Graphene-Based Composite Sensors for Energy Applications

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Overview Of Presentation

Background

Graphene As A Sensor Material

Hypothesis, Goals, & Research Issues

Roadmap & Overview of Project

Update on Key Research Areas

Graphene Synthesis & Device Fabrication

Nanoparticle Nucleation & Growth

Electrical Characterization of Graphene Films & Sensors

Future Work

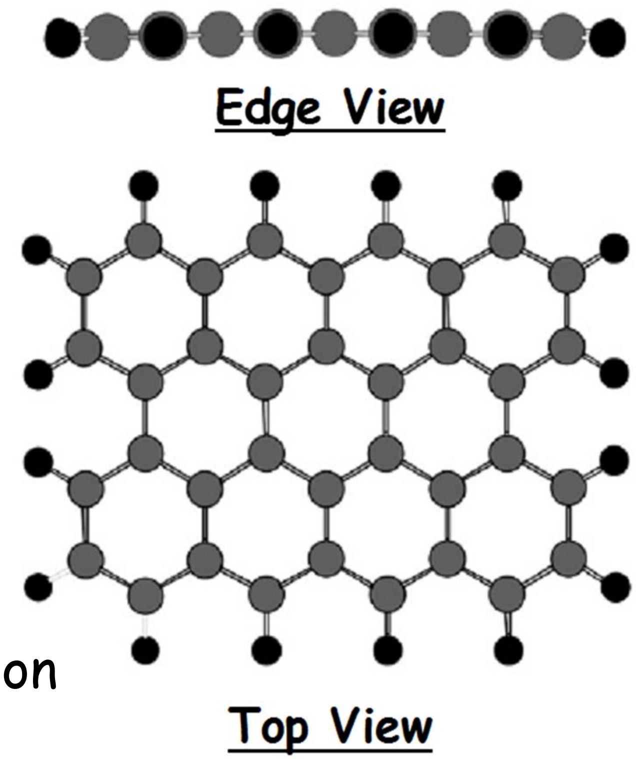
High Temperature Test Unit

Graphene-Nanoparticle Composite Sensors

Graphene As A Sensor Material

Structure of graphene

- Monolayer of sp^2 bonded C-atoms
- p orbitals normal C-monolayer
- Ideally one layer but frequently multilayers



Attributes as gas sensor material

- High charge carrier mobility
- Low charge carrier density / altered by adsorption

- Chemoresistive graphene gas sensors should have a high sensitivity and rapid response

Basic Question: How can target specificity be achieved?

Fundamental scientific issue addressed in this research → **Basic Hypothesis of this Research**

Basic Hypothesis

Gas adsorption mediated by different types of nanoparticles attached to independent chemoresistive graphene sensors can yield a unique electrical response pattern for each adsorbed species.

