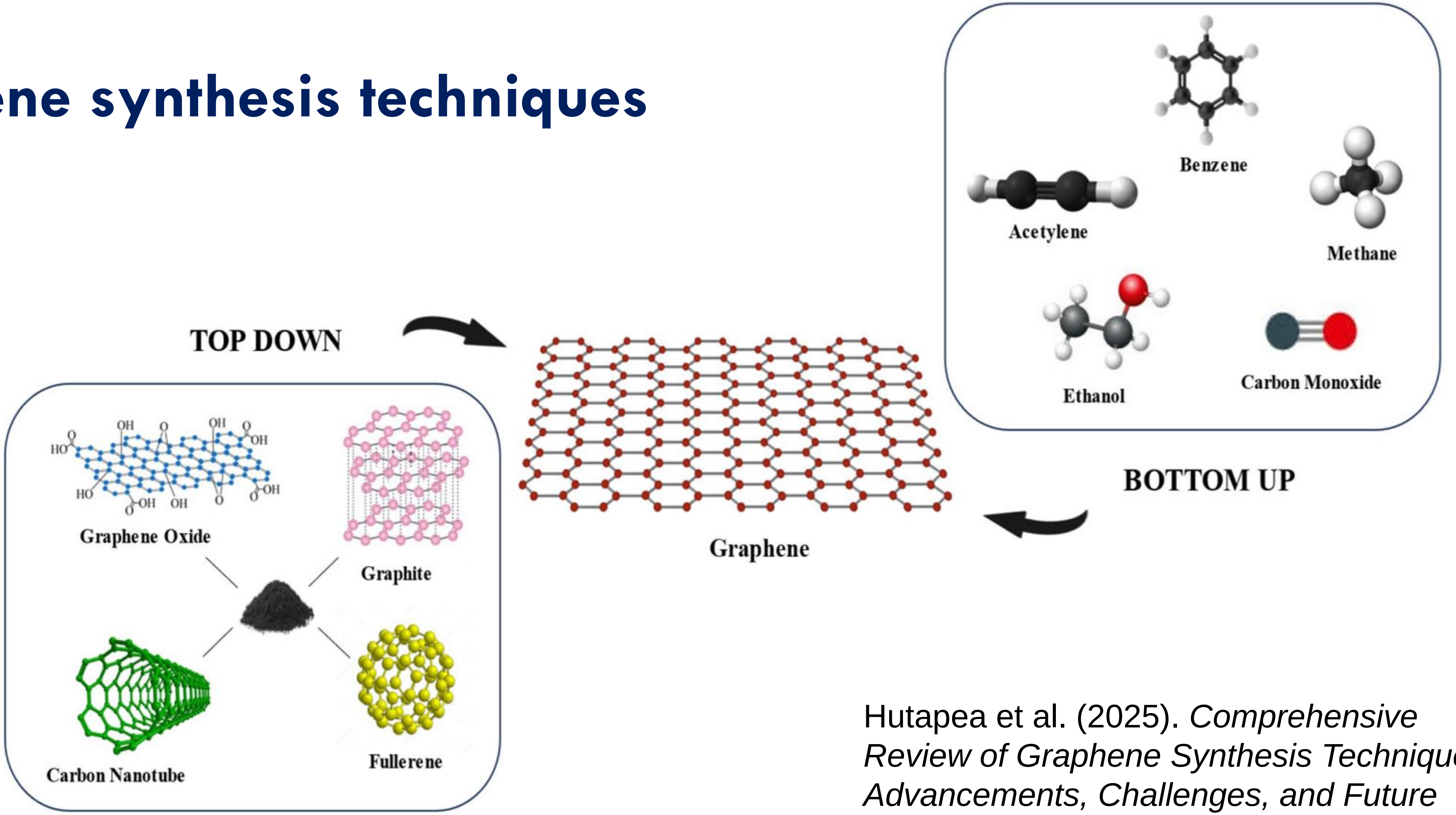
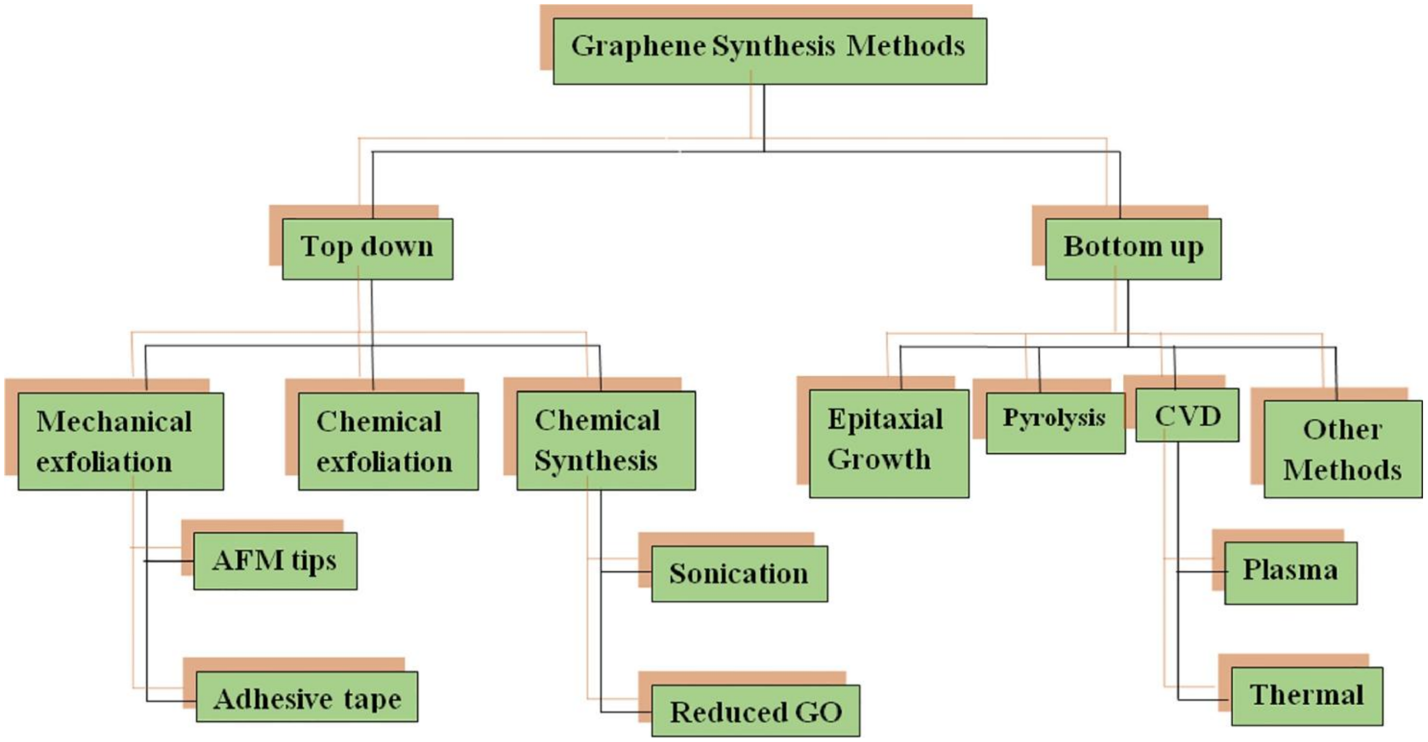
December 2025

