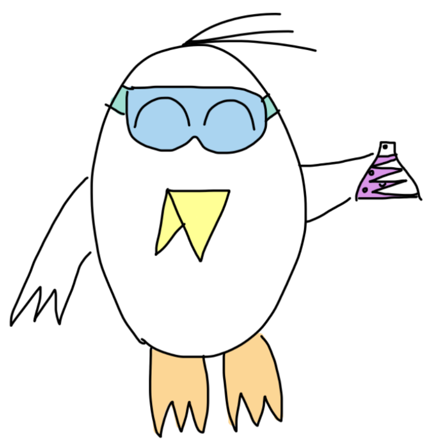
'Iolani Science Olympiad Invitational 2025

Division C

MATERIALS SCIENCE



Team Name ______________________________

Team Number __________

Honolulu
2025

Preliminary information

This lab and exam was written by Raphael Esquivel ('Iolani '25, Harvey Mudd '29). Please do not hesitate to direct any questions after the event to esquivelralphie@gmail.com.

- This is a chemistry event and involves hazardous chemicals. **You must be in proper attire in order to participate**. Participants not in proper attire will not be allowed in the lab.
- The lab staff, including the event supervisor, **reserve the right to remove any competitor from the lab at any time.** The event supervisor will **disqualify** any competitor engaging in dangerous behaviors, including removal of protective attire.
- **Read lab instructions carefully!**
- This event will last **50 minutes**. The lab and exam are to be taken concurrently.
- Each competitor may bring a single 8.5″ × 11″ sheet of paper with information written on it as a reference.
- You may use a graphing calculator. **You may not use your phone or any electronic devices with internet capabilities** for any purposes.
- Once you have been working on the exam for 50 minutes, **you must stop answering questions** and turn it in. Please make sure your **lab equipment is turned off and your experiment in a stable state** before leaving the lab.
- **BE SAFE AND HAVE FUN!**

EXPECTATIONS:

In Science Olympiad, chemistry event supervisors have the following expectations of Science Olympiad team members participating in the Chemistry events:

- Students will have researched proper PPE for the chemistry lab and know what goggles belong to which group and to show up properly attired.
- Students are expected to know how to use standard chemistry measuring instruments, including but not limited to graduated cylinders, thermometers, pH paper, conductivity meters, multimeters, calipers, and rulers.
- Students are expected to know how to use laboratory glassware stated in the rules and standard techniques associated, such as quantitative transfer, meniscus reading, titration, filtration, mixing, cleaning glassware, weighing by difference, etc.

These expectations, as well as many others, can be found on soinc.org. **Competitors who demonstrate incompetence in these lab techniques in a way that endangers themselves or others will be removed from the lab.**

1 Lab instructions

Synthesis of nanoparticles with specific properties is a newly established research area that attracts a great deal of attention. In this lab, you will be synthesizing a zinc oxide nanostructure and analyzing some of its properties. You will find in front of you:

- 8 g sodium hydroxide (NaOH)
- 2 g zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot {}_2H_2O$)
- 1 graduated cylinder
- Bottle with distilled water
- Magnetic stirring plate with stir bar
- Burette with 100 mL of ethanol
- 3 beakers

If you do not know how to use some of the lab equipment **ask a lab supervisor.** If you spill anything, notify a lab supervisor immediately. Keep your goggles on at all times. If you need to defog your goggles, step away from the lab setup and **do not touch your face with gloved hands!** Some of these chemicals can burn or irritate your skin and permanently blind you.

Follow these steps to synthesize your ZnO nanostructures.