Research Goals

Validate the hypothesis for graphene-nanoparticles (G-nP) composites

Develop a G-nP composite "electronic nose" for energy applications

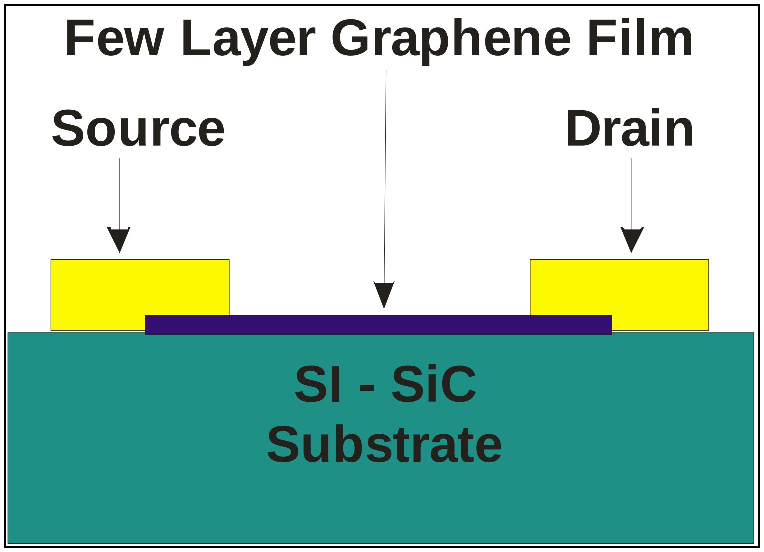
Research Issues

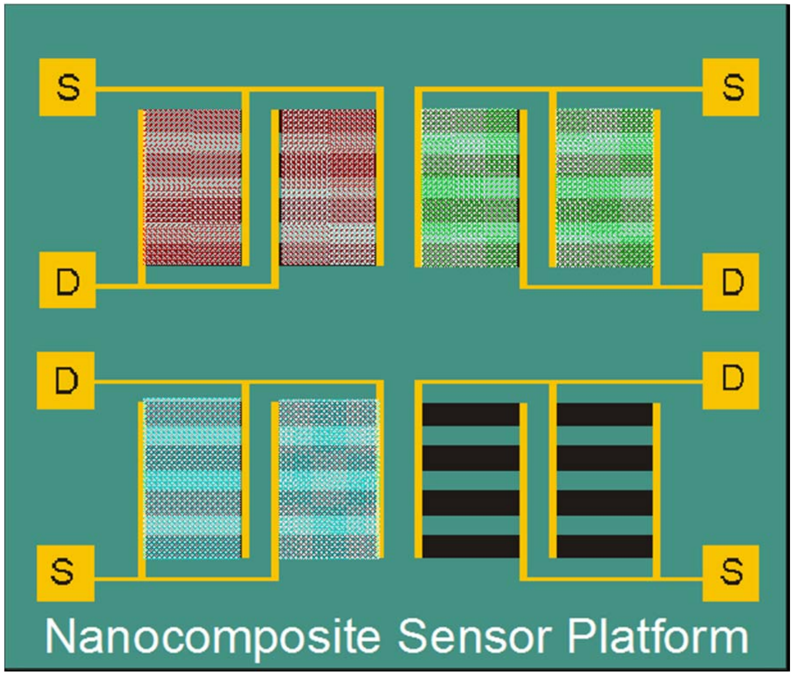
Synthesis of graphene & G-nP composites

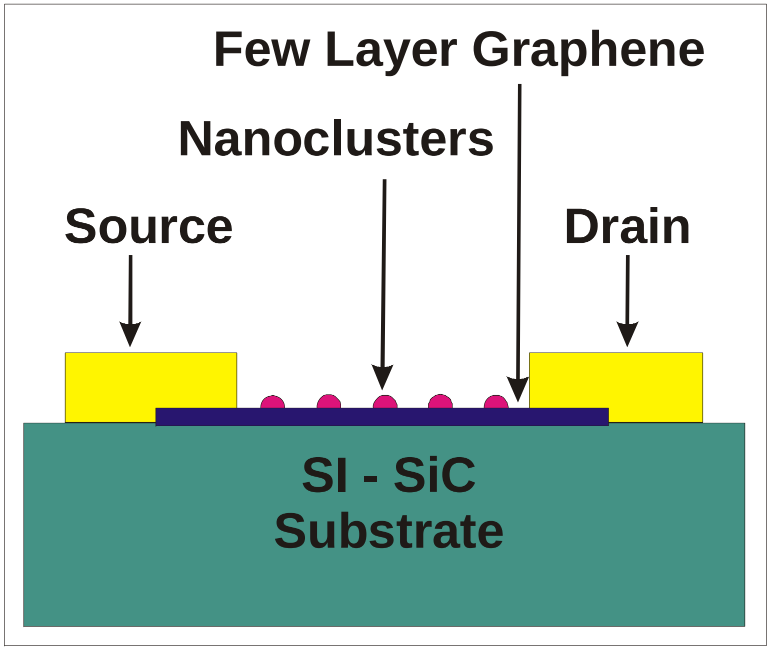
Fabrication of sensor structures

Characterization of thin film & sensor properties

Roadmap & Overview of Project







Synthesis of graphene films

Patterning & contact deposition

Nucleation & growth of nanoparticles

Characterization of electrical properties

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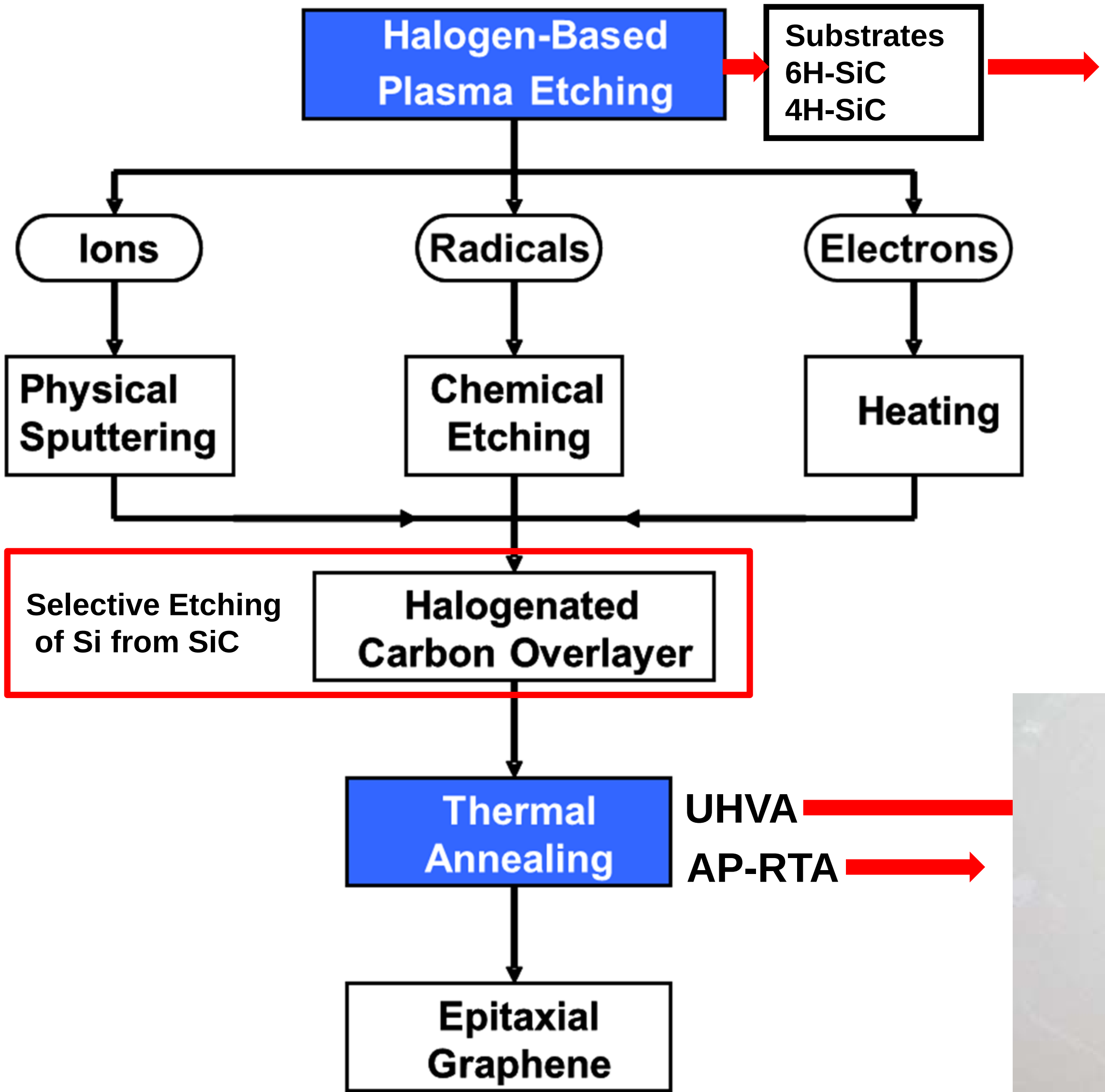
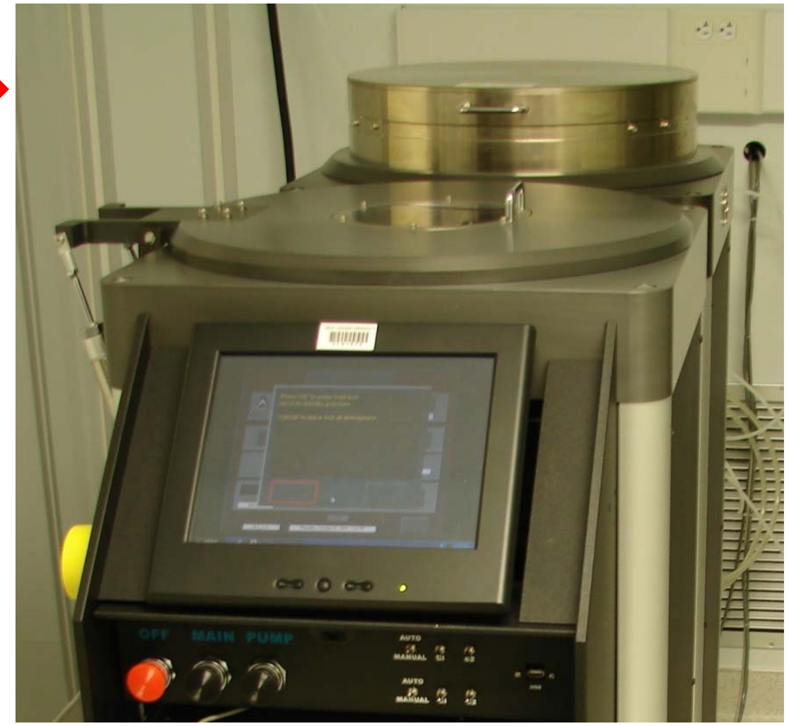
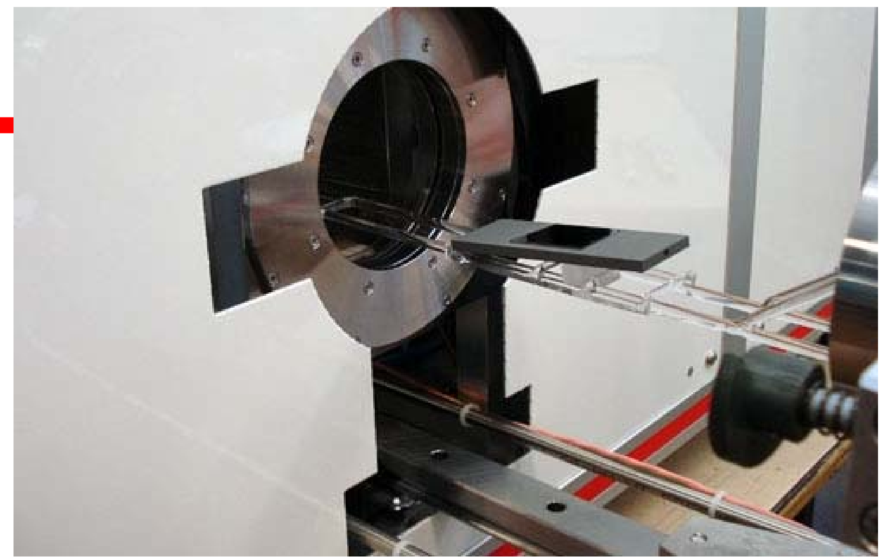
Synthesis Of G/SiC Films