Graphene synthesis techniques



Hutapea et al. (2025). *Comprehensive Review of Graphene Synthesis Techniques: Advancements, Challenges, and Future Directions.* Micro, 5, 40.

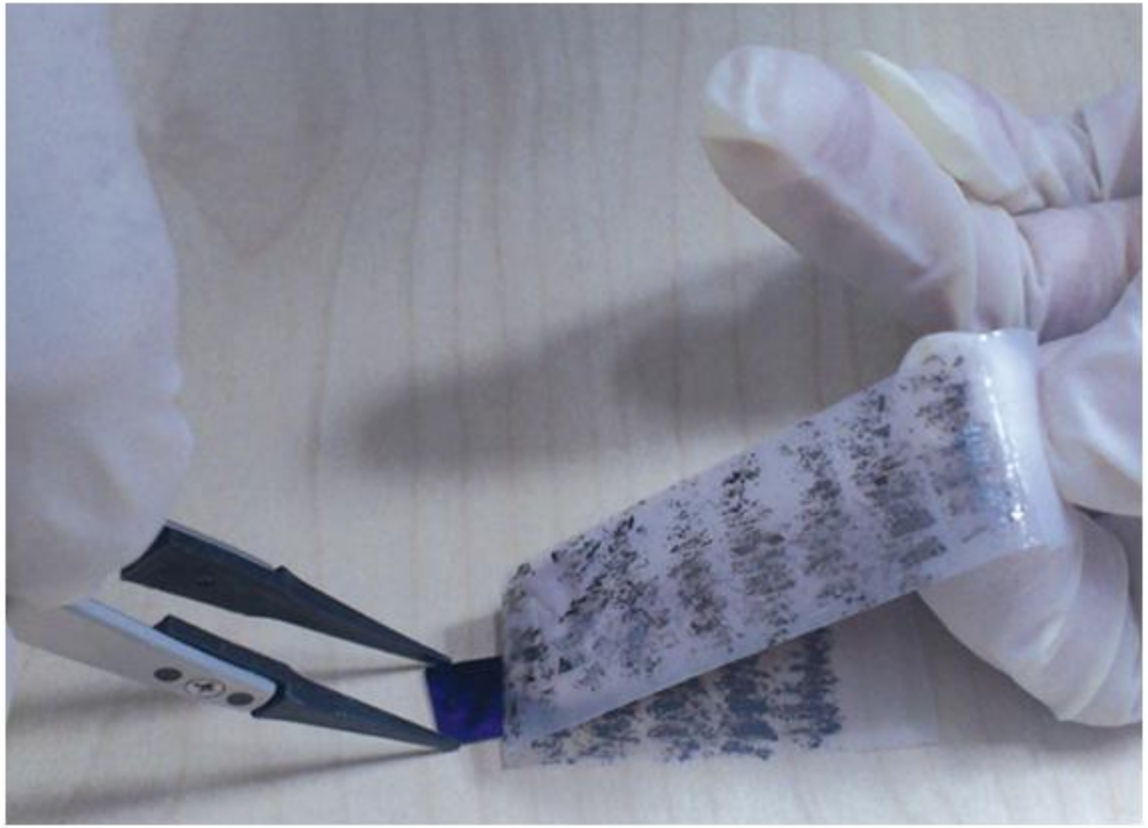
Graphene synthesis techniques



Van Noorden, R. Production: Beyond sticky tape. *Nature* **483**, S32–S33 (2012).

Micromechanical Cleavage

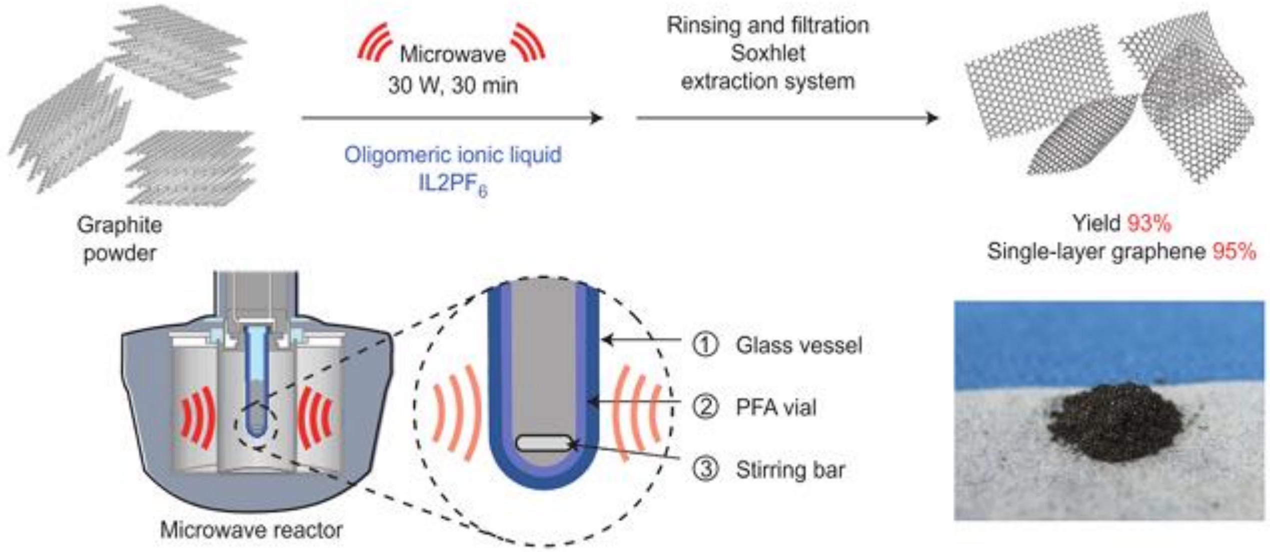
- **Scotch tape method**
  - It relies on overcoming the weak van der Waals forces between graphitic layers
- **Advantages:**
  - Produces the highest quality graphene (high mobility)
- **Disadvantages:**
  - Impractical for large-scale applications (low yield).



