Teacher's Guide **Teacher's Guide**

Turning Fruit Juice into Graphene Quantum Dots

Grade Level: High school and undergraduate

Subject area(s): Chemistry & physics

Time required: Two 50 minute classes and one 90 minute lab

Learning Objectives: Through exploration students will learn the quantum nature of electrons and light including the wave/particle nature of both

Summary: Graphene, a sub-nanometer thick sheet made of carbon, was isolated just over a decade ago (2004), yet swiftly won the Nobel Prize for Geim and Novoselov in 2010 for its properties of high strength, conductivity, and transparency. Students will replicate the procedure used to isolate graphene and make graphene quantum dots from citrus fruit juice. This lab is designed to help students understand the quantum nature of electrons and light, including the wave/particle nature of both. Students will encounter graphene and learn about its strength, conductivity, and transparency. Using "kitchen" science students will use a citrus fruit juice of their choice and analyze any fluorescence produced for comparative brightness and color.

Lesson Background Information: Graphene is a sub-nanometer thick sheet made of carbon atoms bonded in a hexagonal pattern (Figure 1a). It is the strongest yet thinnest material and is an excellent conductor of electricity and heat. Graphite, used in pencils and as a lubricating powder, forms as a mineral in nature and is composed of billions of graphene sheets stacked atop each other (Figure 1b). The sheets are weakly bonded (covalently) with only three of the four possible bonding sites used. This weak bonding structure is what makes graphite "slippery". Until recently, it was thought that a single sheet would curl up on itself and could never be isolated, investigated and used in applications. In 2004, Geim and Novoselov successfully isolated single sheets of graphene using the surprisingly low-tech "sticky tape" method. For their discovery and subsequent characterization of graphene's properties, they won the Nobel Prize for Chemistry in 2010[1]. For an excellent overview of graphene visit the Nobel Prize site listed in the Source section below. Graphene is proposed to be a highly enabling material for electronics because it is very conductive, transparent, and flexible. Because it is useful when only one atom thick, it is projected that all of the world's electronic displays could be coated using only a briefcase full of graphene (15kg). It has a breaking strength 200 times greater than steel and it is the most electrically conductive material known at room temperature[2-3]. A hammock made of a single sheet of graphene would be practically invisible, weigh less than a gram and could support the weight of a baby. All of the promises of graphene are yet to be realized, and the high school students of today will be among the

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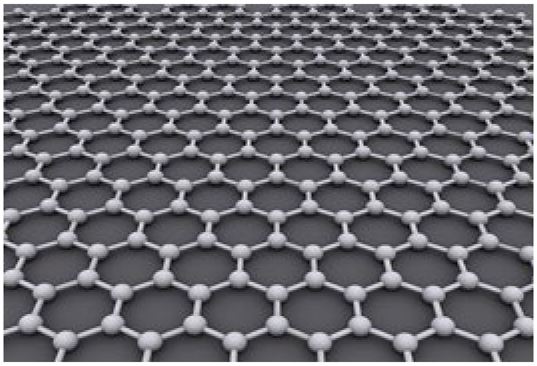
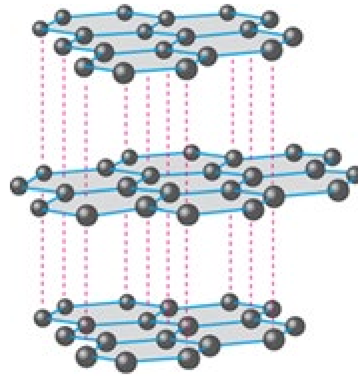
researchers and engineers who figure out how to make and use it for the next decade's technology.



1a.



1b.