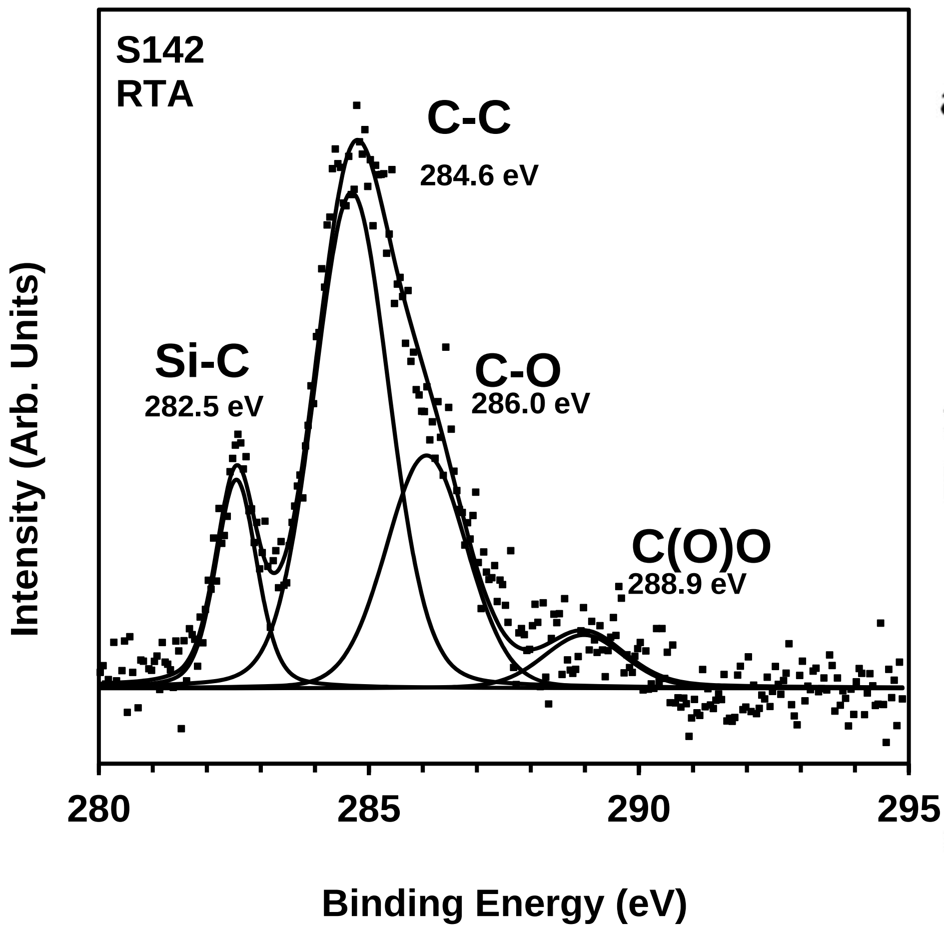


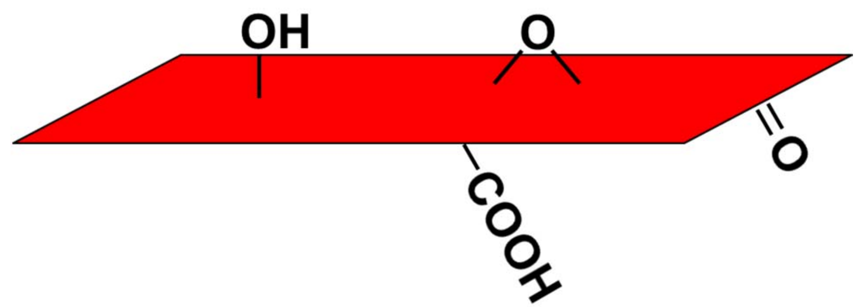


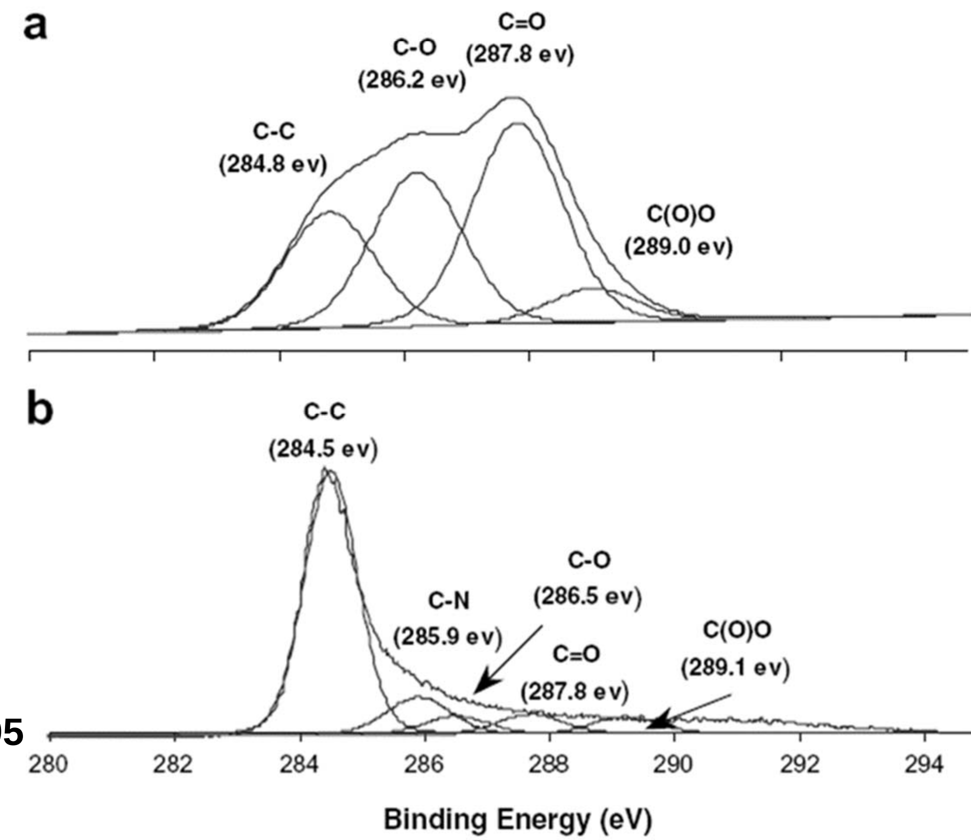
Stinespring & coworkers, J. Vac. Sci. Technol. 30 (2012) 030605.

Surface Chemistry of AP-RTA G/SiC Films

XPS of C1s



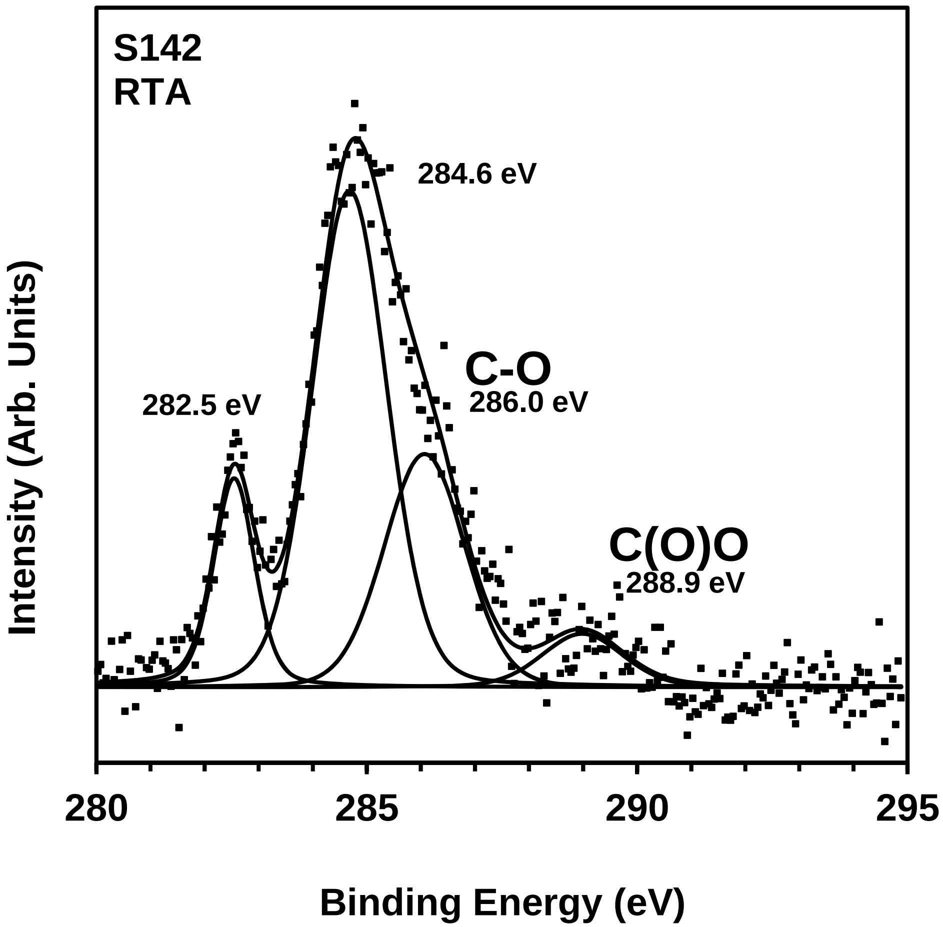


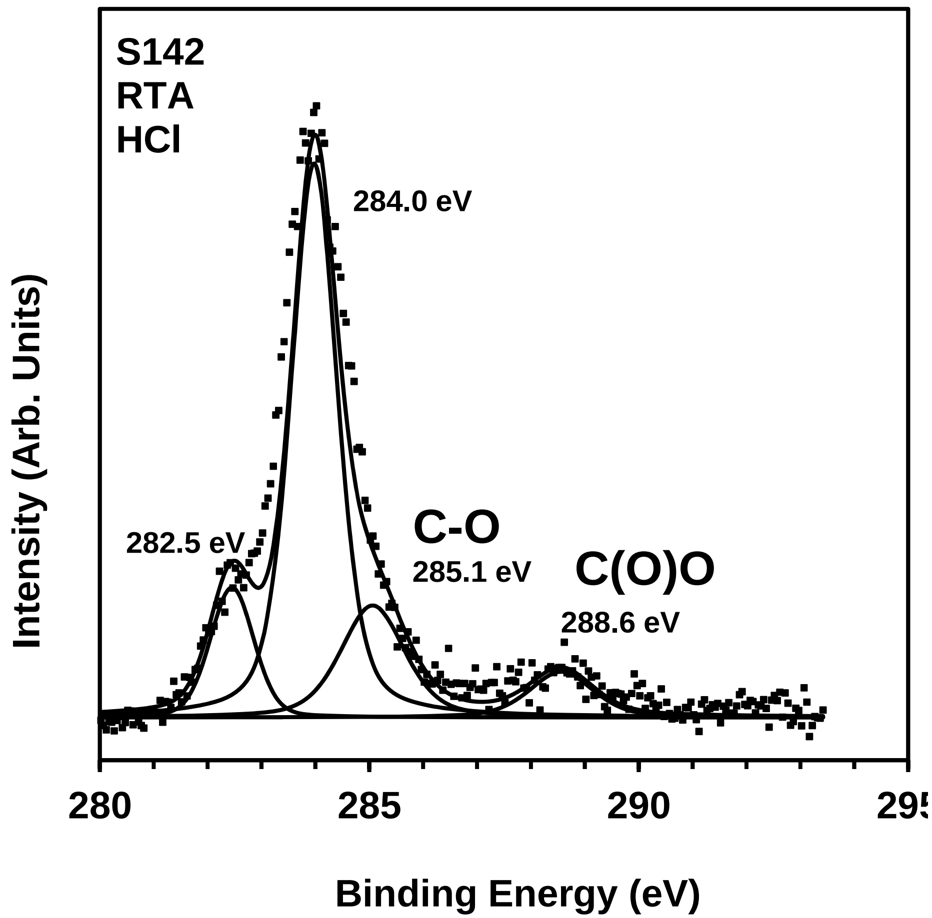


a) Graphene oxide and b) hydrazine reduced GO

Stankovich et al., Carbon 45(2007)1558-1565.