Van Noorden, R. Production: Beyond sticky tape. *Nature* **483**, S32–S33 (2012).

Microwave-Assisted & Ionic Liquids

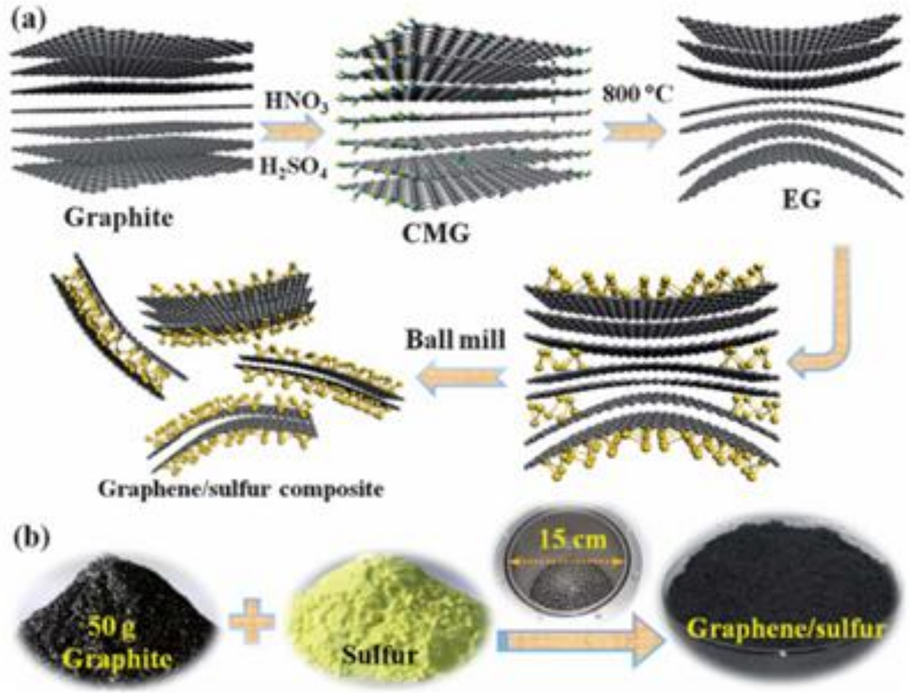
- **Procedure:**
  - Graphite is suspended in oligomeric ionic liquids and irradiated with microwaves.
  - Microwaves generate in situ HF species from the ionic liquid decomposition, which intercalates and aids exfoliation.
- **Advantages:**
  - **Ultrahigh throughput:** 93% yield with 95% selectivity for single-layer graphene..
- **Disadvantages:**
  - Requires specific molecularly engineered ionic liquids.
  - Requires specific work-up (Soxhlet extraction) to remove decomposed ionic liquid contaminants.



Matsumoto, M., Saito, Y., Park, C. *et al. Nature Chem* **7**, 730–736 (2015).

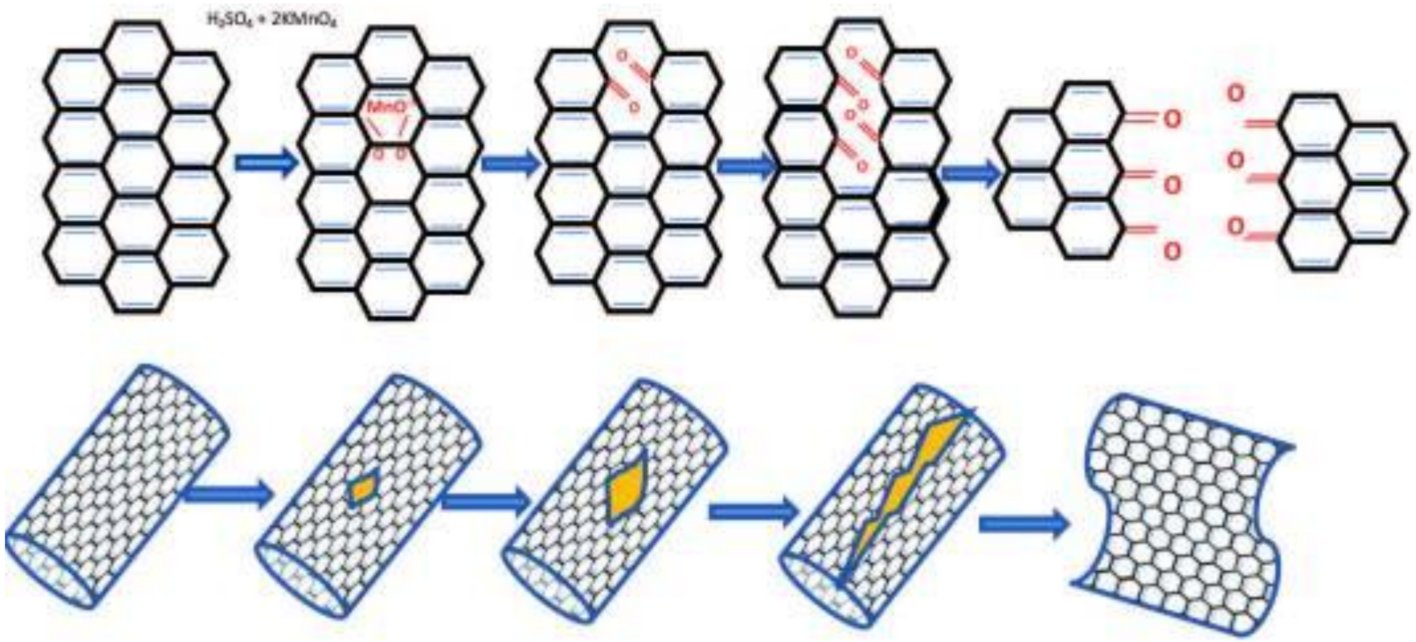
Electrical Explosion & Ball Milling

- Treated graphite flakes with sulfuric/nitric acid, then rapidly heated to 800 °C to create edge-opened graphite.
- Ball milling with elemental sulfur, which acts like “Scotch tape” to exfoliate graphite layers.
- Produce highly conductive, low-defect graphene sheets with uniformly anchored sulfur for high-performance Li–S batteries.



