Production and Characterization of Graphene and other 2D Nanomaterials: An AP High School Inquiry Lab

By Alison Fielding

TIMING AND LENGTH OF INVESTIGATION – teacher section

- **15 minutes: Teacher Preparation Time**
  Set up materials and prepare solutions
- **175 minutes : Total Student Time**
  80 minutes: Prelab Guiding Questions and Notebook Preparation
  70 minutes: Investigation
  15 minutes: Data Collection and Computation
  10 minutes: Postlab Assessment
  20 minutes: Additional Activities
  2 hours: Follow-up Experiment/Fieldtrip

This lab is designed to be a final project to be performed in May after the AP exam.

✓ **CENTRAL CHALLENGE**

You will develop the production and characterization of nanomaterials to determine the identity of an unknown.

✓ **CONTEXT FOR THIS INVESTIGATION**

You are working in the semiconductor industry on a research and development team. Your team has the job of producing graphene and other nanomaterials in an inexpensive, large-scale capacity. Once you have researched and chosen a method to produce the material, you will then characterize it, using the suggested protocol, to prove you have successfully produced that material.

✓ **ALLIGNMENT TO THE AP CHEMISTRY PROGRAM – teacher section**

Primary Learning Objective

- **L.O. 2.29:** The student can create a representation of a covalent solid that shows essential characteristics of the structure and interactions present in the substance. [See **SP 1.1**]

Secondary Learning Objective

- **L.O. 2.30:** The student is able to explain a representation that connects properties of a covalent solid to its structural attributes and to the interactions present at the atomic level. [See **SP 1.1, 6.2, 7.1**]

✓ SKILLS – teacher section

Prior Skills
Students should be able to:
- Use lab equipment to accurately measure volume and mass;
- Use vacuum filtration, hot plate and centrifuge;
- Operate a Spectrophotometer or Vernier probeware;
- Use a multimeter and microscope;
- Proper solution preparation.

Developing Science Practices, Instrumentation, and Procedural Skills

Lab Activities	Science Practice
Accurately operate and read a spectrophotometer or spectro-vis apparatus.	Spectroscopy
Apply the information from the graph to determine the bandgap in millivolts and then use that information to determine an unknown	SP 2.2: The student can *apply mathematical routines* to quantities that describe natural phenomena.
Form a research question and hypothesis.	SP 3.1: The student can *pose scientific questions.* SP 3.2: The student can *refine scientific questions.*
Design a procedure/data-collection strategy from given background materials to determine the unknown 2D nanomaterial given.	SP 4.2: The student can *design a plan* for collecting data to answer a specific scientific question. SP 4.1: The student *can justify the selection of the kind of data* needed to answer a particular scientific question. SP 6.4: The student can *make claims and predictions about natural phenomena* based on scientific theories and models.

✓ PREPARATION – teacher section

Materials
The initial investment for the chemicals and instrumentation in this lab can be expensive, but your materials will last for years. You can perform this lab with only graphite and have the students make graphene to save money. The author of this lab applied for a grant at a local semi-conductor company to cover the initial costs of the chemicals, blenders, bath sonicator and balance. The Vernier Spectrophotomers were already in the lab.

• Isopropanol • Graphite • Tungsten IV sulfide • Molybdenum IV sulfide • Molybdenum IV selenide • Boron nitride	• Centrifuge and tubes • Dry, bleachless, dishwasher detergent	• Multimeters, at least 5
• Hand blender, bath sonicator or kitchen blender (you need at least 2 different types to choose from)	• Quantitative filter membranes .22µm in pore size	• Spectrophotometer and cuvettes
• Vacuum filtration set-up	• Acetone, distilled water	• Microscope slides w/cover slips
• 10 hotplates	• Mini spatulas	• Balance capable of mg precision
• Weigh paper		

Safety and Disposal
- Graphite is slightly flammable, store in flammable cabinet and avoid open flame
- MoS_2, WS_2, BN and $MoSe_2$ cause eye and skin irritation – wash immediately
- Isopropyl alcohol should be used under the fume hood and should not be inhaled causes eye and skin irritation – wash immediately, flammable store in flammable cabinet and avoid open flame
- BN should be mixed under the fume hood
- A prelab quiz is recommended regarding safety for this lab

Prelab Preparation
- For 10 lab groups, prepare 1000ml of a 30% IPA solution to use as the solvent for all five solutions. 30ml isopropanol in 70ml distilled water. Make sure you have 99% to begin with. Have storage bottles for all solutions available. They have long shelf lives.
- Students will prepare the additional solutions needed. Cover the labels on the bottles so your students don't know what solutions they are mixing.
- Make sure materials are available on the bench tops or in a central location.