1. Put the zinc acetate dihydrate in a beaker. Measure 15 mL of distilled water with your graduated cylinder and pour into the zinc acetate dihydrate beaker. Put magnetic stir bar in and begin stirring.
2. Put sodium hydroxide in the other beaker. Measure 10 mL of distilled water with your graduated cylinder and pour into the sodium hydroxide beaker. Put magnetic stir bar in and begin stirring.
3. Let stir for 5 minutes. (You can start answering some questions during this time, but pay attention to your lab setup).
4. After well mixed, pour the sodium hydroxide solution into the solution containing zinc acetate with a constant stirring by magnetic stirrer for about 5 minutes.
5. Place flask under burette and add ethanol one drop at a time until a white precipitate is formed. To add one drop at a time, quickly rotate the handle on the right side of the burette by 180 degrees.

Now, we will characterize our nanostructures. We will use UV-Vis absorption spectroscopy to estimate the optical bandgap energy of the ZnO. The UV-Vis spectrophotometer shines ultraviolet and visible light through the sample and measures how much light is absorbed at each wavelength; by seeing where the sample strongly absorbs, we can learn a lot about its properties.

1. Gently swirl the beaker containing your sample so the suspension is homogeneous.
2. Shine a laser through the beaker and record what you observe; compare with what happens when you shine a beaker in water.
3. Dilute your suspension by transferring 2 mL of your ZnO mixture into a clean beaker and adding 8 mL of distilled water. Mix gently until uniform.
4. Fill a clean quartz cuvette 2/3 full with your diluted solution and wipe the outside with a Kimwipe. Once you have your cuvette, come see the event supervisor.

You will analyze your data and observations on page 6.

2 Questions (27 points)

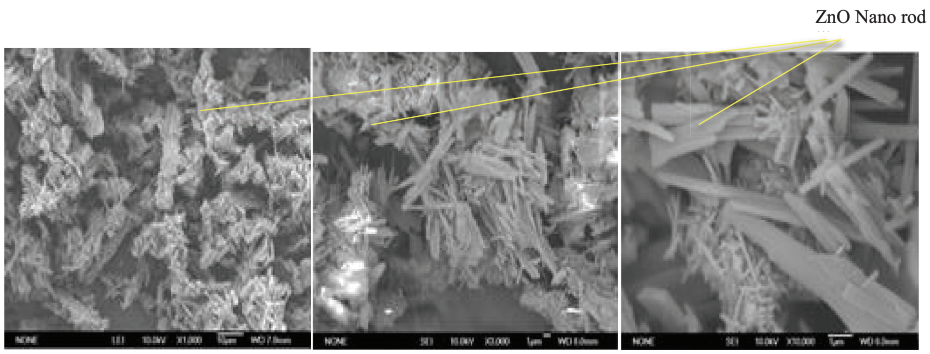
You will answer questions about the experiment. (Tip: do not begin answering these questions before having started stirring your solutions.)

1. (1 point) What is the name of this method of producing nanomaterials? Sol-gel

2. (1 point) Circle the type of method of production of nanomaterials that we are using.

   Top-down   Bottom-up

   Below is a micrograph showing images of zinc oxide nanostructures, synthesized using the same method you just did!



3. (1 point) Which type of microscopy technique was most likely used to capture these images?
   A. Transmission electron microscopy (TEM)
   B. Scanning electron microscopy (SEM)
   C. Atomic force microscopy (AFM)
   D. Optical microscopy

4. (1 point) These nanostructures are classified as which type of nanomaterial?
   A. 0D nanomaterial
   B. 1D nanomaterial
   C. 2D nanomaterial
   D. 3D nanomaterial

5. (5 points) Circle all correct classifications of ZnO nanorods.
   A. Ceramic
   B. Polymer
   C. Excitonic
   D. Oxide nanomaterial
   E. Photocatalytic
   F. Magnetic
   G. Ferromagnetic
   H. Ferrimagnetic
   I. Ferroelectric
   J. Piezoelectric

6. (1 point) Why do ZnO nanorods often exhibit very high mechanical strength compared to bulk ZnO?
   A. Dislocations are easily generated and move freely
   B. Surfaces and small volumes suppress dislocation motion
   C. The material becomes amorphous
   D. The grain boundaries dissolve during loading