Lin, T. *et al.*, *Energy Environ. Sci.* (2013). DOI: 10.1039/c3ee24324a

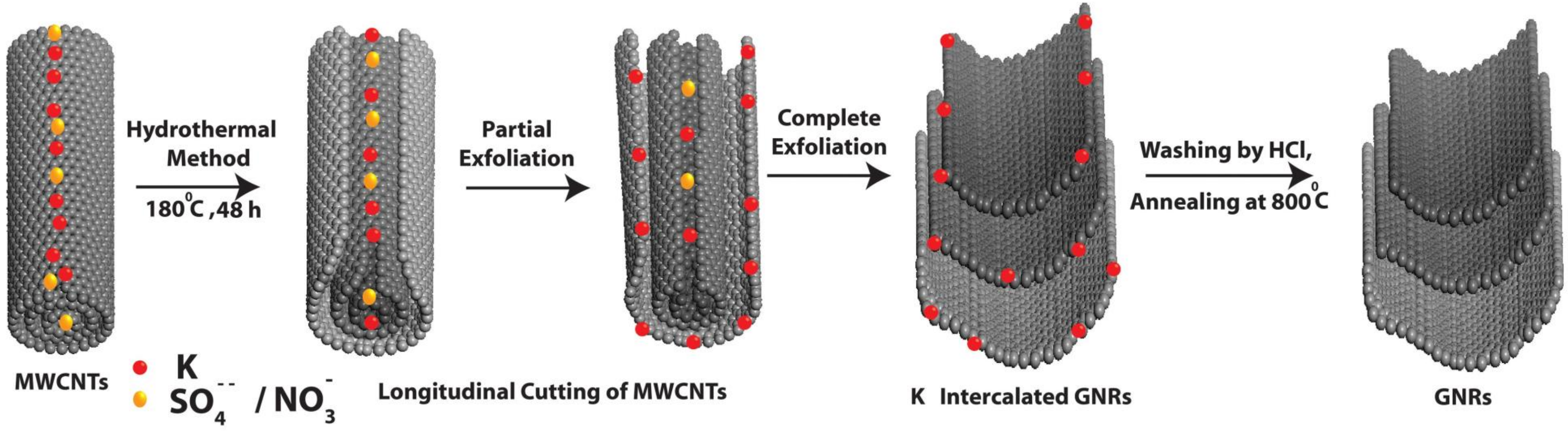
Unzipping carbon nanotubes



By **ion intercalation**

Kosynkin D Higginbotham A Sinitskii A Lomeda J Dimiev A Longitudinal unzipping of carbon nanotubes to form graphene nanoribbons. Nature . 2009;458:872–876

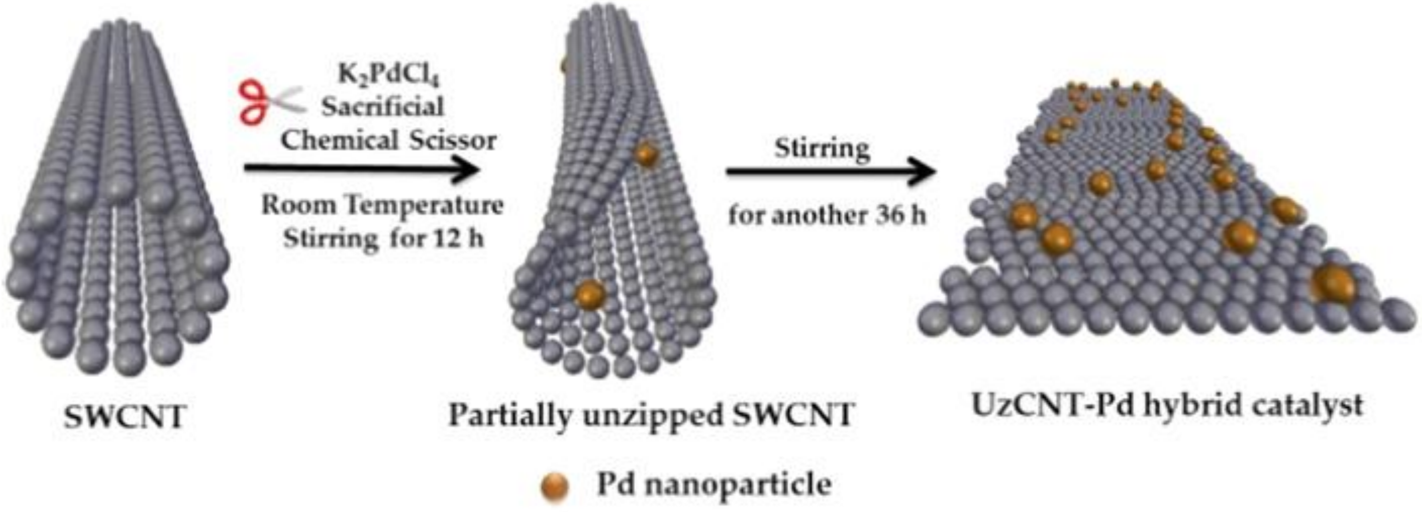
Carbon nanotubes unzipping mechanism



- Potassium, sulfate, or nitrate ions intercalation creating defects and internal pressure.
- This intercalation weakens C–C bonds along the tube axis and promotes longitudinal exfoliation, producing graphene nanoribbons.

Shinde, D. B.; Majumder, M.; Pillai, V. K. Sci. Rep. 2014, 4, 4363.

