Towards Cleaner Graphene Catalyst Removal

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NSF National Science Foundation
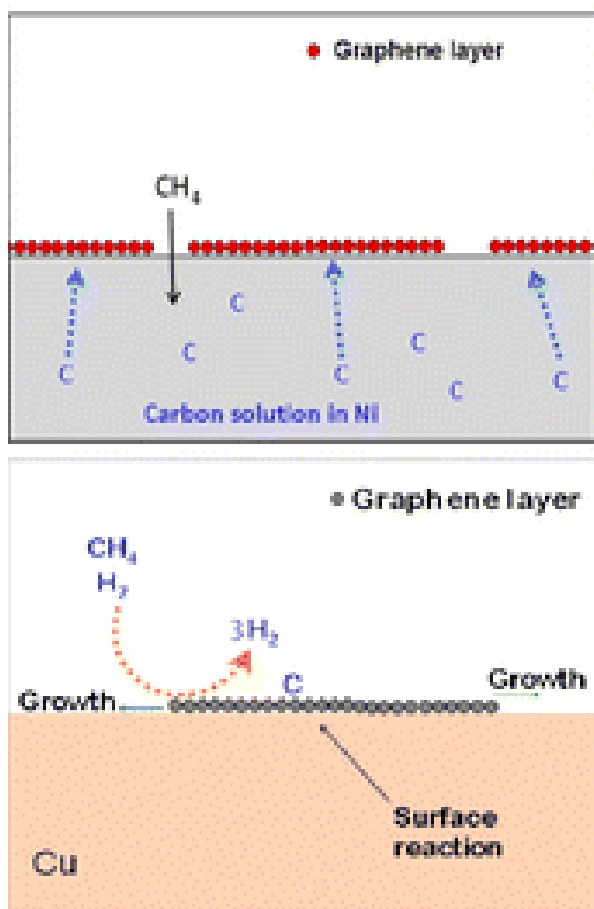WHERE DISCOVERIES BEGIN

Overview

- **Exciting Applications of Graphene**

- **Synthesis and Characterization**

- **Challenges**

- **Etching Improvements**

- **Summary and Future Recommendations**

Exciting Applications of Graphene

- 2D, one-atom-thick layer of carbon atoms arranged in a hexagonal lattice
  - Conductivity
  - Transparency
  - Flexibility

- Applications include:
  - Photovoltaic cells
  - Field effect transistors
  - Electronics (replacement for Indium Tin Oxide)

- Limiting Factor: lack of process for large-scale, high-quality production
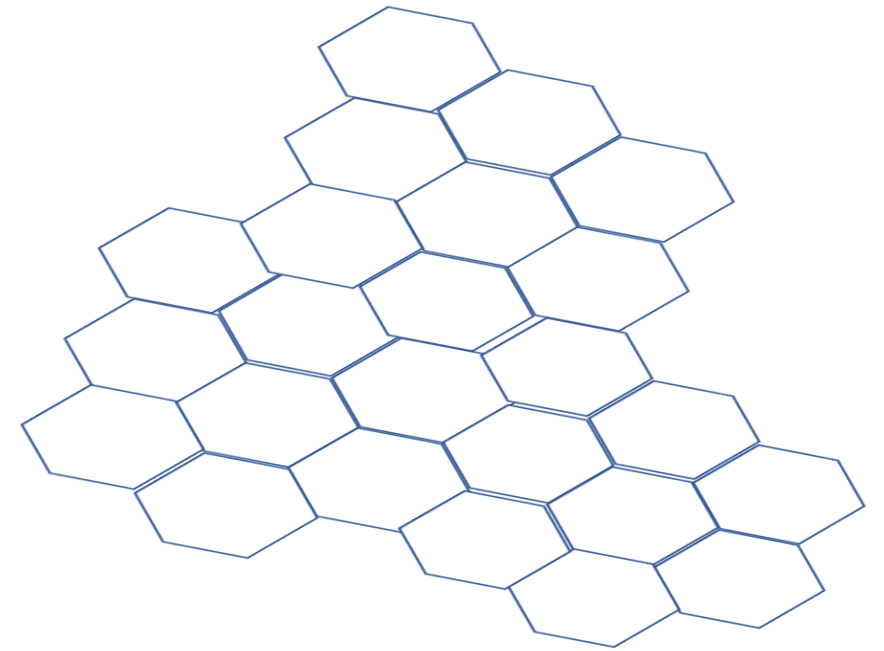
Chemical Vapor Deposition Synthesis

Zhang, Y.; Zhang, L.; Zhou, C. "Review of Chemical Vapor Deposition of Graphene and Related Applications". Acc. Chem. Res. 2013, 46, 2329– 2339.