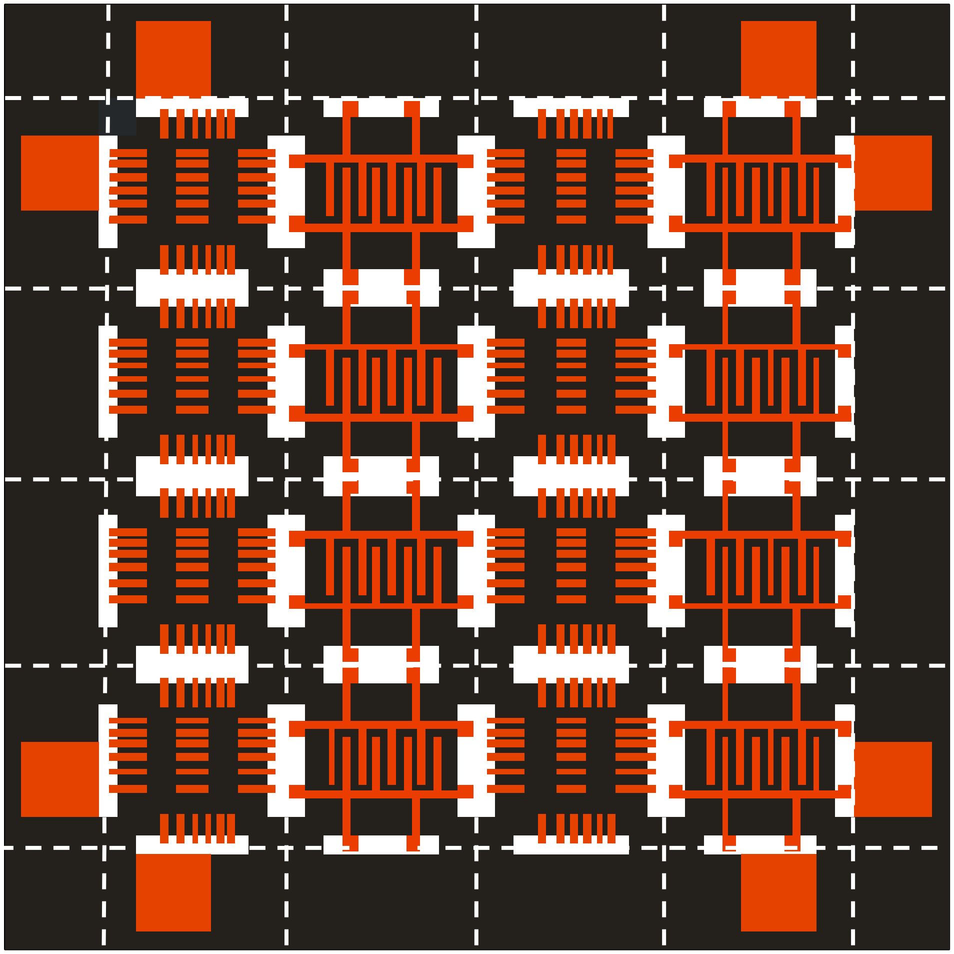
Post Synthesis Surface Modification





The ability to control the surface defects is important since they influence electrical properties & serve as sites for particle nucleation

Device Fabrication



- Grow uniform G/SiC film on 1 cm x 1 cm substrate
- Use shadow mask & oxygen ICP-RIE to remove graphene & form SiO_x strips while protecting 2 mm x 2 mm graphene regions
- Use shadow mask and e-beam evaporation to produce Au/Ti device patterns
- Use wafering saw to produce 2.5 mm x 2.5 mm die for testing
- TLM pattern - electrical properties
- Sensor pattern – sensor testing

Nanoparticle Nucleation & Growth on Graphene

Solution based nanoparticle nucleation and growth chemistries

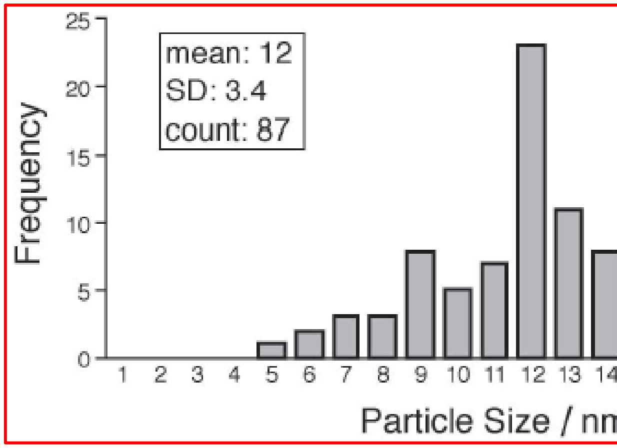
Studies to date include Ag, Au, Pt, Ir, TiO_2 nanoparticles

<u>Simple</u> Reaction Mechanisms

$$AgNO_3 + NaBH_4 \Rightarrow Ag + \tfrac{1}{2} H_2 + \tfrac{1}{2} B_2H_6 + NaNO_3$$

<u>Simple</u> Preparation Sequence

- Immerse graphene in (10mM $AgNO_3/H_2O$)
- Add reducing agent (25mM $NaBH_4/H_2O$)
- Incubate mixture at room temperature
- Remove & wash in DI water

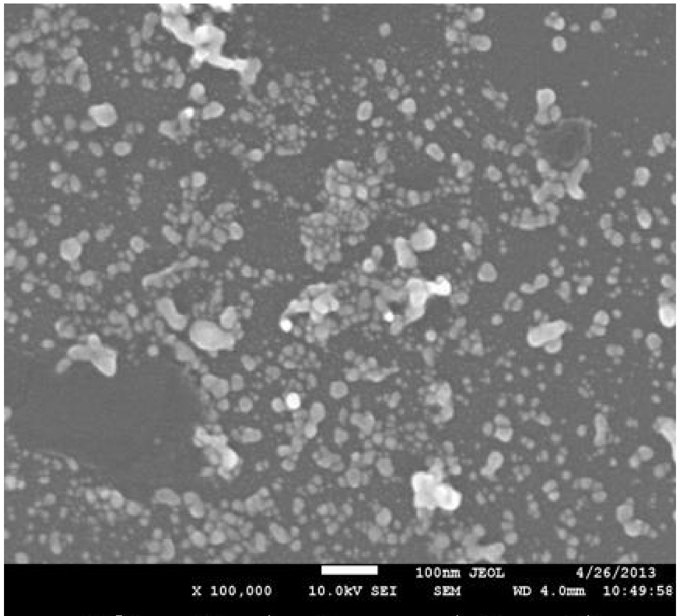


Solomon et al., J. Chem. Ed. 84 (2007) 322-322.