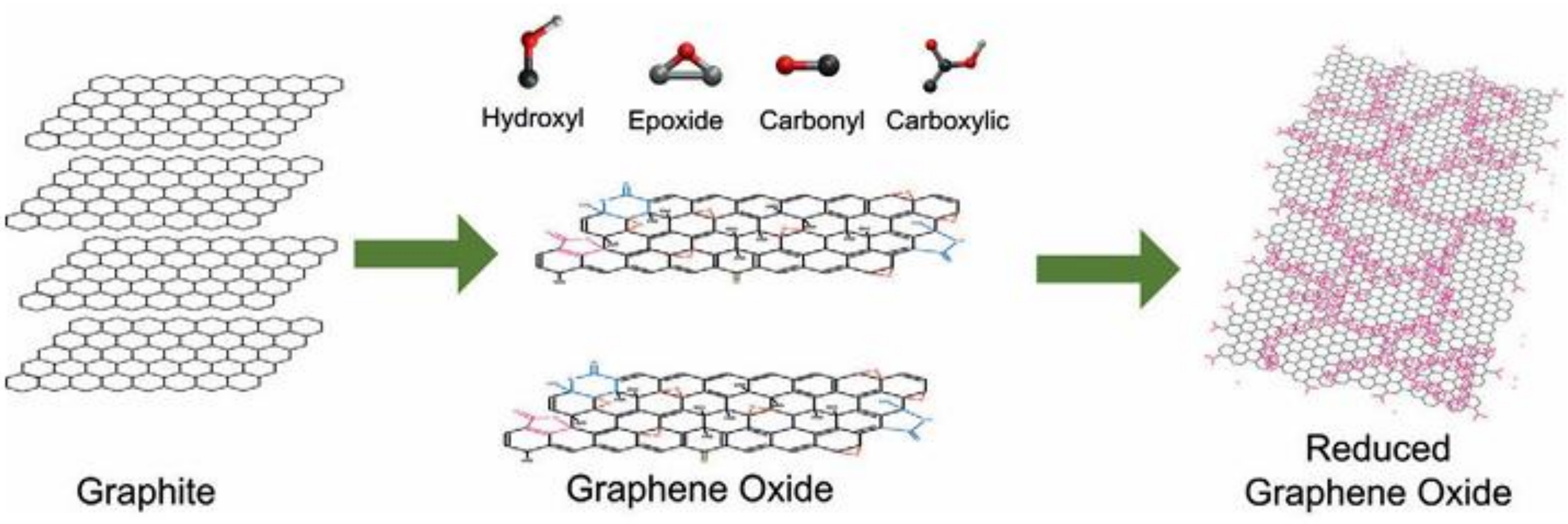
Carbon nanotubes unzipping mechanism



- Palladium complex ($PdCl_4^{2-}$) is used in water at RT
- Pd complex acts as a chemical “scissor”
- highly electrocatalytic hybrid

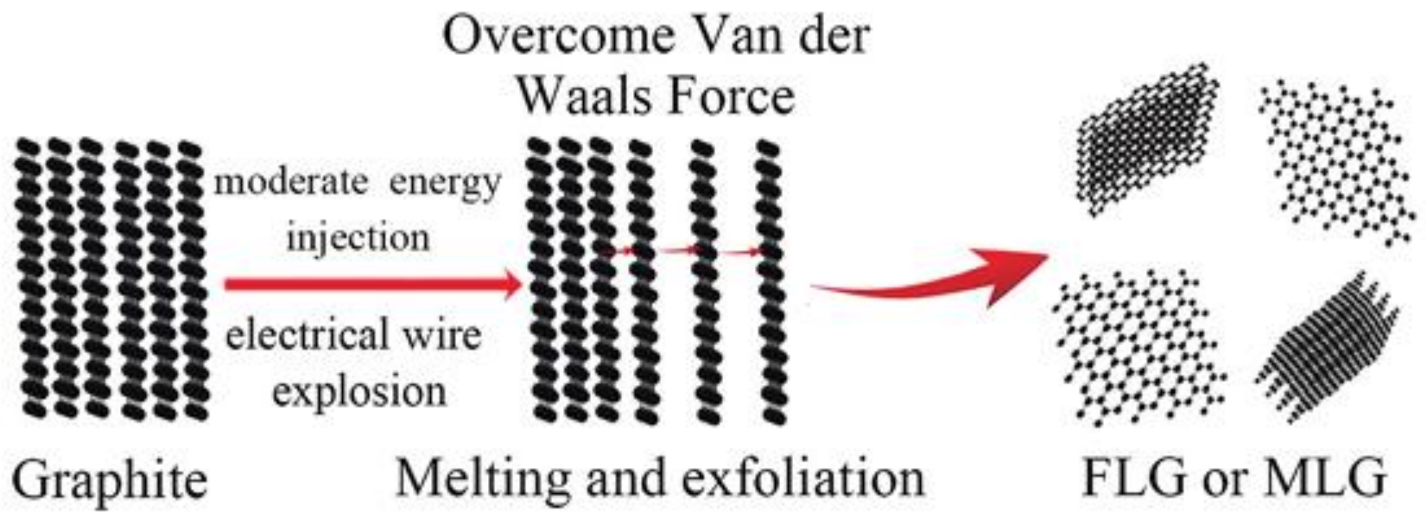
Mondal, S.; Ghosh, S.; Raj, C. R. *Unzipping of SWCNT for Electrocatalytically Active Graphitic-Carbon/Pd Hybrid Catalyst.* **ACS Omega**, 2018, 3, 622–630.

Graphene oxide reduction



- Graphite can be oxidized using different procedures in the presence of strong acids.
- GO flakes are functionalized with epoxy and hydroxyl groups above.
- Partial recovery of electronic properties is possible after reduction treatment.
- Current approaches cannot fully remove defects.