- Ni or Cu film heated to 900°C-1000°C to allow carbon atom dissolution

- Mixture of H_2/C_2H_2 gas introduced into chamber; carbon ions dissolve in metal film

- Cu surface reaction is self-limiting

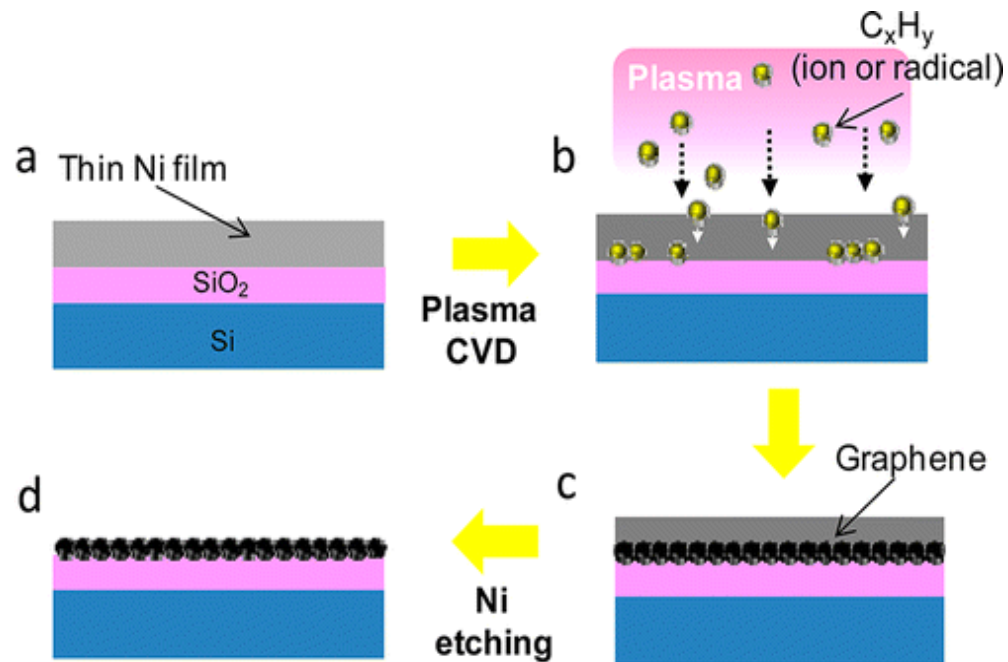- As Ni cools, carbon precipitates out on top

Polymer Mediated Transfer
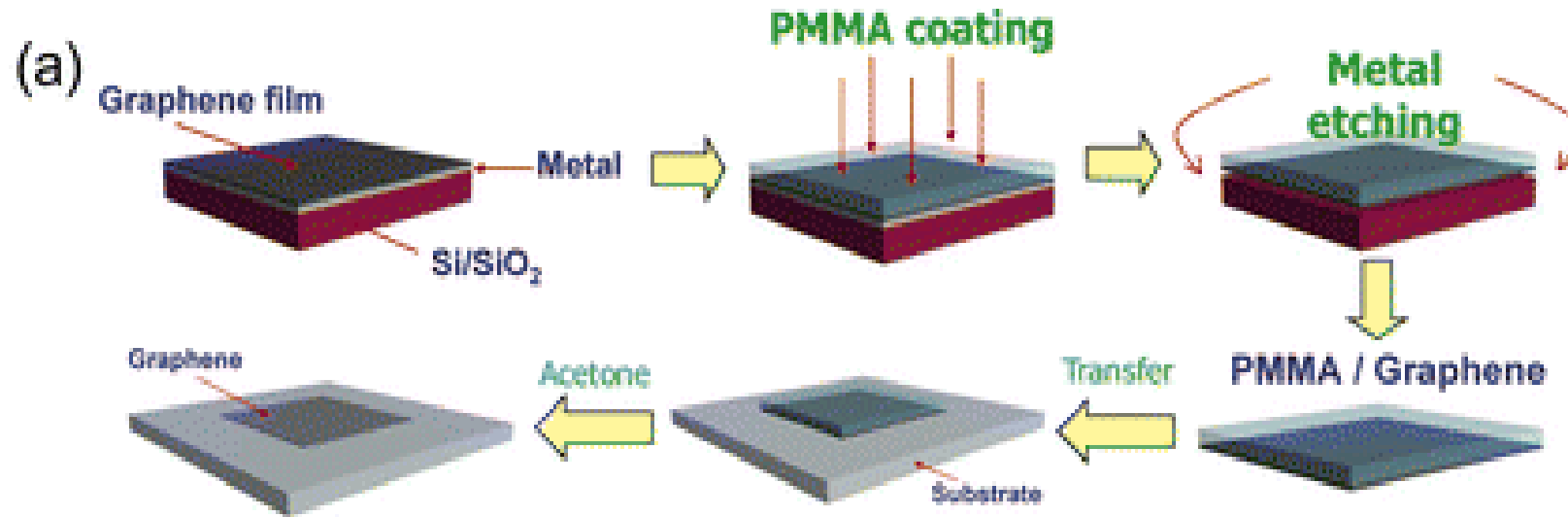
Zhang, Y.; Zhang, L.; Zhou, C. "Review of Chemical Vapor Deposition of Graphene and Related Applications". Acc. Chem. Res. 2013, 46, 2329– 2339.