7. (1 point) When mechanically loaded beyond the elastic limit, ZnO nanorods most often fail by:
   A. Ductile necking due to extensive dislocation motion
   B. Creep deformation from diffusion along grain boundaries
   C. Brittle cleavage fracture along crystallographic planes
   D. Localized grain growth that relieves internal stress

8. (1 point) Compared to bulk ZnO, what would you expect the ZnO nanorods you synthesized to exhibit regarding their melting temperature?
   A. Nanorods would have higher melting temperature because smaller rods have stronger surface bonds
   B. Nanorods would have lower melting temperature because a larger fraction of atoms are at the surface with weaker bonding
   C. The melting points would be the same because chemical composition is unchanged
   D. We do not have enough information to predict how the melting temperatures compare

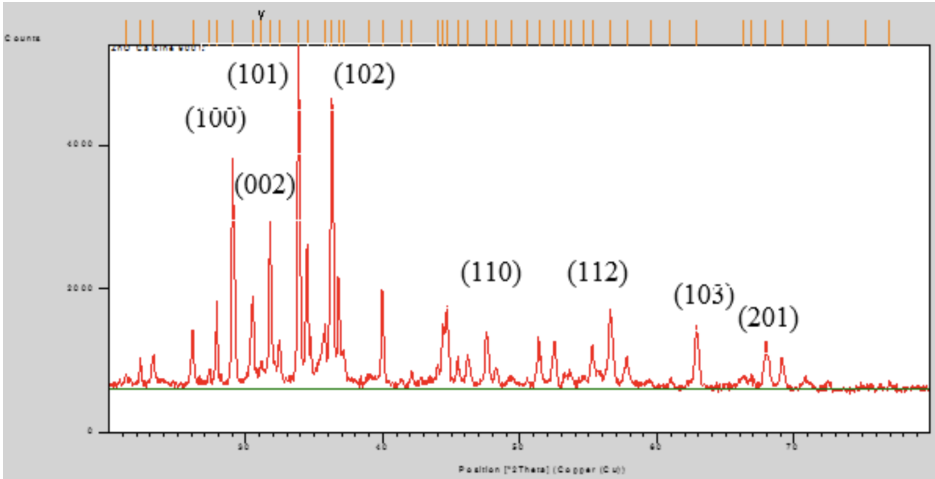
9. (1 point) As the diameter of ZnO nanorods decreases to the nanoscale, quantum confinement effects become significant. Which of the following statements best describes the impact of quantum confinement on the optical properties of ZnO nanorods?
   A. The band gap decreases, causing a red shift in the absorption spectrum.
   B. The band gap increases, leading to a blue shift in the absorption spectrum.
   C. The band gap remains constant, but the exciton binding energy decreases.
   D. The band gap fluctuates randomly due to surface defects.

10. (2 points) During the synthesis of ZnO nanorods, how does increasing the concentration of sodium hydroxide (NaOH) typically affect the morphology of the product? Why?

Solution: Increases nucleation rate, leading to shorter and smaller nanorods.

11. (2 points) Why does ethanol make the nanorods precipitate? (Identify what properties ethanol has that leads the ZnO to precipitate and why this happens)

Solution: Water has a high dielectric constant, stabilizing ions like Zn^{2+} and OH^- in solution. Ethanol has a much lower dielectric constant. Mixing ethanol with water reduces the solution's ability to keep ions dissolved.



Above is data from a sample of ZnO nanorods produced using this method.

12. (1 point) What technique produced this type of diagram? X-ray diffraction

13. (1 point) What quantity is shown on the horizontal axis? What about the vertical axis? Diffraction angle, intensity

14. (2 points) Identify the crystal structure this represents. Wurtzite

15. (6 points) Fill in the blanks.

Pyroelectricity is the property of a material to generate an electric voltage when its temperature changes. This occurs only in crystals that lack inversion symmetry, because these crystals possess a permanent polarization that can increase or decrease with temperature. ZnO exhibits this property because its structure is non-centrosymmetric and the Zn^{2+} and O^{2-} ions are displaced along the c-axis, creating a built-in dipole that changes as the lattice expands or contracts with temperature.