Figure 1a. Graphene from: https://commons.wikimedia.org/wiki/File:Graphen.jpg
Figure 1b. Graphite from: http://chemhume.co.uk/ASCHEM/Unit%201/Ch3IMF/Images%203/hexagonal_structure.jpg

Quantum effects play an important role in the conductive properties of graphene, because the sheet structure limits how energy can spread i.e. not up or down, but only within the sheet (across). This 2D confinement of electrons increases the speed of electrical conduction by forming what is known as a 2D Electron Gas, in which the electrons behave as relativistic, mass-less particles (discussion of this is beyond the scope of this activity). To help students understand quantum mechanics you may want them to explore two video games which will help them understand the quantum world: *Particle in a Box* and *Psi and Delta* http://learnqm.gatech.edu/.

Graphene can be made into small discs, either by breaking up large sheets or reacting it with smaller carbonizing molecules. Depending on how they are made and what chemical groups are along the edges, they exhibit fluorescence in UV light; usually emitting green or blue light (Figure 2).

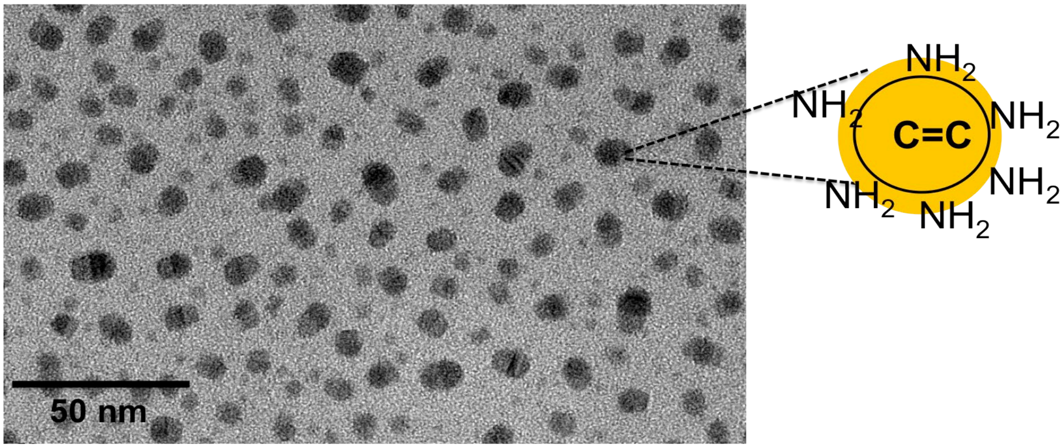


Figure 2. Graphene quantum dots with amine edge groups, imaged by electron microscope, Credit: Titirici Research Group, used with permission. (https://titiricigroup.org/)

A surprisingly simple method for making these fluorescent particles is to heat citric acid on a hotplate at 250°C until it turns yellow-orange, then quenching the reaction with a dilute alkali (ammonium hydroxide or sodium hydroxide). The citric acid carbonizes with the heat, losing water and making more carbon-carbon bonds until small discs of graphene are formed. Students will take this methodology even further into the "kitchen chemistry" realm by using a citrus fruit juice of their choice and analyzing any fluorescence produced for comparative brightness and color.

Nanoparticles that interact with light are often called "quantum dots" because their behavior is only understandable using the quantum physics concepts of energy bands and light with quantized energy (photons). See Quantum Dots lesson for further information - https://www.nnci.net/node/5335. Quantum dots can only be excited using photons of high enough energy (violet or UV) and not lower energy light such as red or green. Quantum dots are being used in high quality TV and phone screens because of their better color output.[4, 5]

The photoelectric effect won Einstein the Nobel prize in 1905 and shows that light energy is quantized (light as a particle) in a way that is related to wavelength/color. Young's double slit experiment demonstrates that light has wave-like properties (destructive interference).[6] See a good animation of the experiment at NanoHub (https://nanohub.org/resources/4916) or YouTube (https://www.youtube.com/watch?v=DfPeprQ7oGc). These two experiments give rise to the concept of wave-particle duality. In the introductory cadmium selenide quantum dot activity below, students observe how shorter wavelengths of light have higher energy and that fluorescence is a quantum phenomenon that only appears with a high enough energy of light.