- Catalyst typically etched with $FeCl_3$ or other chemical etchant
- Polymethyl-methacrylate (PMMA) coat is applied to preserve graphene shape
- PMMA/graphene column transferred onto Si wafer and cured before PMMA removal with acetone

Direct Graphene Synthesis

Inductively Coupled Plasma
Chemical Vapor Deposition
(ICPCVD)

a) Ni film heated to 500°C to allow carbon atom dissolution

b) Mixture of H_2/C_2H_2 plasma introduced into chamber; carbon ions dissolve in Ni film

c) As Ni cools, carbon precipitates on top **and** in between the Ni and Si substrate

d) Ni is etched away with $FeCl_3$ to reveal only graphene left on the surface

Kato, Toshiaki and Rikizo Hatakeyama, "Direct Growth of Doping-Density-Controlled Hexagonal Graphene on SiO2 Substrate by Rapid-Heating Plasma CVD". ACS Nano 2012, 5, 10, 8508-8515.
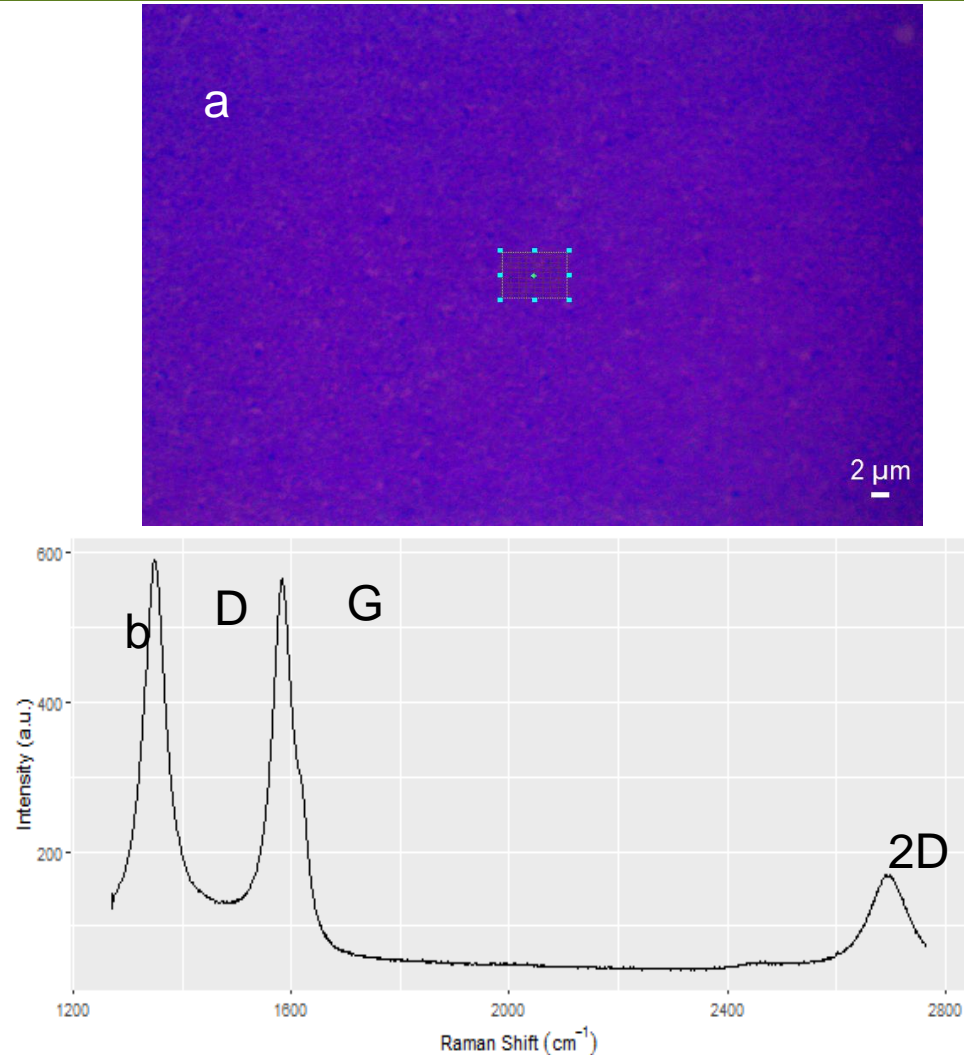
Graphene Characterization

a) **Optical Microscopy**
- Easy tool to spot large details and residues.
- Provides general sense sample cleanliness.

b) **Raman Spectroscopy**
- Utilizes Raman scattering to measure signal strength
- 2D/G: Layering
- D/G: Defects

Figure 1. **a)** Optical image of an electrically dissolved Ni graphene sample in 1:10 H_2SO_4/DI and **b)** corresponding Raman spectrum.