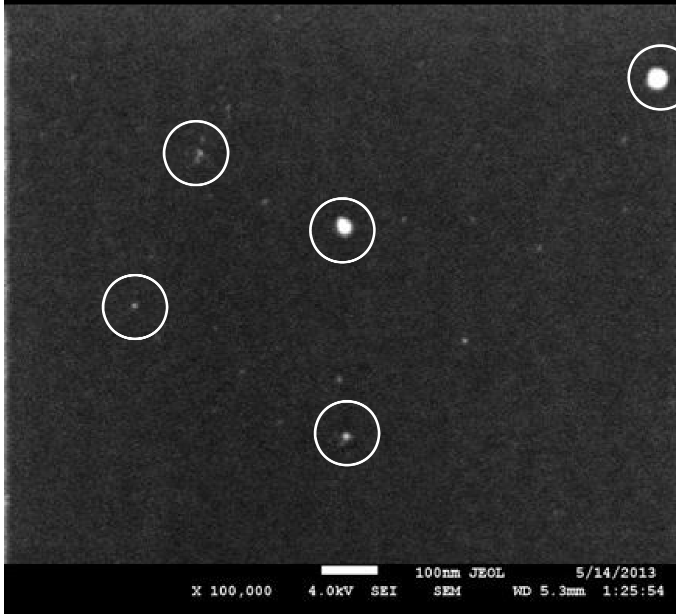
Key Parameters

- Solution concentrations
- Incubation time
- Surface defect levels

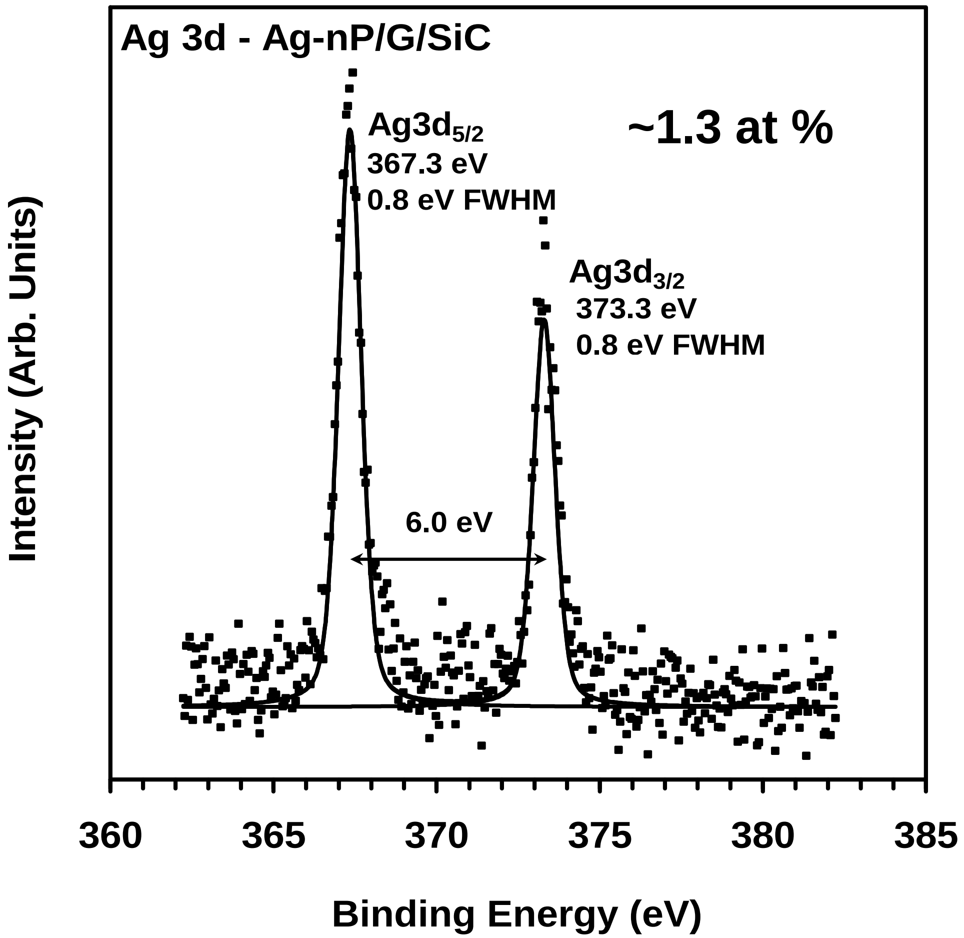
Ag Nanoparticle Nucleation & Growth



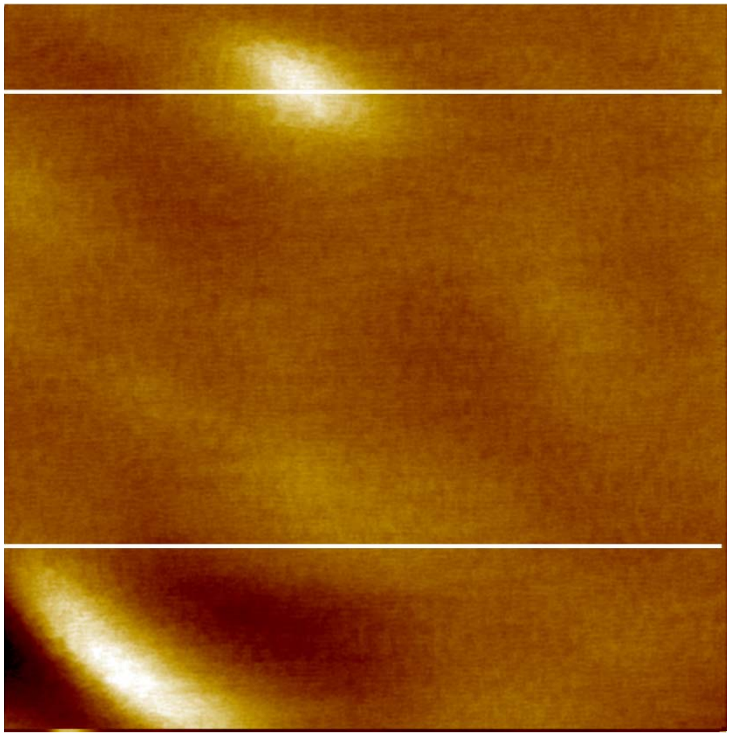
After Nucleation and Growth

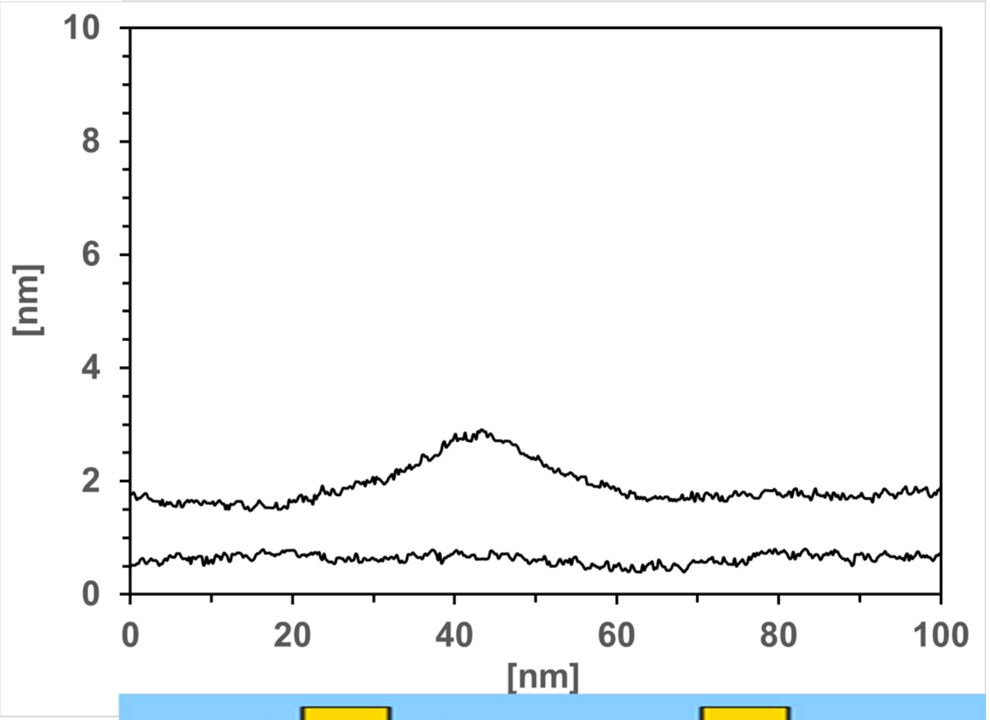


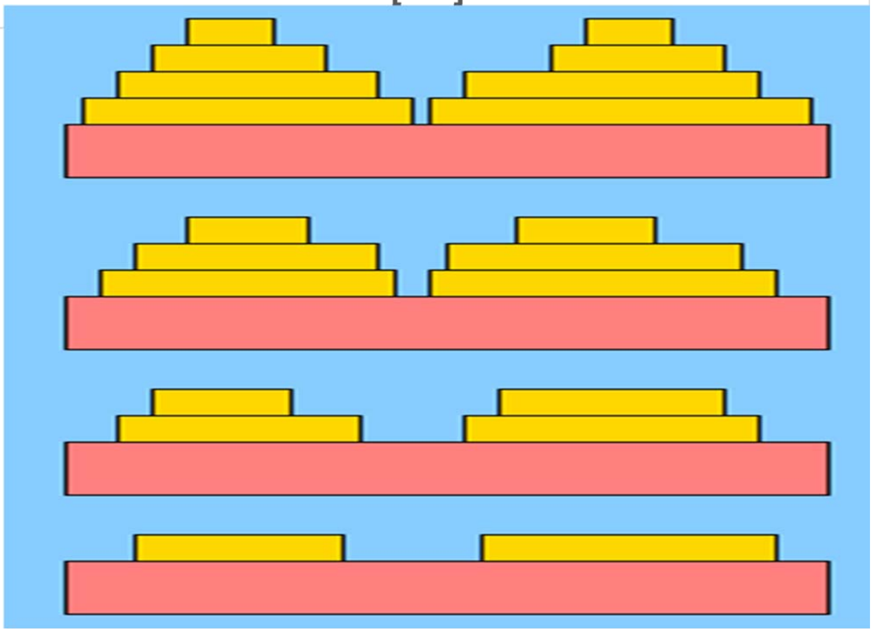
After 5 min Sonication in Acetone



Au Nanoparticle Nucleation & Growth





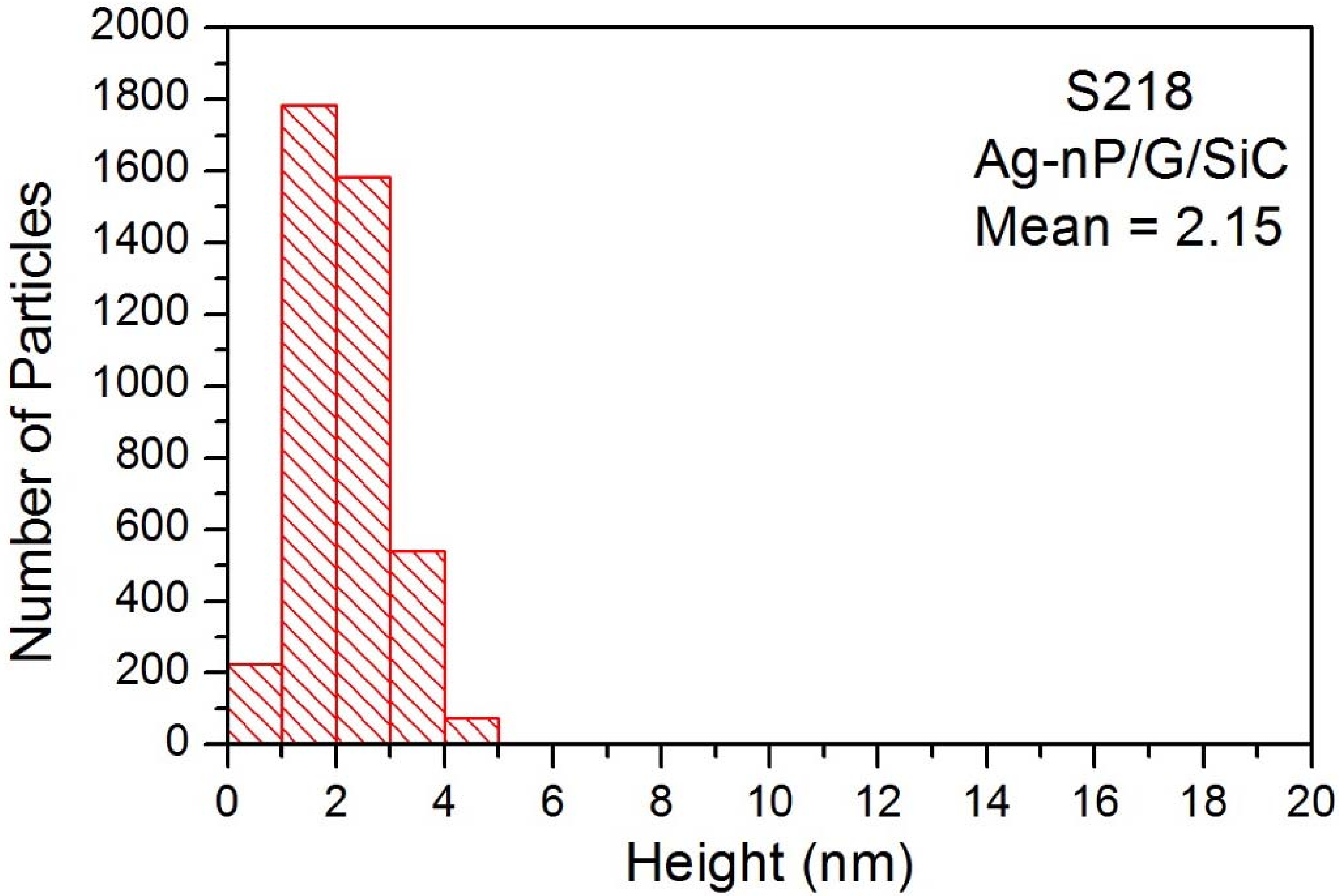