Electrical explosion of graphite sticks

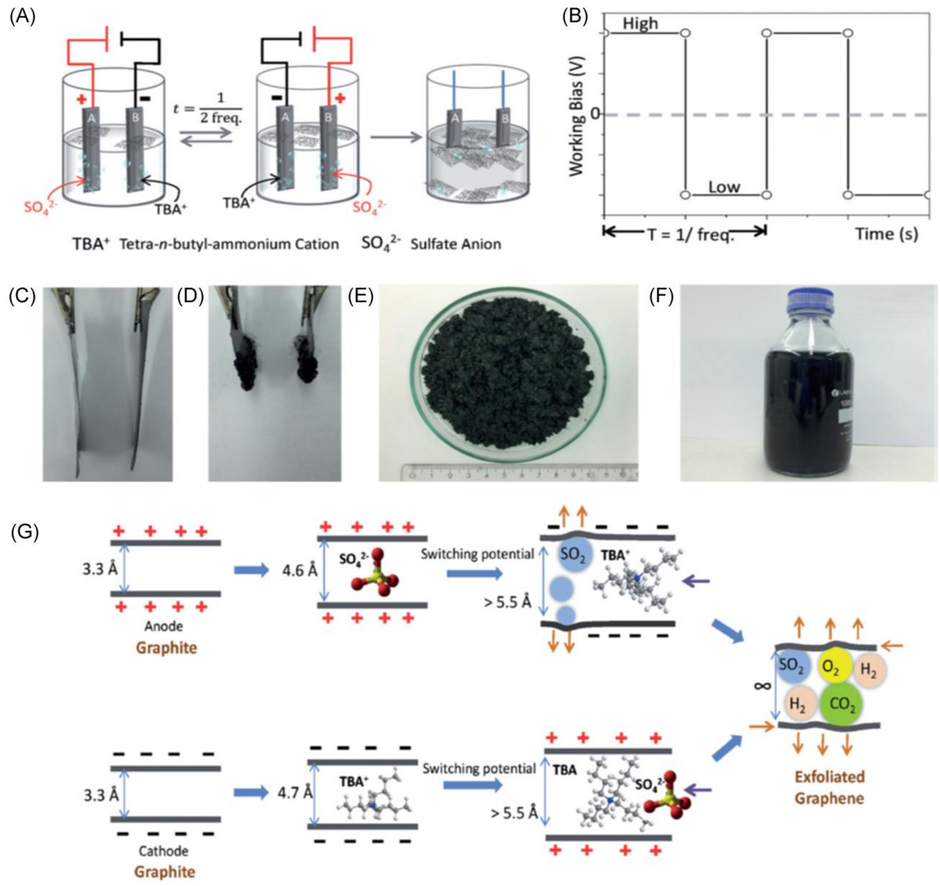


- Electrical explosion of high-purity graphite sticks submerged in distilled water
- Injecting specific amounts of energy into the graphite to melt it and overcome van der Waals forces
- Precise control of the charging voltage, 22.5–23.5 kV, is critical for optimizing the yield of high-crystallinity mono-layer graphene.

Gao, X. *et al.*, *Nanoscale* 9, 10639–10646 (2017).

Electrochemical exfoliation of graphene

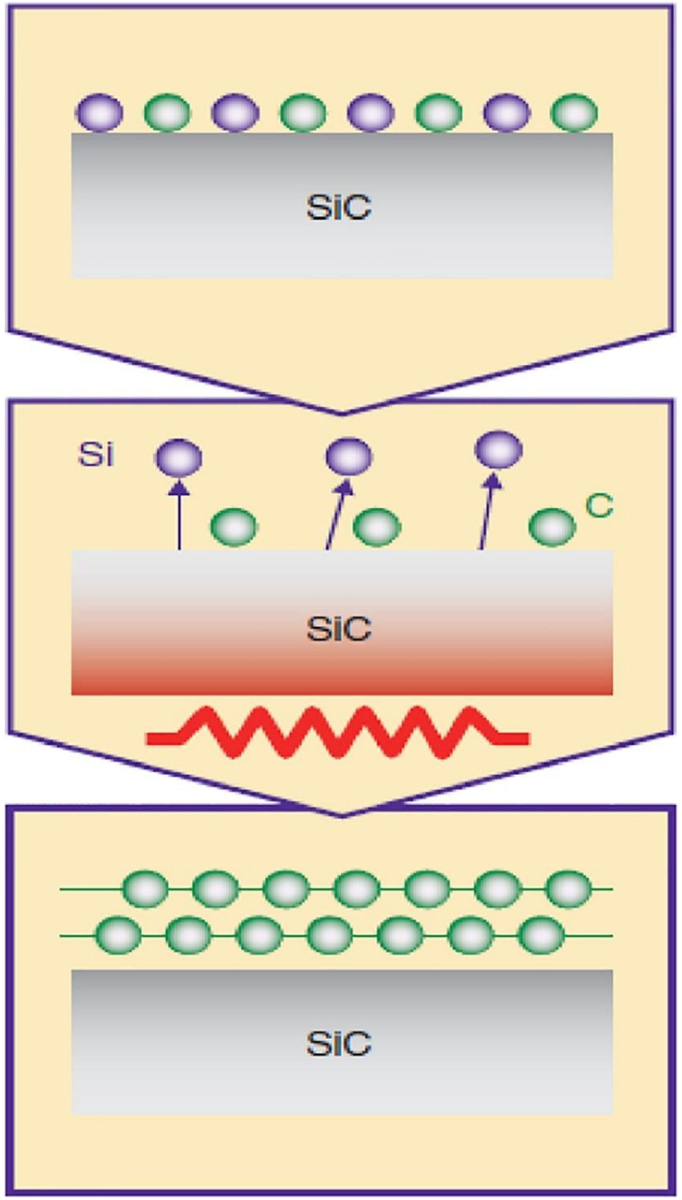
- At the anode, oxygen-containing radicals (HO•, O•) attack defects in graphite and allow sulfate ions to enter between layes
- When polarity switches, intercalated sulfate ions form gas bubbles, creating space for large TBA^+ ions to enter.
- At the cathode, flat TBA^+ ions fit between graphene layers; sulfate ions intercalate when polarity reverses.
- Resulting graphene consists mainly of 1–3 layers, with a high carbon/oxygen ratio



Liu et al. (2019). Carbon Energy, 1(2), 173–199.