Challenges with Graphene Growth

- Initial quality of graphene is difficult to determine
  - Unsure if defects are caused by growth conditions or by the etching process introducing residue and causing deformities
  - $FeCl_3$ can be harsh on grown graphene

- Residues affect graphene device performance
  - Metal ions
  - Polymer residues

- Alternatives to direct wet etching with $FeCl_3$ to analyze true graphene quality
  - Electrochemical Ni Delamination
  - $FeCl_3$ Vapor Etching
  - Electrochemical Ni Dissolution

Electrochemical Delamination (Attempted)

- Samples placed in 1.0M NaOH solution with Pt foil electrode

- Voltages set between 1.5-2.5V for times ranging from 15 seconds to 30 mins using potentiostat

- Graphene delaminated along with metal film

Delaminated Cu film

Ni film

1.0M NaOH solution

Pt foil

Nickel
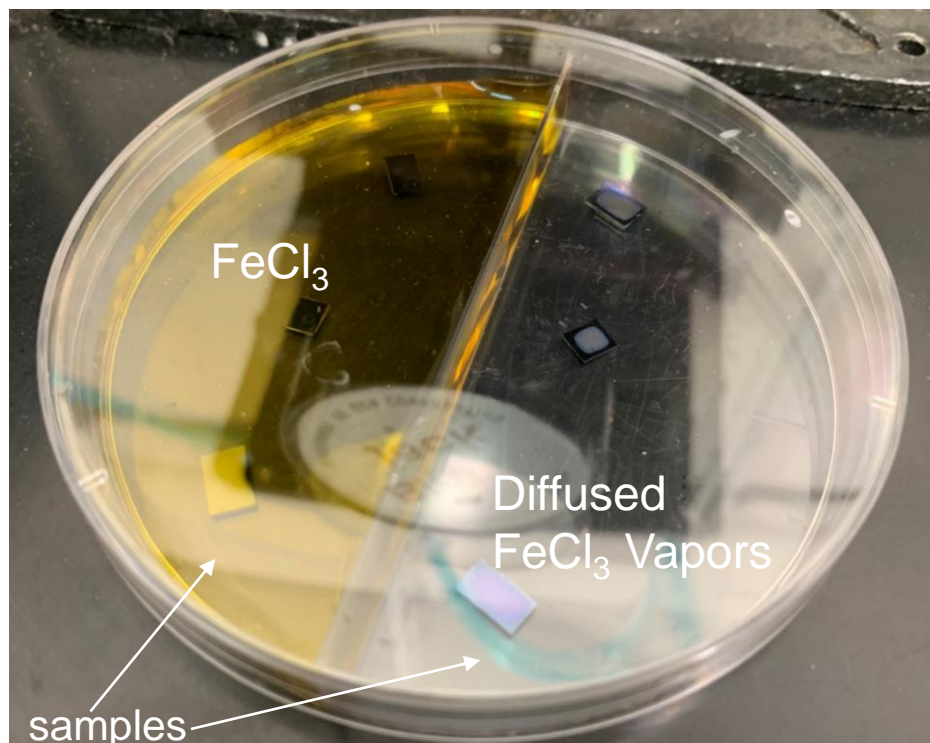
Graphene

Silicon

Graphene

Silicon
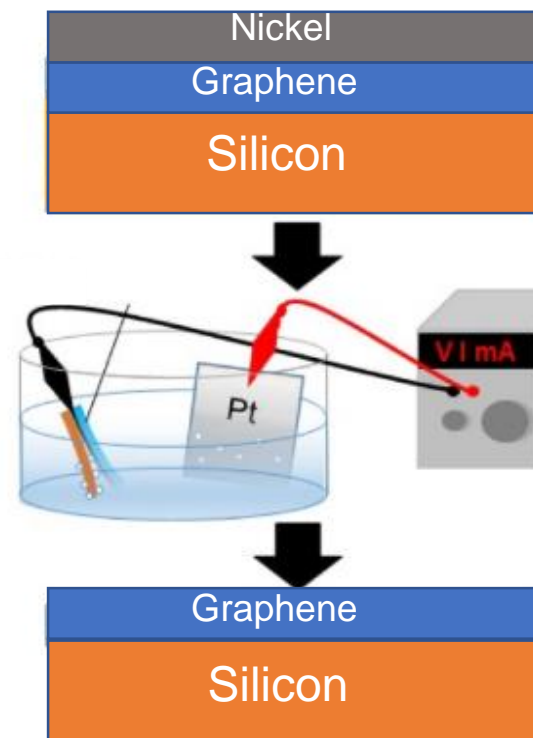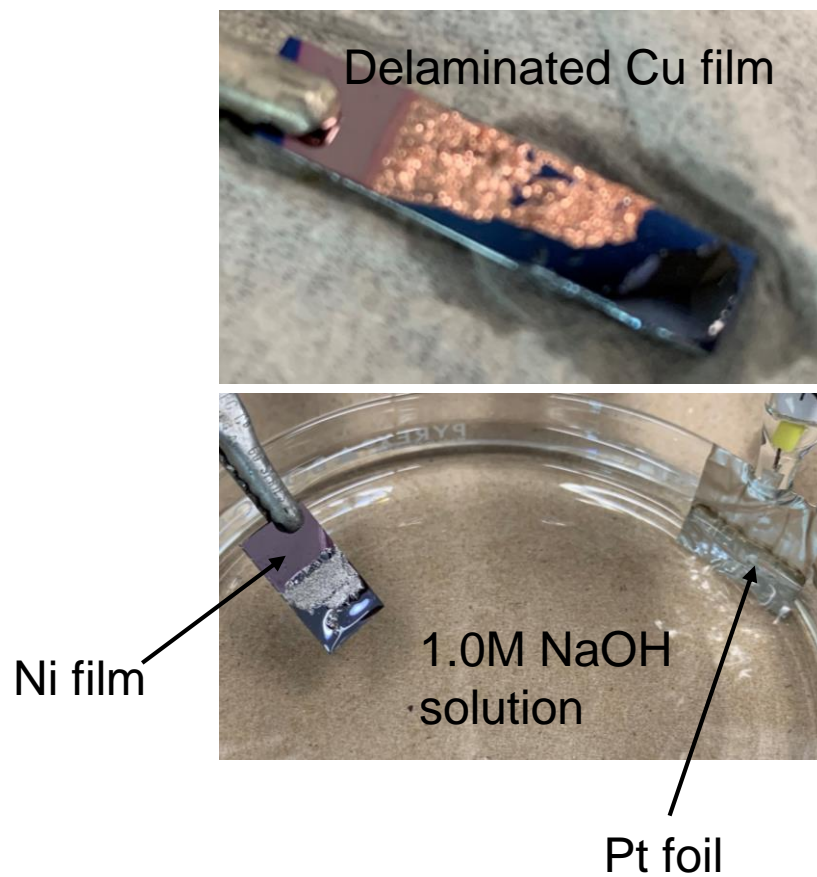
Wet and Vapor FeCl₃ Etching