100 nm x 100 nm AFM Image of Au nP/G/SiC (S170) RMS ~ 0.2 nm

- **Ultrasonically removed particles are spheroidal**
- **Associated with homogeneous nucleation & deposition from solution**

- **Attached nPs are pyramidal**
- **Suggests heterogeneous nucleation with Volmer-Webber growth**

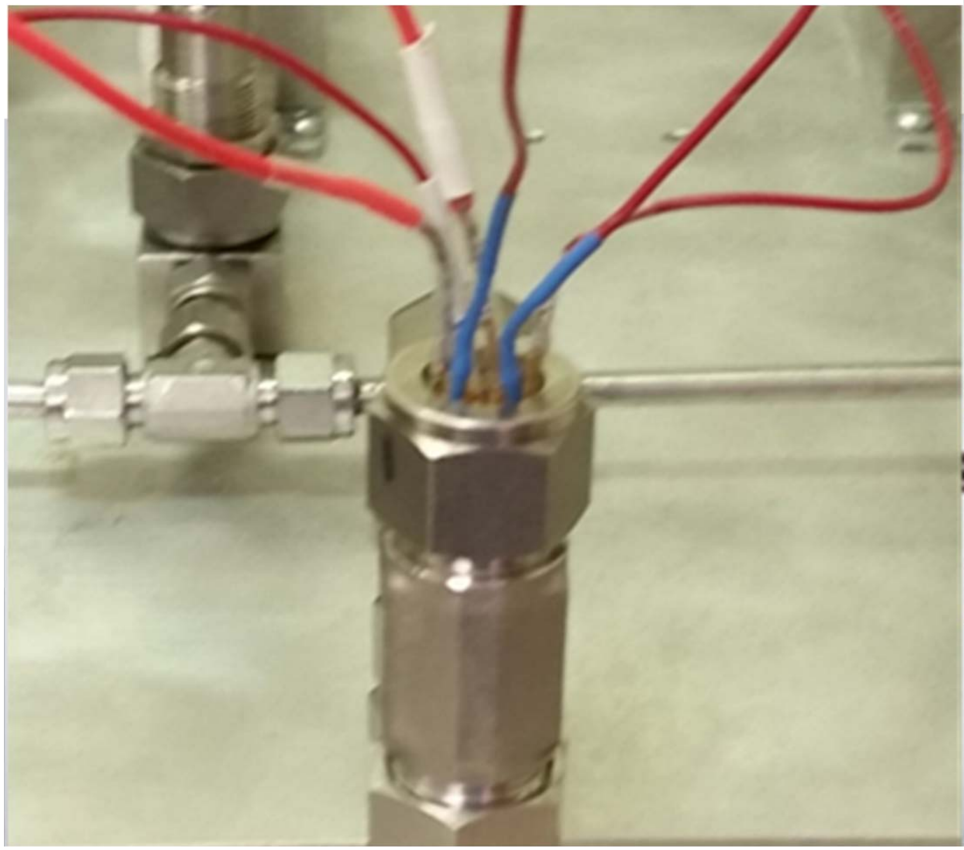
Particle Size Distributions



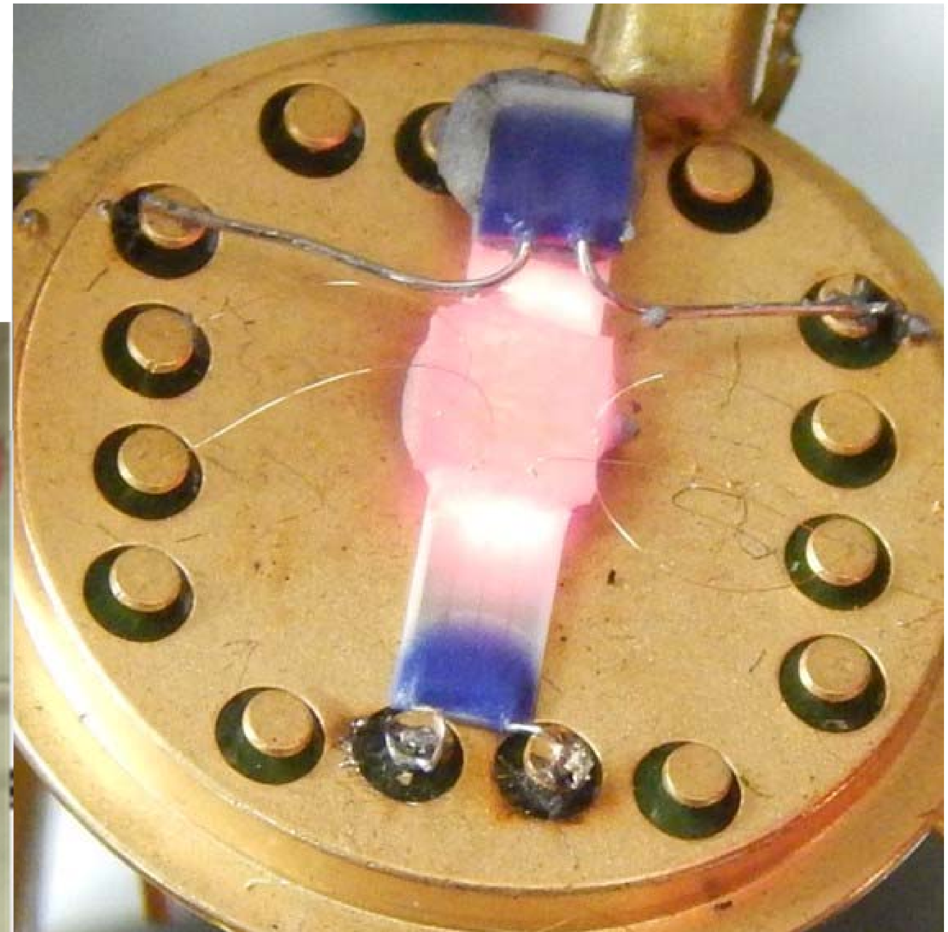
Sensor Platform and Test Unit

- Sensor mounted on microheater with RTD for control of temperature (≤700 °C)