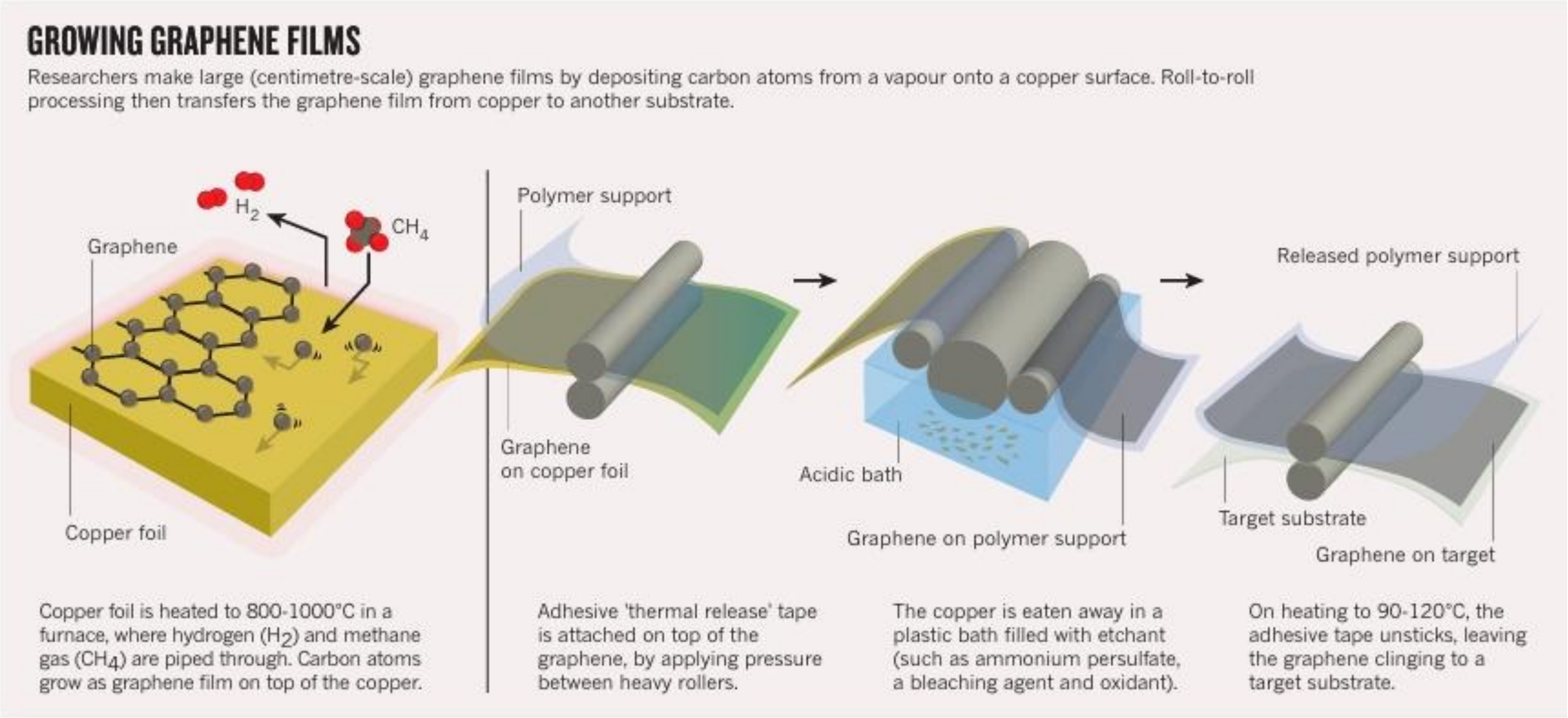
Epitaxial growth of Graphene (SiC heating)

- Thermal decomposition of SiC
- Si atoms desorb from the surface and the C atoms left behind naturally form few layer of Graphene
- Temperature, pressure, surface and catalyst all affect the quality of graphene
- No transferring to a substrate is required



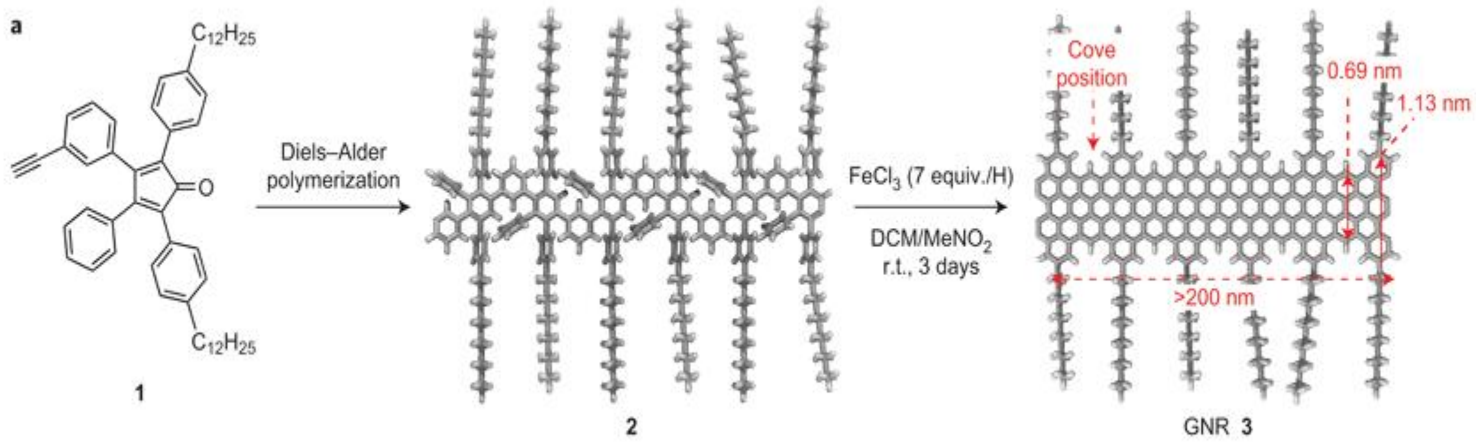
Abdel Ghany, N. A.; Elsherif, S. A.; Handal, H. T. “Revolution of Graphene for Different Applications: State-of-the-Art.” *Surfaces and Interfaces*, **9** (2017): 93–106.