Figure 2. Small graphene growths are processed in wet and vaporous environments in a divided Petri dish.

Wet FeCl₃ Etching

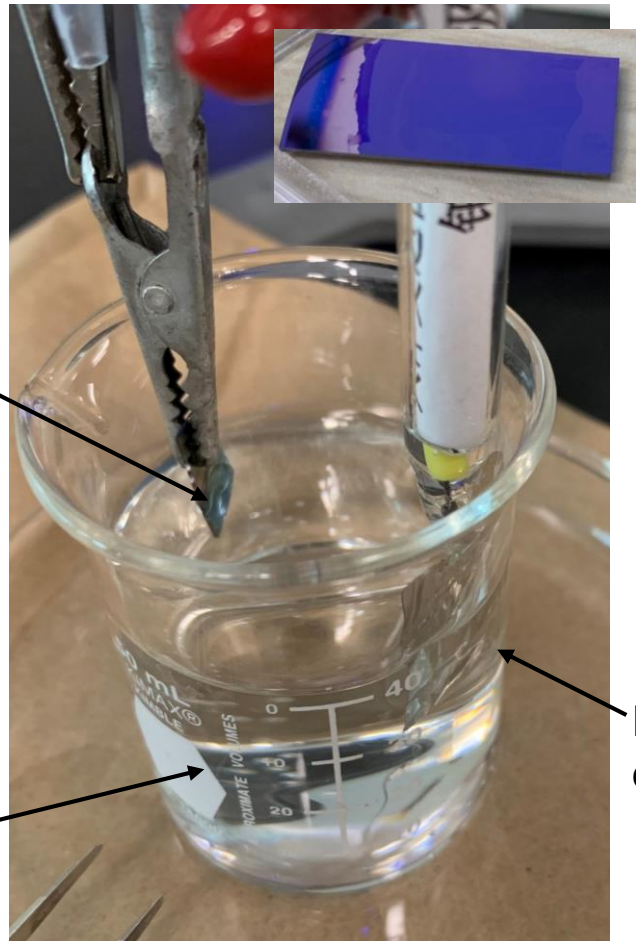- FeCl₃ dissolves Ni catalyst
- Usually requires a few hours
- Cleaned in deionized (DI) water baths

Vapor FeCl₃ Etching

- FeCl₃ vapors have capacity to dissolve Ni catalyst
- Typically requires 24+ hours
- Cleaned in DI water baths
- Goal: reducing deformations