✓ **PRELAB GUIDING QUESTIONS – Student homework or done as a class**

Please answer the following in complete sentences on a separate sheet of paper. This will be graded prior to the investigation.

1. Watch the following video, http://youtu.be/InPjLsLPA44
   i. What is the purpose for using a centrifuge?

ii.   Why do you think it's necessary to counterbalance your tubes during your use of the centrifuge?

iii.   What would happen if this wasn't done properly?

2. Please visit this URL, http://chemistry.stackexchange.com/questions/815/how-to-find-the-band-gap-for-a-compound

    i.   What is the formula you would use to calculate a band gap in electron volts using an absorption spectrum?

3. It will be necessary for you to mix your prepared solution for this lab at high speeds for varying amounts of time in order for the desired nanosheets to form. Here are the methods available to you:

    i.   Hand Blender – operates for a maximum of 20min before overheating

    ii.   Kitchen Blender – you will need to run for 1 full hour with the aid of a surfactant to obtain sheets

    iii.   Bath Sonicator – you will need to run this form 4 hours to overnight to obtain sheets

Based on this information, which method will you use and why?

4. Please visit the following URL, http://nadp.sws.uiuc.edu/cal/PDF/MultimeterUse.pdf

    i.   Are the multimeters that are in out lab considered switched or auto range?

    ii.   What does Ω stand for? What does it measure?

    iii.   When testing the voltage of a system, where do you want your dial set at?

Answers to prelab guiding questions – Teacher section

1.

    i.   The purpose for centrifugation is to separate the solid and liquid phases or to produce a precipitate.

    ii.   It is necessary to use a counterbalance in a centrifuge or it will become unbalanced.

    iii.   If the test tubes aren't balance properly, the centrifuge will begin to knock and possibly break if it isn't stopped immediately.

2.

    i.

$$E(eV) = \frac{1239.84187 \text{ eV nm}}{\lambda(nm)}$$

3. The two best methods for the students to choose are the blenders or the bath sonicator. Make sure they have chosen a method before they begin.

4.   i.   The multimeters are switched.

    ii.   Ohms, resistivity

    iii.   On the setting just lower than the expected voltage.

✓ **EXPLAINATION TO STRENGTHEN STUDENT UNDERSTANDING**

2D Material Overview

Watch the following Youtube videos as a class for an overview on nanomaterial applications:

http://youtu.be/SXmVnHgwOZs

http://youtu.be/ndJlgTkm0oQ

✓ PREPARATION

Materials

30% Isopropanol solution	Centrifuge and test tubes Test tube rack	Multimeter
Hand blender, bath sonicator or kitchen blender	Quantitative filter paper ruler	Spectrophotometer and cuvettes
Vacuum filtration set-up	Acetone, distilled water	Microscope slides w/cover slips
Hotplate	Methanol	Balance capable of mg precision
Weigh paper	Mini spatulas	Unknown 1-5
volumetric pipettes		

Safety and Disposal

Include Safety Data Sheet, MSDS, information on health hazards, handling and disposal measures for all listed chemicals in your lab notebook. Do not exceed 2-3 lines in your lab notebook.