Cadmium selenide nanoparticles show fluorescence that is dependent on their size. Students will observe how they fluoresce (or don't) under different colors (wavelengths/energies) of light. Asked to predict which is the largest particle and which is the smallest and give their reasoning. Further discussion of this can be found in the Quantum Dots lesson noted earlier.

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Sources:

1. Nobel Prize in Physics 2010: https://www.nobelprize.org/nobel_prizes/physics/laureates/2010/popular.html
2. Discovery of Graphene: http://www.aps.org/publications/apsnews/200910/physicshistory.cfm
3. Graphene: http://graphene.nus.edu.sg/content/graphene
4. Quantum Dots Go on Display: http://www.nature.com/news/quantum-dots-go-on-display-1.12216
5. Android Authority: http://www.androidauthority.com/samsung-lg-quantum-dot-displays-391966/
6. Quantum Mechanics, Spectral Lines: http://www.colorado.edu/UCB/AcademicAffairs/ArtsSciences/physics/PhysicsInitiative/Physics2000/quantumzone/index.html
7. http://titiricigroup.org/biofuels/

Pre-requisite Knowledge: Students should understand atomic structure, chemical bonds, electrical conduction and fluorescence.

Materials:

- Graphene kit (see materials source below and alternative materials to kit)
- Clear Scotch tape
- CdSe nanoparticles sets (Sargent Welch CENCO® , NN-Lab, or Navillum Nanotechnologies (Quantum Dots)
- Variety of Photon LED lights (at least red, green, blue and violet/UV)
- Basic spectroscope (optional, for determining LED wavelengths)
- citrus fruit (orange, lime, lemon, students may bring their own to try)
- hotplates, one per group
- 50ml glass beakers, five per group
- mesh cover for beakers (prevents splashes)
- safety eyewear
- tongs for handling hot beakers
- dilute ammonium hydroxide solution (grocery store ammonia works fine)
- clock or timer
- glass pipettes/droppers
- (2) 5 or 10 mL Syringes
- 2 syringe filters (.2 or .45µm)

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Advance Preparation: Purchase materials, which may be found here:

Source/Website	Material
Graphene Supermarket** (https://graphene-supermarket.com/Graphene-Kit-Beginner-s-Value-Package.html)	Graphene Value Kit (~$125)
Fisher Scientific (http://www. fishersci.com) Educational Innovations (https://www.teachersource.com/category/s?keyword=uv+light)	Mini UV lamp, battery operated, 365nm There are many sources for handheld UV lights
Sargent Welch CENCO® Quantum dot kit https://www.sargentwelch.com/store/product/18800022/cenco-quantum-dots-uniform-particle-size **NN-Labs** https://www.nn-labs.com/ **Navillum Nanotechnologies** www.navillum.com	Quantum dot sets are expensive. For example the CENCO® Quantum Dots sold in quantities of one set of four is ~$300
Flinn Scientific Spectroscopic http://www.flinnsci.com/store/Scripts/prodView.asp?idproduct=17157&noList=1	Basic spectroscope at ~$9.50 each
LED lights - Photon Microlights http://www.photonlight.com/	We use the photon microlight for the LED lights. They come in a variety of colors.

** An alternative to the graphene kit would be to purchase graphite flakes (available at most scientific suppliers) and use a glass slide instead of a piece of wafer. Graphene sticks best to silicon but the slide is a possible substitute.

Safety Information: Hot liquids – hot objects should be handled with tongs. Wear safety eyewear. Ammonia is irritant to skin. Wear gloves.