Electrochemical Ni Removal
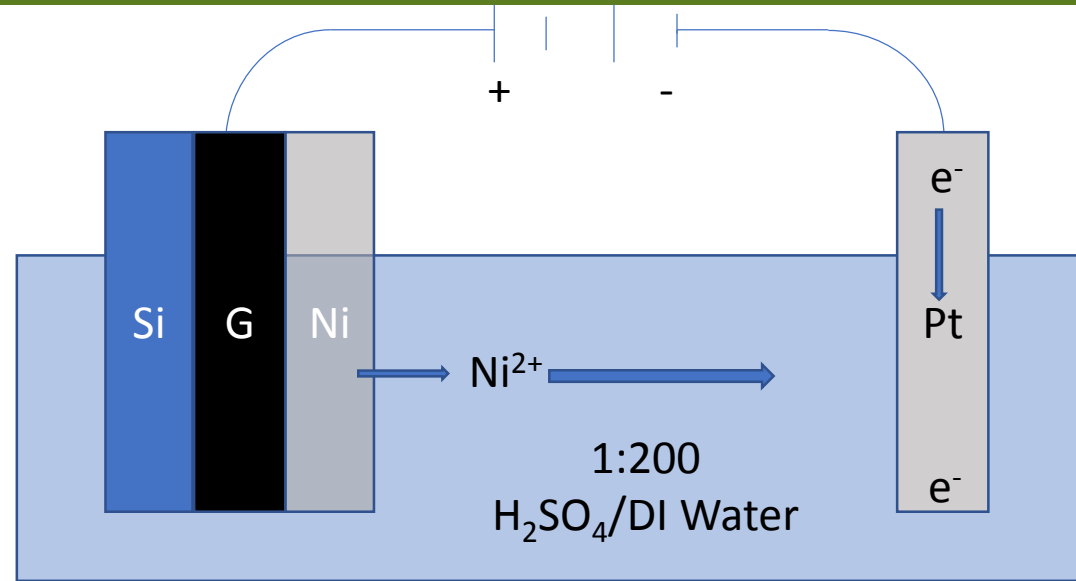

sample (unetched/etched regions)

Ni-graphene sample
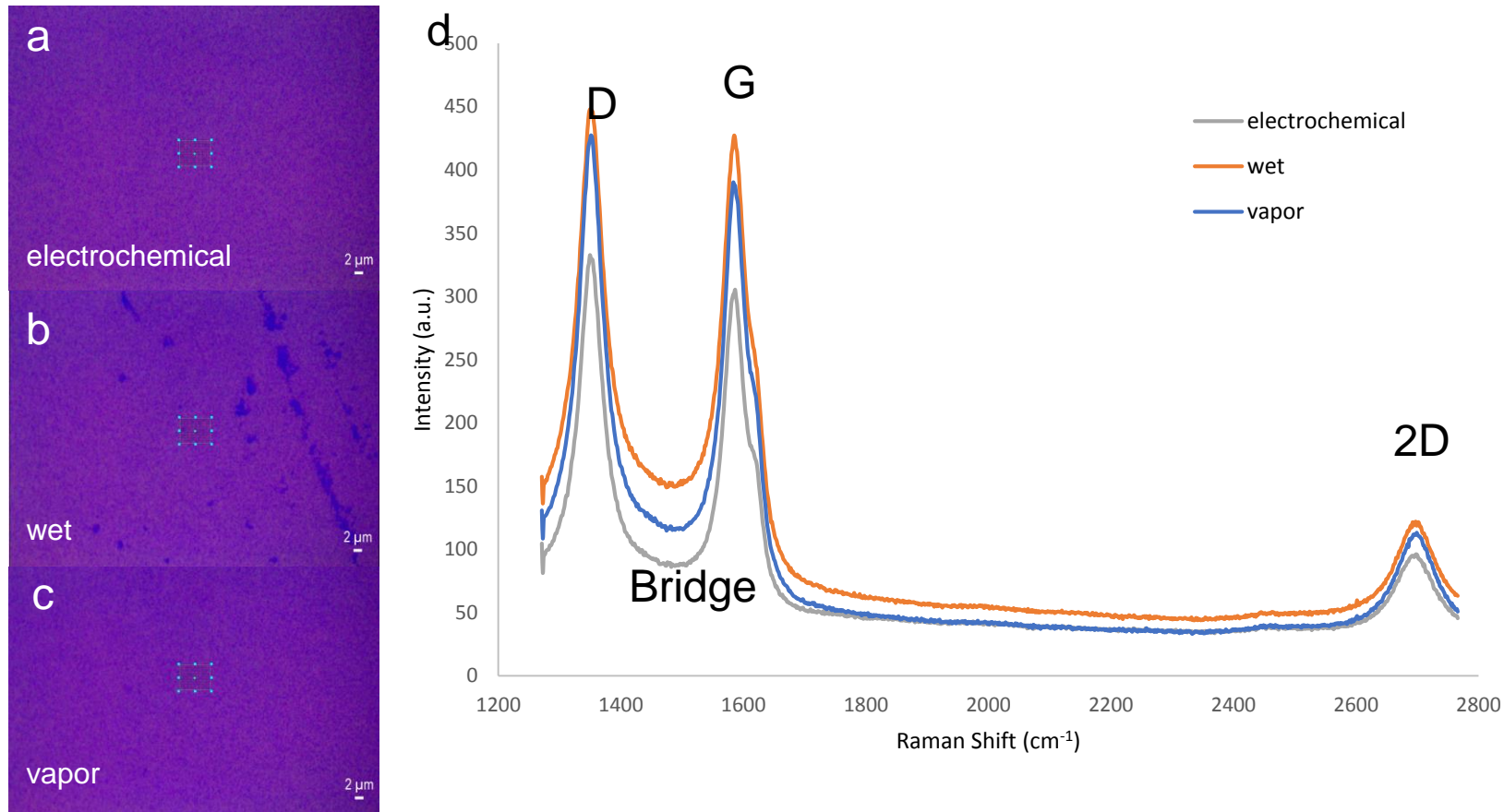
Sulfuric acid solution