- Sensor platform mounted in test unit

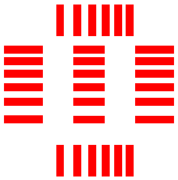


16 Pin Transistor Outline Header

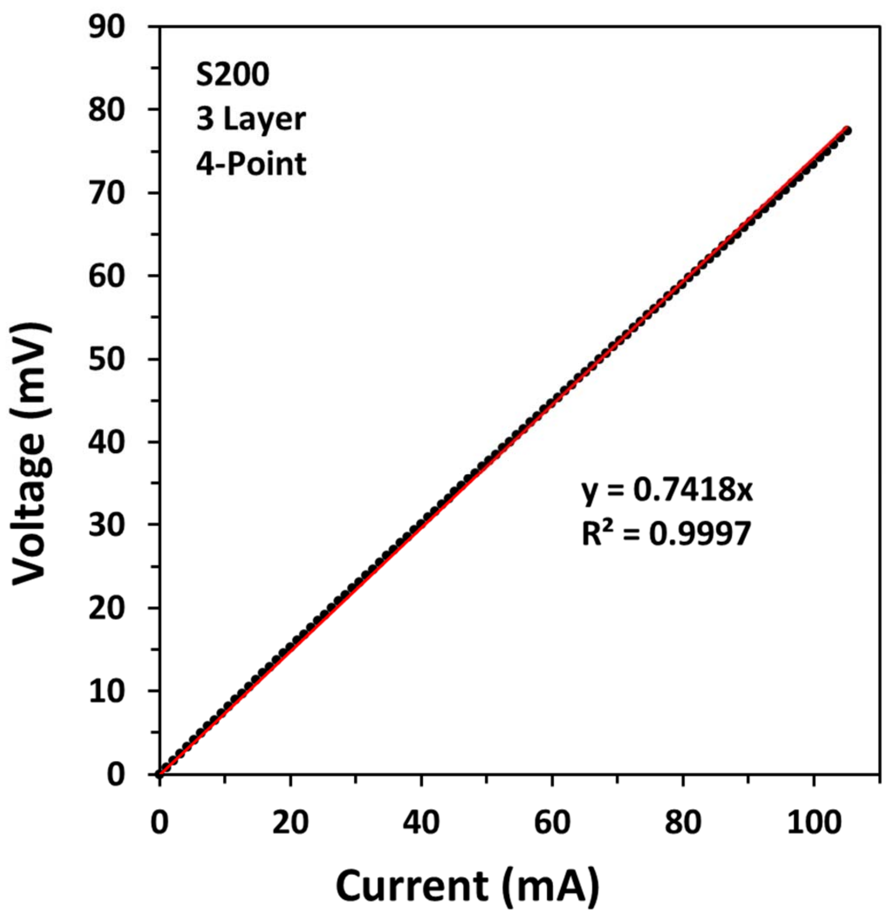


- Used for electrical characterization of both films & sensors

Electrical Characterization of Graphene Films



- Four point characterization
- Select four collinear contacts
- Obtain I-V characteristics



- Slope = R_{sd} (sheet resistance of device)

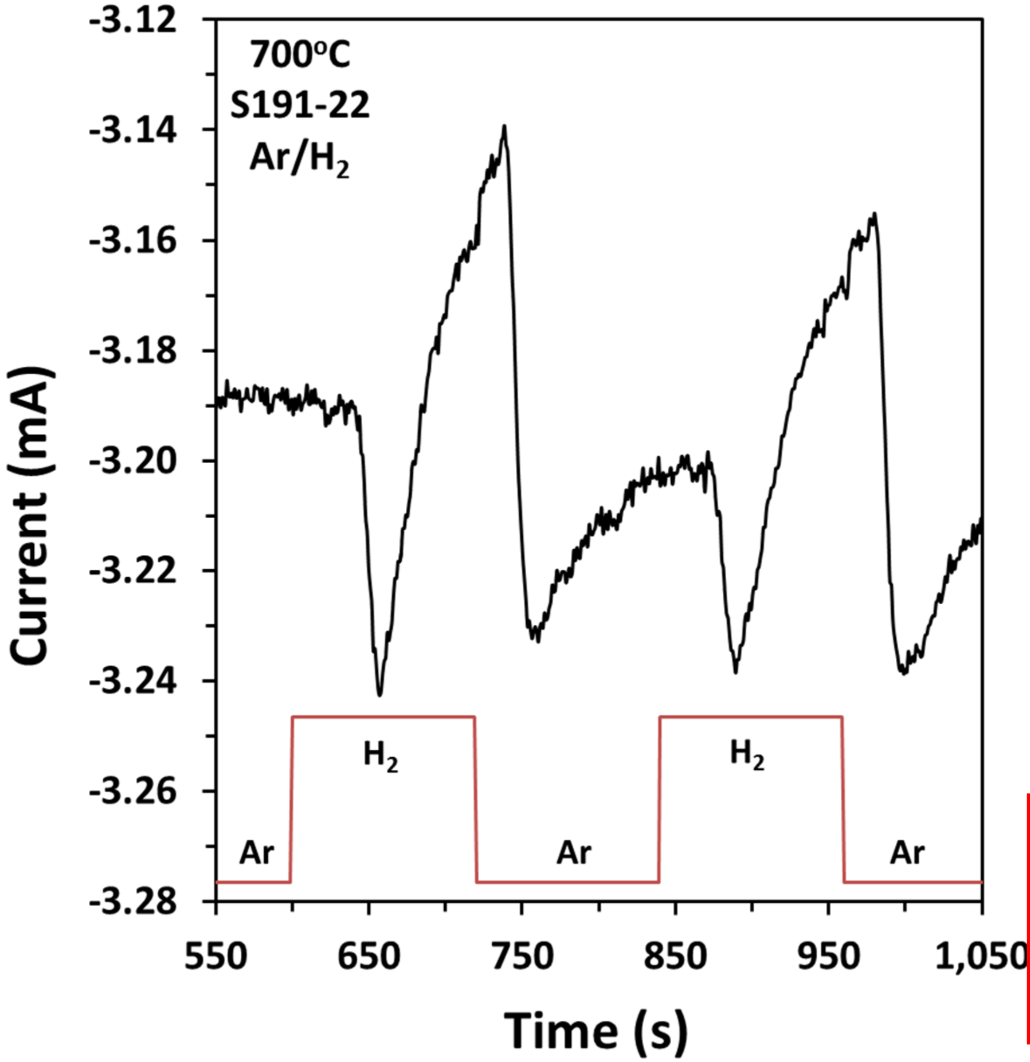
$$\frac{1}{R_{sd}} = \frac{1}{R_{ss}} + \frac{1}{R_{sf}}$$

- Measure R_{ss}
- Calculate R_{sf}
- Calculate $\rho_f = R_{sf} \times \tau_f$
- Typical values for 3 layer films

$\rho_f = 0.13 \pm 0.02\ \mu\Omega\text{-cm}$

Sensor Characterization

- Two point characterization
- Select source and drain contacts
- Measure two point I-V characteristics



- Effects of temperature
- Effects of composition
- Response to different gases
  - H_2/Ar
  - CO/Ar
- Pulse test
  Response due to combined thermal & chemical effects

- Need
  Constant temperature test bed
  Extend to T > 700°C

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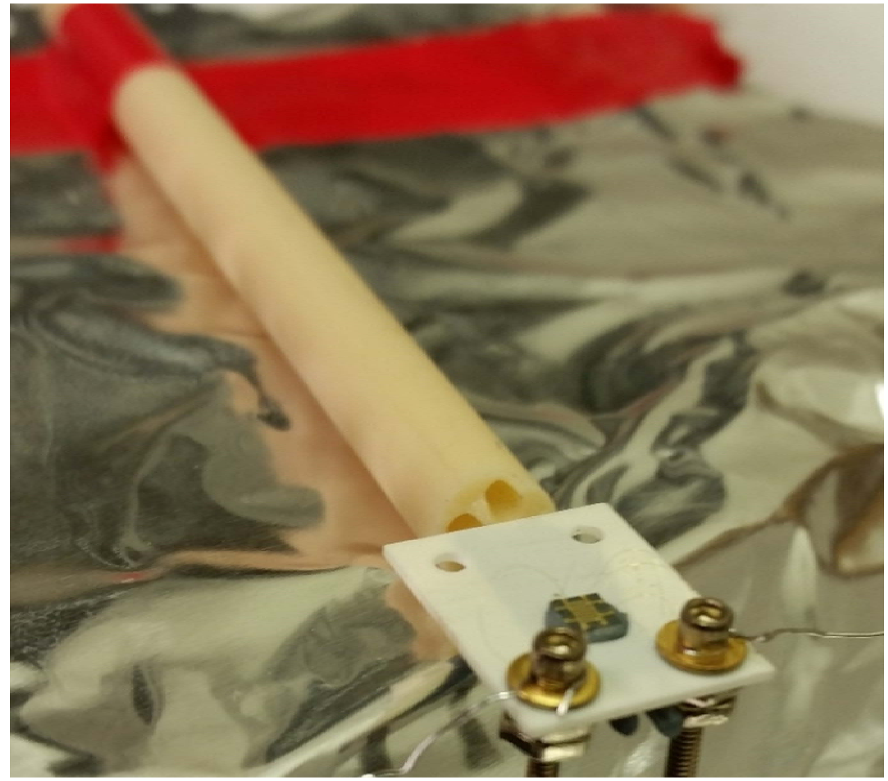
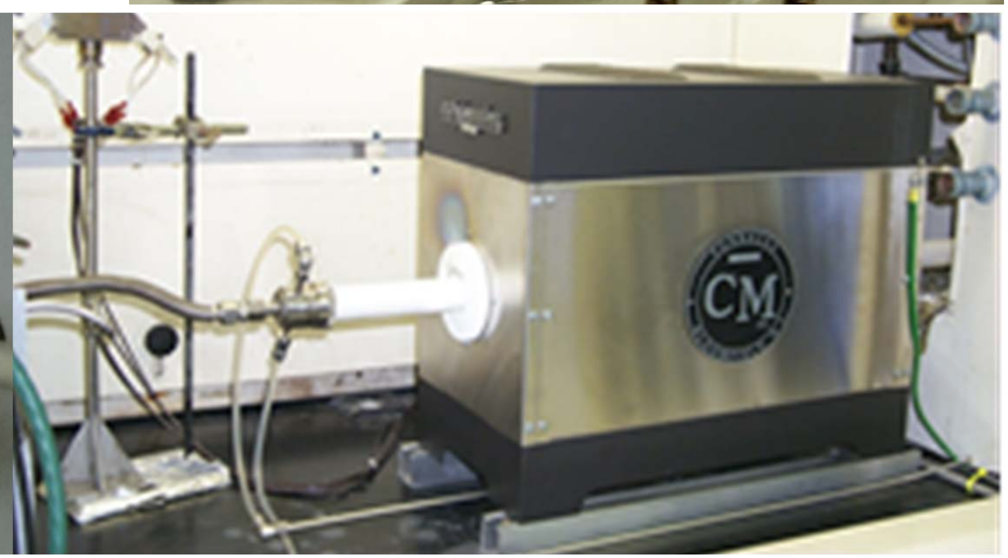
High Temperature Test Unit