Vocabulary and Definitions:

Nanometer: *A billionth of a meter (1 x 10^{-9}). About 100^{th} the width of a human hair or about 4 atoms wide.*

Nanoparticles: *Particles which are particles between 1 and 100 nanometers. At this scale, surface properties are often stronger than bulk properties.*

Quantum Dot: *A nanoscale size semiconductor that has optical and electrical properties that differ from larger particles and bulk material. The color light that a QD emits is directly related to its size*

Fluorescence: *The emission of light by certain substances that have absorbed light or other electromagnetic radiation. It is a form of luminescence. The absorbed light is of a shorter*

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wavelength than the emitted light (longer wavelength) and has lower energy, than the absorbed radiation.
Graphene: *A sub-nanometer thick sheet of carbon known for its high strength, conductivity , and transparency*.
Graphite: *Crystalline form of carbon with the atoms weakly bonded in a hexagonal structure.*

Suggested Teaching Strategies:

Time	Activity	Goal
Pre-lesson Home-work	**View the following:** *https://www.youtube.com/watch?v=Mcg9_ML2mXY* *www.youtube.com/watch?v=rphiCdR68TE* https://www.youtube.com/watch?v=lvi3nG2Mwsw	To introduce graphene and to familiarize students with "stick tape" method for isolating graphene.
Day 1	**Graphene Intro and Isolation**	
15 min	Introduce students to the topic of graphene. Discuss Sci Show video on graphene previously assigned for homework: Q) What interesting properties does graphene have? Q) Why do you think we are not using it already? Q) What would you use it for? Demonstrate how to use tape method to peel apart layers (see video above)	To prepare students for isolating graphene and thinking about quantum effects.
20 min	Students use tape and graphite to attempt to get a graphene layer.	Experience how accessible science can be.
10min	Discussion: What techniques might we use to convince ourselves that we only have a single layer?	Students look for evidence and propose further tests.
Day 2	**Quantum Dots**	
10 min	Lead discussion on light What is light? Huygens Vs Newton. Wave vs Particle. Suggest show double slit animation.	To get students to ask questions and propose reasoning.
20 min	Distribute CENCO quantum dots and photon microlight sets to students. Students investigate behavior.	To allow students to collect evidence and propose hypotheses.

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10 min	Discuss ideas about color and fluorescence.	Core concept: Energy of light is related to its color. Fluorescence has energy barrier that must be overcome. This demonstrates that light must be absorbed in packets with an energy that is related to color.
3 min	Clean up.	To prepare workspace for next class.
1 min	Ask students to bring citrus fruit/juices for lab tomorrow	Materials needed for lab.
Day 3	**Making Quantum Dots lab**	
10 min	Graphene can be made as tiny discs. These discs fluoresce and might be useful in medicine because they are non-toxic. Researchers have found they can build discs from carbonizing citric acid or from sugars or proteins.	Intro to lab concept.
50 min	Students heat citrus juice to investigate whether it will make fluorescent quantum dots.	Removing samples at different times to investigate fluorescence formation. Gathering data to remake conclusions based on reasoning.
10 min	Students compare fluorescence of samples to examine for differences in color/brightness.	
10 min	Discussion with additional questions (why was a particular juice good or bad? How long did you heat the sample? Suggestions for further purification?)	Reasoning based on data
5 min	Clean up.	To prepare workspace for next class.

Directions for the Activity:
Ask students questions to review what they already know:

1. Example: What happens during a *chemical reaction? Chemical reactions occur when the reactants (particles) come into contact with each other and form new products.*
2. Example: What factors affect what products are formed? *It depends on whether or not the reactant atoms are compatible (it depends on the number of valence electrons in the atoms); whether the atoms will interact fast enough to make a new product.*

Forming Graphene Procedure: The Sticky Tape method is a simple method and consists of repeatedly folding tape over a piece of graphite to pull layers of graphite apart. The difficult part is transferring the graphene sheet to a place where you can examine it. Usually this is achieved by pressing it onto a silicon wafer with a silicon dioxide coating then examining under

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a light microscope. The video www.youtube.com/watch?v=rphiCdR68TE gives a good tutorial of the process. If a wafer piece is not available, you can try a glass slide.

Cleanup: Tape with graphite can be put in the trash. Pieces of silicon wafer can be washed and reused or disposed of as “sharps” waste.