Pt foil electrode

Ni removal process

Si G Ni

Ni^{2+}

1:200
H_2SO_4/DI Water

e^-
Pt
e^-

+   -

Schematic of Ni removal

- With applied potential Ni dissolves in 1:200 H_2SO_4/DI Water, leaving only graphene

- Vastly reduced chemical concentration compared to $FeCl_3$

- Requires around 30 mins

- Reduces necessary chemical volume

- Higher concentrations reduce time

Etch Comparison

Figure 3. Optical images of a(n) **a)** electrochemical Ni removal, **b)** wet $FeCl_3$ etch, and **c)** vapor $FeCl_3$ etch, with **d)** superimposed Raman spectra.

- Wet chemical etching exhibits strongest signal.
- Graphene quality appears relatively consistent.
  - Wet etch has more noise
- Electrochemical method reduces D/G bridging.
  - Wet: 4:1 D/bridge
  - Vapor: 5:1 D/bridge
  - Electrochemical: 6.8/1 D/bridge

Etch Comparison

electrochemical   wet   vapor
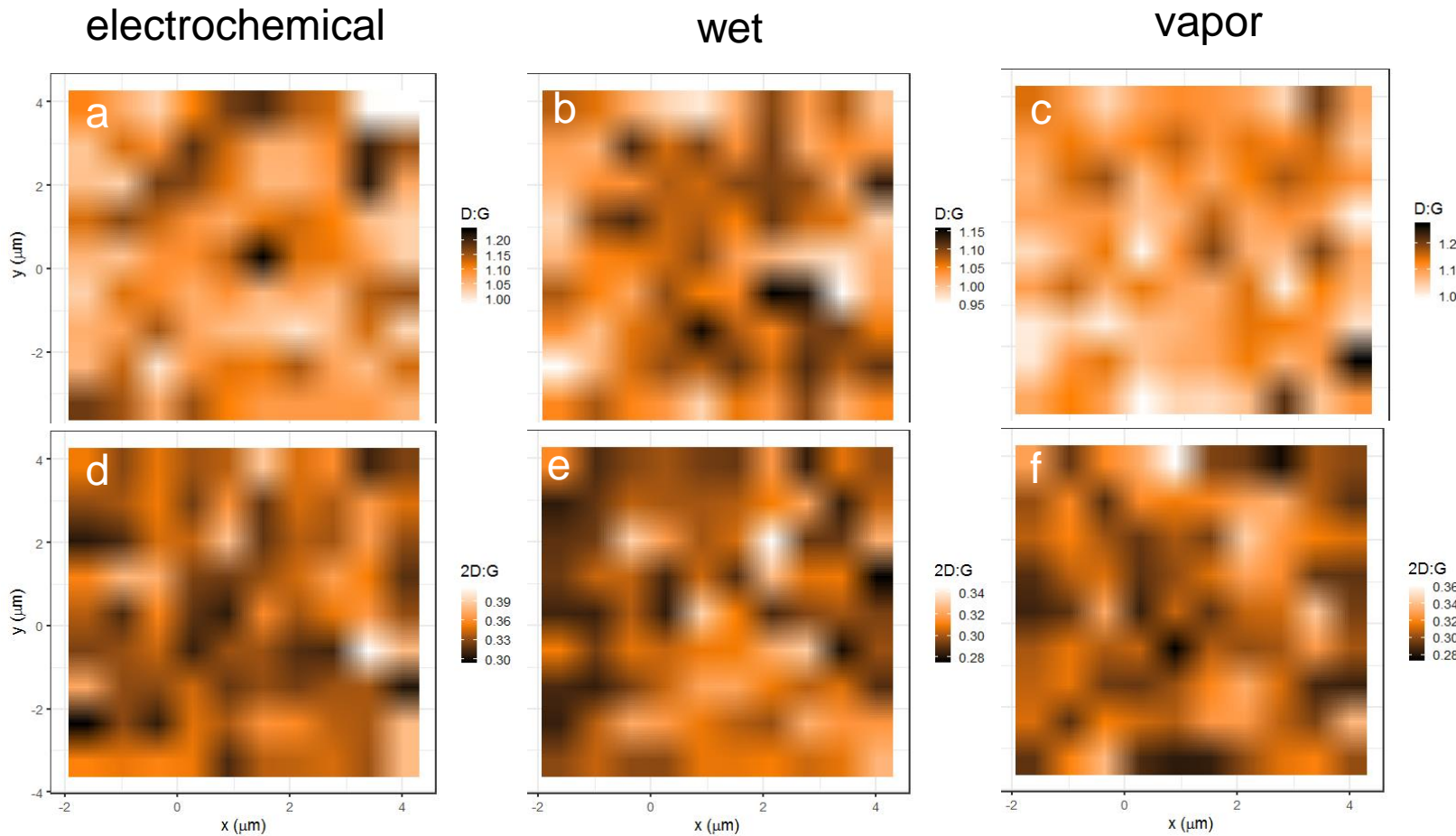
Figure 4. D:G ratio maps of **a)** electrochemical Ni removal sample, **b)** wet FeCl$_3$ etch, and **c)** vapor FeCl$_3$ etch, with **d), e), f)** respective 2D:G ratio maps