✓ INVESTIGATION

Procedure

1. Develop a **research question** based on the Central Challenge.
2. Based on the prelab exercises write down the exfoliation method you chose.
3. As a class, prepare 200ml of each unknown as a 2mg/ml concentration in the 30% IPA provided, write down exactly how you did this. Also, calculate molarity (M), show all work with significant figures for BOTH calculations.
4. If you are using the blender, add 2g of Cascade detergent.
5. Obtain 100ml of a single unknown per group. Record your number.
6. Use your mixing method of choice on your solution for the recommended time. You will next use a centrifuge in two steps:
    i. Centrifuge all 100ml of material for 5 minutes. Collect the liquid, being careful not to disturb the precipitate, and put it into new test tubes.
    ii. Centrifuge the collected liquid, or supernatant, for an additional 15 minutes. Collect the supernatant again and put into a clean, small beaker.
7. Run an absorbance spectrum, absorbance vs wavelength, on your exfoliated material using your Vernier Spectrovis Plus. You do not need to calibrate, however, you do need to print the graph and affix it to your lab notebook in the data section. Remember to save your data on the Labquest 2 before printing.
8. After comparing your graph with the graphs provided below, state a **hypothesis**.
9. Next, set up a vacuum filtration with a porcelain funnel. Obtain a filter membrane from your teacher and hook up your apparatus to a hose leading from a pump.
10. Filter half of your remaining solution and place the filter paper in the drying over for 10 minutes.
11. Repeat with the rest of the solution. Bring one filter paper to your teacher.
12. Place the other paper face down on a microscope slide and place in an acetone vapor bath for 20 minutes. Set your hot plate close to 80°C. Then, add enough acetone to fully cover the slide. Allow it to heat then leave overnight.
13. Dry the slide in the drying oven 10 minutes and observe your sample under a microscope.

14. Measure the voltage and resistance. Record in the Data Section of your notebook.
15. Place the sample slide in the case provided for Scanning Electron Microscopy at Hewlett Packard during our fieldtrip.

Data Collection and Computation

1. Compare your data with the data below. Clearly identify the nanomaterial you were given. Include your absorbance spectrum in this section of your write-up.
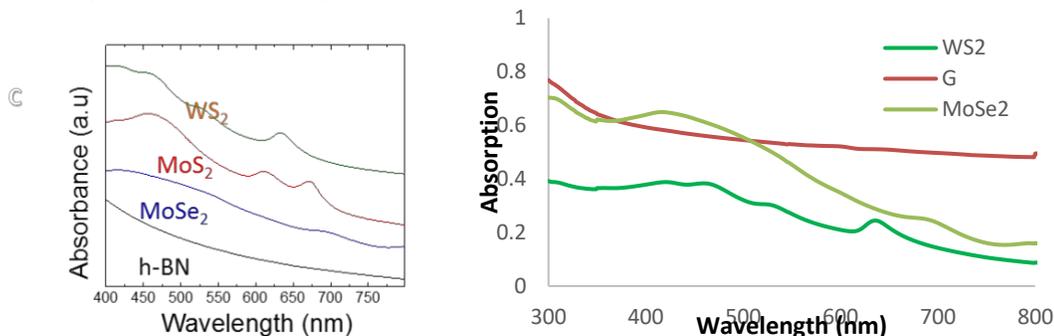
2. Resistivity/conductivity test - record

Argumentation and Documentation

In the conclusion of your lab, identify your unknown, justify the procedure you chose, the instrumentation you used, and the selection of the kind of data needed to determine the identity of your unknown. Please use these guiding questions; which tests were significant? Which tests were of no help at all? Why?

✓ POSTLAB ASSESSMENT

On a separate sheet of paper please answer the following in complete sentences. This will be turned in along with your lab write-up.

1. What instrumentation did you use to suspend your unknown within the solvent? Why?
2. What is a supernatant? Why was it important to collect only the supernatant during this experiment?
3. What is a surfactant? Molecularly, how does it help suspend the nanosheets?
4. Draw a picture representation, including charges, from #3.

Additional Activities

1. While taking conductivity/resistivity measurements, shine a light on the coverslip with the leads from the multimeter on each end. Try it with different colors of light. Record all measurements. What would be the practical applications?
2. As an application of Ohm's Law, paint incremental lines of silver paint on your filter paper and measure resistivity over distance using a multimeter. Brainstorm the practical applications.

Follow-up Experiment

Develop a partnership with a local company that has a Scanning Electron Microscope (SEM) or Transmission Electron Microscope (TEM) that can properly prepare your samples and allow you to use their microscope to view them.