Growing graphene films



Van Noorden, R. Production: Beyond sticky tape. *Nature* **483**, S32–S33 (2012). https://doi.org/10.1038/483S32a

Liquid-Phase Exfoliation-graphene nano ribbons



- Diels–Alder polymerization of tailored monomers with solubilizing alkyl chains.
- Precursors "graphitized" into well-defined GNRs by intramolecular oxidative cyclodehydrogenation using $FeCl_3$.
- Produced >200 nm GNRs

Narita, A. *et al.*, *Nat. Chem.* 6, 126–132 (2014)

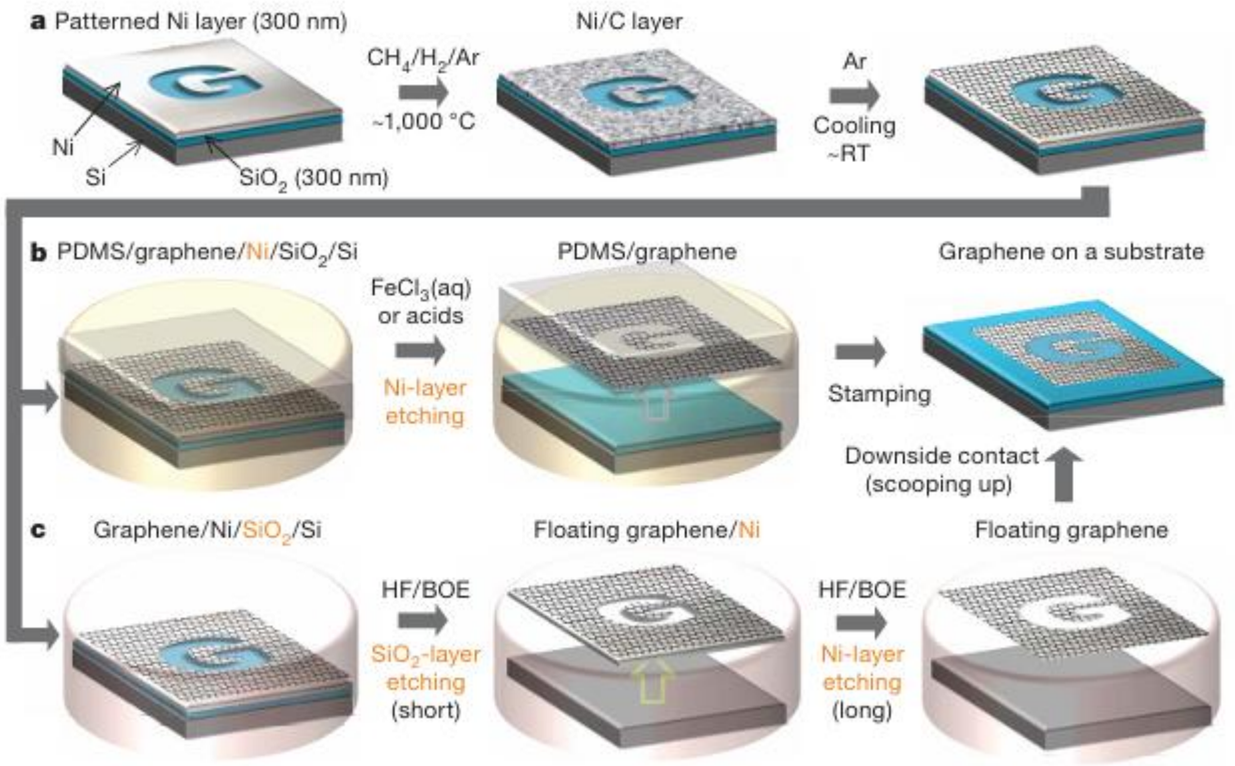
Graphene growth by CVD

Chemical Vapor Deposition (CVD)-Graphene growth based on thermal decomposition and surface diffusion, yielding uniform layers.

- In PECVD, plasma-induced ion bombardment and localized energy input accelerate nucleation but increase defects and vertical growth
- Laser-CVD uses focused heating for patterned growth,
- TCVD enhances efficiency through controlled thermal conditions.

Graphene films on a large scale using CVD on nickel layers

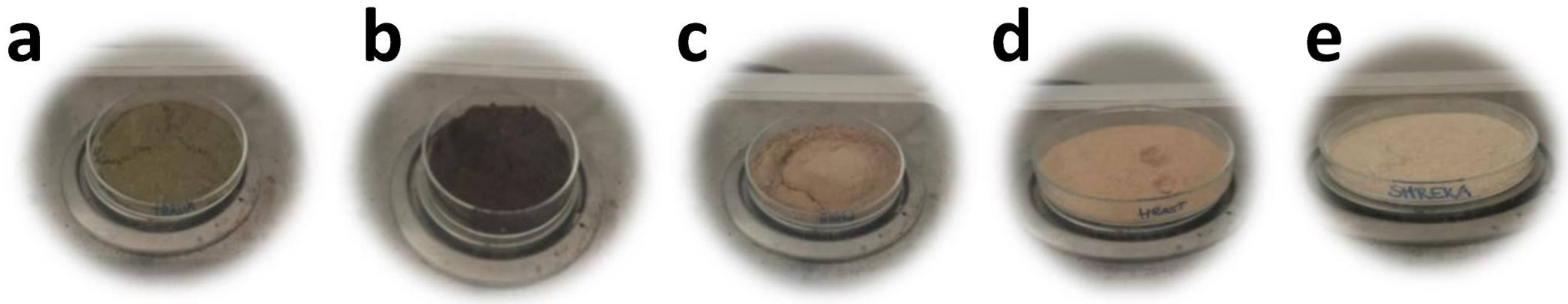
- Patterned graphene grown on thin nickel layers.
- Etching with $FeCl_3$ (or acids) and transfer using a PDMS stamp.
- Etching with BOE or HF solution and transfer of graphene films (RT, −25 °C).



PDMS-Polydimethylsiloxane

Kim, K., Zhao, Y., Jang, H. *et al.* *Nature* **457**, 706–710 (2009).

Graphene by biomass pyrolysis



(**a**) grass ; (**b**) coffee sludge ; (**c**) brewery sludge (B-BS); (**d**) wood chips, and (**e**) wood chips

biomass -pyrolysis process under inert atmosphere -biochar (carbon-rich solid residue) - modify the biochar chemically -graphene-like material

Plenča et al. (2023). Materials, 16, 7658.

Advantages and disadvantages of Top-down synthesis

Top-down methods, such as mechanical exfoliation, oxidation-reduction, unzipping carbon nanotubes, and liquid-phase exfoliation,

- are highlighted for their scalability and cost-effectiveness,
- albeit with challenges in controlling defects and uniformity.

Hutapea,J. et al. Micro 2025, 5, 40

Advantages and disadvantages of Bottom-up synthesis

Bottom-up methods, including chemical vapor deposition (CVD), arc discharge, and epitaxial growth on silicon carbide,

- offer superior structural control and quality
- but are often constrained by high costs and limited scalability.

Hutapea,J. et al. Micro 2025, 5, 40

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Thank you!

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