Goals for high temperature unit

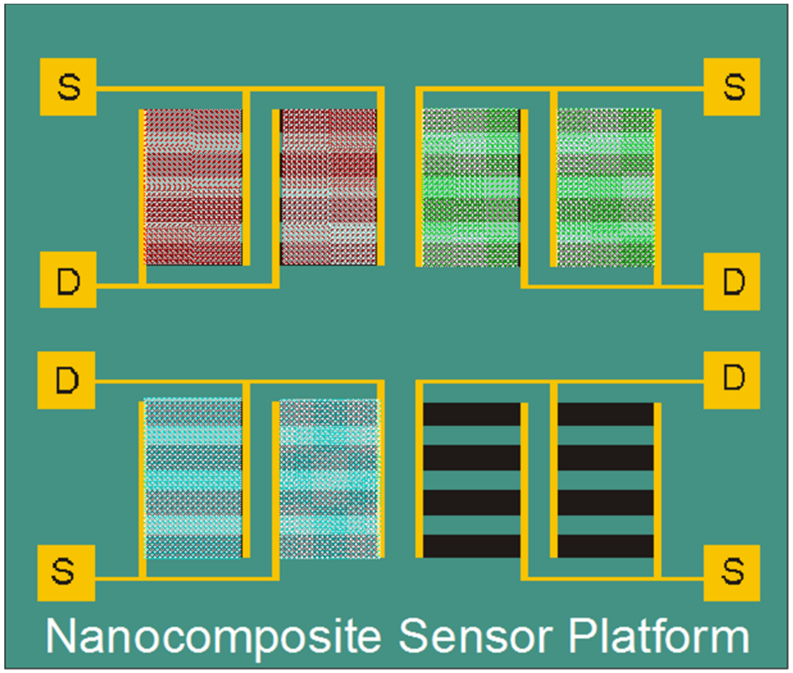
- Constant temperature test bed
- Temperatures 700 – 1000°C+ range

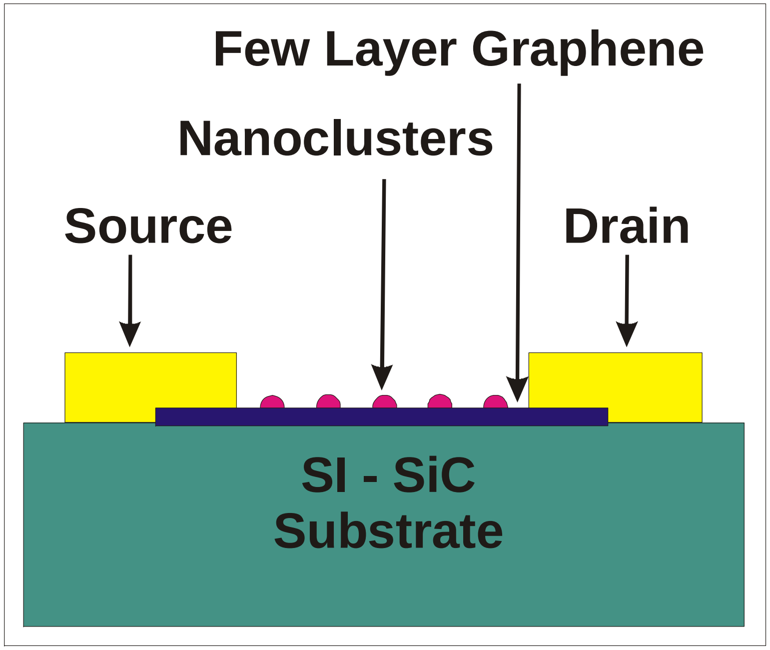


Graphene-Nanoparticle Composite Sensors

Goals for G-nP sensor studies

- Standardize fabrication
  - Control nP size distribution
  - Control surface coverage of nP
- Characterize G-nP sensor response
  - Sensitivity
  - Selectivity





- Extend measurement range
  - Temperatures to 1000°C+
  - Additional nP systems
  - Additional gas species
- Future applications areas
  - Temperature sensors
  - Pressure sensors
  - Liquid species sensors

Acknowledgments

University Coal Research Program

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PhD Students

- Saurabh Chaudhari – Graphene synthesis & sensor fabrication
- Andrew Graves – Sensor characterization

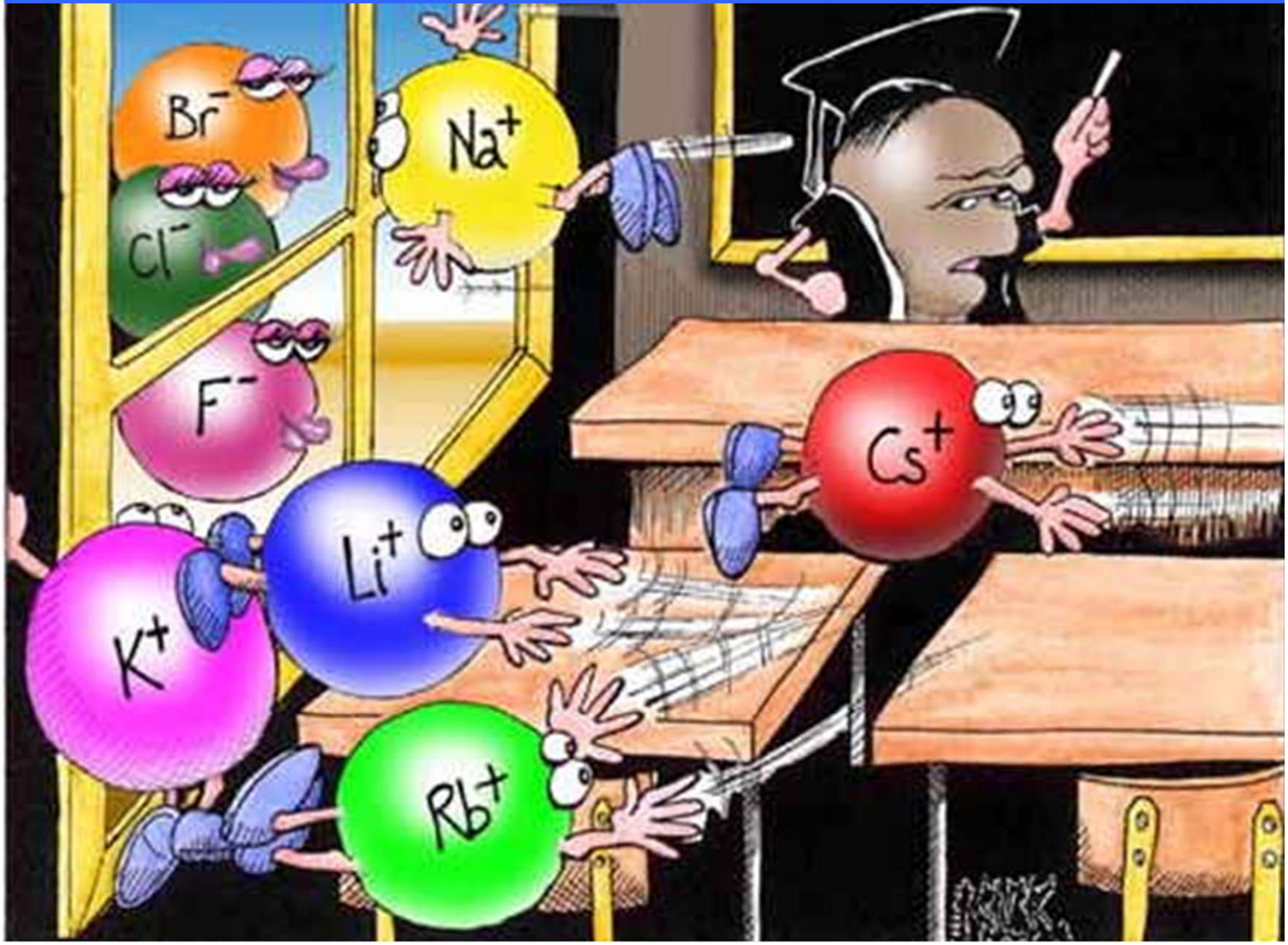
Undergrad Students

- Megan Cain – Particle nucleation and growth
- Jason Miles - Particle nucleation and growth (grad spring 2014)
- McKenzie Mills – Surface modification (grad spring 2014)

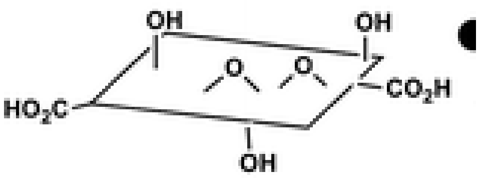
WVU Shared Research Facilities

- NSF EPSCoR Research Infrastructure Improvement Cooperative Agreement
- WV EPSCoR / Higher Education Policy Commission & WVU

QUESTIONS



"Perhaps one of you *gentlemen* will tell me just what you find so attractive outside that window . . . ?"



Graphene Oxide