3 Characterization (40 points)

Make sure you get your plot from the event supervisor before starting this part. The plot itself is worth 20 points. You will turn it in along with your completed test.

16. (2 points) What happened when you shone the laser in the mixture with the ZnO? How did it compare to shining the laser in water? Why does this happen?

Solution: In water, you can't see the beam. In the colloid, you can see the beam, and it scatters. This happens because the nanoparticles have a different refractive index from the surrounding medium, so incoming light interacts with them and is scattered

17. (1 point) (Tiebreaker #1) What is the name of this optical effect? Tyndall effect

For the next part, you will find the following facts helpful:

- The energy of a photon is $E = h\nu = \frac{hc}{\lambda}$. Here, h is Planck's constant, c is the speed of light, ν is the frequency, and λ is the wavelength. You can use $hc = 1240\ \text{eV} \cdot \text{nm}$.
- Absorbance A is related to the absorption coefficient α via $A = \alpha L$, where L is the cuvette path length. Here, use $L = 1\text{cm}$.

The graph you have obtained from your sample is a Tauc plot, a common way to estimate the optical bandgap of a semiconductor. For ZnO, which is a direct bandgap material, we plot $(\alpha h\nu)^2$ vs $h\nu$. The straight-line portion of the curve represents where electrons begin to absorb enough energy to move from the valence band to the conduction band.

18. (4 points) Determine the bandgap energy by extending the linear region backward until it intersects the x-axis; the x-value of the intersection is your estimate of the optical bandgap of the ZnO nanoparticles you synthesized.

$E_g =$ should be somewhere >3.3eV

19. (2 points) Fill in the blanks.

The bandgap is the minimum energy needed to excite an electron from the valence band into the conduction band so that it can participate in electrical conduction.

20. (3 points) Did your spectrum show any defect-related absorption (e.g. a small shoulder around 420-500 nm? What specific synthesis step could have introduced these defects? (Answer this question even if you do not have such a shoulder on your spectrum)

Solution: A shoulder at 420-500 nm indicates defect-related absorption from states in the bandgap, typically due to oxygen vacancies or zinc interstitals. These defects are introduced during the NaOH addition/precipitation step, where rapid, strongly basic nucleation produces non-stoichiometric, defect-rich ZnO.

21. (3 points) Looking at the linear region of your Tauc plot, was the slope steep or shallow? What does this indicate about the crystallinity in your ZnO nanorods? Explain how slope relates to crystallinity.

Solution: If the linear region of the Tauc plot is steep, this indicates that nanorods have high crystallinity; sharp absorption edge means electronic transitions are well-defined and there are few defect states or structural disorder. Otherwise, a shallow slope means the absorption edge is smeared out by defects, lattice disorder, size variability, or surface states.

22. (2 points) It is possible to make LEDs with ZnO nanorods; in fact, these are often better for LEDs than bulk ZnO powder. How does the rod-like morphology improve LED performance compared to bulk ZnO powder?

Solution: Rod-like, vertically aligned ZnO nanostructures improve LED performance because they provide fast, low-defect paths for carriers and guide light out of the device more efficiently than a disordered bulk powder layer.

23. (3 points) If you were to make an LED with the nanorods from your sample, what color would it be? Which steps in your synthesis would you modify to change the color, and why? (Hint: How does nanorod size correlate to bandgap?)

Solution: $\lambda = \frac{1240}{E_g}$**. Typically this would be around** < 400 **nm, in the near-UV/violet range. Smaller nanorods → stronger quantum confinement → larger** E_g **→ shorter** λ **(bluer/UV), and vice versa. To control the size of nanorods, change** NaOH **concentration, which changes the supersaturation and nucleation/growth rates; less** NaOH **means larger rods so red-shifted, and vice versa.**
+1 point for λ**, +1 for how size changes color, +1 for how to change size**