- Ratio maps are similar across the board.
- Reveals fairly defect dense, multilayer graphene
- Somewhat expected as samples are from the same graphene growth.
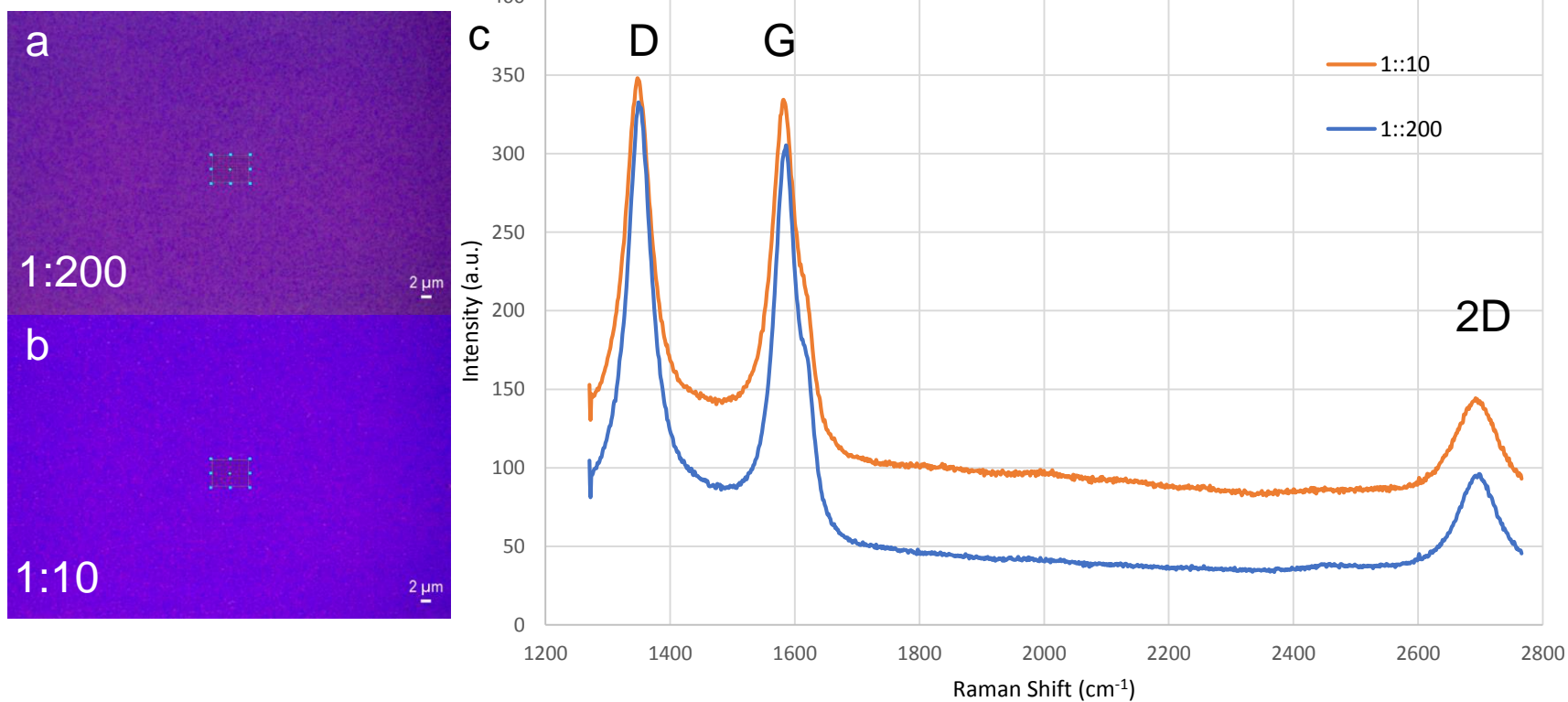
Solution Concentration

Figure. Optical images of a(n) **a)** electrochemical Ni removal in 1:200 H_2SO_4/DI solution, **b)** in 1:10 H_2SO_4/DI solution, and **c)** superimposed Raman spectra.

- Higher concentrations of solution reduce etching time.

- Potential to dramatically reduce processing times and chemical waste.

Conclusions and Future Insights

- Quality of synthesized graphene appears low
  - High D/G and low 2D/G ratios through all methods
  - Similar Raman spectra
    - Strength
    - Noise

- Electrochemical Ni removal saves time
  - Reduces D/G bridging effect

- Higher concentrations of sulfuric acid lead to faster Ni dissolution
  - Minor amounts could lead to less contamination
  - Find right parameters for efficient etching

- Residue analysis with Scanning Tunneling Microscope
  - Reveal contaminants left using Energy Dispersive X-ray Spectroscopy

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