Using Fruit Juice to Form Graphene Quantum Dots: The main thrust of this activity is to have students propose lines of reasoning and check them with observations. The activity has students thinking critically while doing something at the cutting edge of science. The overall procedure is each group heats up two different fruit juices until they boil dry (see Student Worksheet for directions). They will re-dissolve the residue in a mild alkaline solution, filter it, and check it for fluorescence. The research field is quite active and some groups are focusing on using food as a starting material for graphene quantum dots. Nobody has reported using fruit juices yet (as of August 2014), so students really are doing new research. There is an array of methods researchers have used to make graphene quantum dots and, as yet, there is no obvious pattern to the reported fluorescence. A collection of the colors and edge groups of graphene quantum dots reported by researchers is below:

Color	Edge groups
Blue	Benzene rings, nitrogen groups
Blue	Nitrogen, carboxylic acid (COOH)
Blue	Phosphate
Blue	Nitrogen, oxygen
Blue	carboxylic acid (COOH)
Cyan	Nitrogen, oxygen, sulfur
Green	Oxygen, nitrogen
Green	Oxygen
Green	Nitrogen groups, carbon chains
Green	Polyphosphate
Green	Rich in carbon-oxygen bonds
yellow	Nitrogen rich
Yellow	Carboxylic acid (COOH), nitrogen
Infrared	Large polymer chains

Cleanup: Heated fruit juice residue can be washed down the sink.

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Assessment:
Review the findings with students:

- A fluorescent substance can be made by heating fruit juice.
- Scientific literature reports that heating citric acid makes fluorescent graphene nanodisks.
- These fluorescent particles might have useful medical applications.

See rubric in Student sheet. Essentially students answer four questions and give a reason for each of their claims which should include details from what they already know. Their explanations should be supported by their observations.

Additional Resources

- SciShow - Graphene: The Next Big (but thin) Thing https://www.youtube.com/watch?v=Mcg9_ML2mXY
- Materials Today, Volume 16, Issue 11, November 2013, Pages 433–442 (DOI: 10.1016/j.mattod.2013.10.020)
- Making Graphene 101, Ozyilmaz' Group http://www.youtube.com/watch?v=rphiCdR68TE
- Introducing Graphene http://www.nanowerk.com/nanotechnology/introduction/introduction_to_nanotechnology_4.php
- The Power of Graphene; lesson from Try Engineering with good information. (http://www.tryengineering.org/sites/default/files/lessons/graphene_0.pdf)
- Quantum Dots Explained: What are Quantum dots and Why are they so awesome? http://www.trustedreviews.com/opinions/quantum-dots-explained-what-they-are-and-why-they-re-awesome#MpSIEtZYjAxpGf49.99
- Quantum Dots (Wikipedia). http: https://en.wikipedia.org/wiki/Quantum_dot

Optional: Activity extension
Students who have a good grasp of the content of the lab can be further challenged with these questions:

1. Why do scientists insist on arguing from evidence? *Without evidence to support an idea, it is merely a story. Once supporting evidence is found, a scientist should look for evidence that counters the idea. If no contradictory evidence can be found, the idea can be used as a model to predict outcomes. A basic tenet of science "Newton's flaming laser sword" can be summarized as "what cannot be settled by experiment is not worth debating".*
2. What are the current issues stopping graphene being used in inventions? *Large pieces of graphene are very difficult to produce in quantity and with high quality. Graphene nano-disks aren't as bright as other fluorescent materials.*

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Student Worksheet (with answers in red)

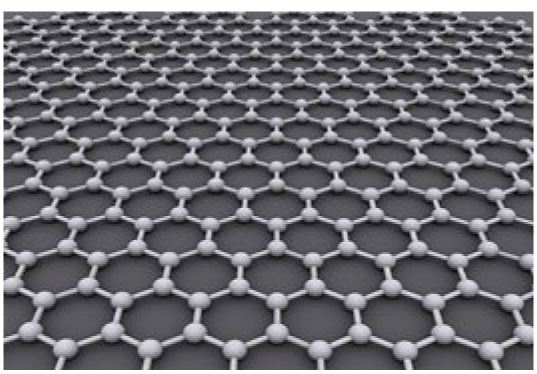
Graphene Quantum Dots from Fruit Juice

Safety
Hotplates: Use tongs to move hot beakers. Hot liquids: Safety eye-wear required.
Ammonia is irritant to skin. Wear gloves.

Introduction

Graphene, a nanoscale material, is a form of carbon that has potential to be a great material for many uses. Graphene is a one atom thick, two dimensional material which consists of carbon atoms densely packed into a honeycomb-like crystal lattice. It exhibits interesting electrical, optical, mechanical, thermal properties. Electrically, it is a semiconductor. Graphite, used in pencils, consists of billions of graphene sheets stacked atop of each other.

Quantum dots are nanoscale semiconductors which emit light. Unlike many materials used to make quantum dots for fluorescence, such as cadmium selenide, lead sulfide, and indium arsenide, graphene has very low health concerns. Graphene quantum dots are being explored by nanoscience researchers because of their interesting properties such as low toxicity, stable flouresence, chemical stability, and quantum effect. In fact, a super low-tech method of making quantum dots is to heat citric acid until it carbonizes to make blue-green fluorescing nano-discs. In this activity, you will create such nano-discs. You will take it even more low tech by using fruit juice, not pure citric acid. How will your choice of fruit juice affect the fluorescence of the quantum dots?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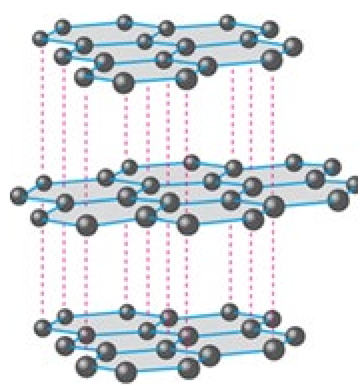
1b.

Figure 1a. Graphene from: https://commons.wikimedia.org/wiki/File:Graphen.jpg
Figure 1b. Graphite from: http://chemhume.co.uk/ASCHEM/Unit%201/Ch3IMF/Images%203/hexagonal_structure.jpg

Part I. **Making Graphene:**
You will watch, either in class or as homework, videos on graphene and the tape method to create it from a piece of graphite. You teacher will supply you with a piece of graphite and clear tape to create your own graphene.

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Questions:

1. How successful were you in creating graphene? Based on what evidence?
2. What might improve your ability to make graphene?
3. Do you think a light microscope is the best tool to observe your results?
    1. If not, what tool would you use and why?

Part II. Making Graphene Quantum Dots

Procedure:

1. Turn on your hotplate to 250ºC
2. Put 5 ml of fruit juice 1 into a 50 ml beaker and label it well.
3. Put 5 ml of fruit juice 2 into a 50 ml beaker and label it. Put both beakers on the hotplate near the center, cover with the mesh and heat until dryness (about 10 minutes). Carefully watch to avoid burning. Record the time the juices first start to boil. Make observations of what happens to the juice.
4. When the juice has boiled dry, record the time, remove the beakers from the hotplate with tongs and place them on a heat-proof surface and let cool for 1 minute.
5. Slowly add 5ml of sodium bicarbonate solution to each beaker and stir.
6. Extract your samples into a syringe and then fit a filter disc to the end of the syringe. Filter your sample back into the beaker to remove any large particles.
7. Using the pipette, put a drop of your two products side by side on a glass slide. Label which drop is what juice with marker.
8. Observe the drops under ultraviolet light (also called UV or blacklight) in the viewing box.
9. Compare your results with other groups. Does your prediction seem to fit with the observations? Does another group have a prediction that fits better? Do you have a new idea of how to predict the outcome?

Record your observations:

Example: Measurements of Objects

	Start Appearance	**Heating Notes**	**End Appearance**	**UV Color**
Juice 1	*Orange opaque*	*Started boiling at 2 minutes. Went brown in one patch before the rest. Took another 2 minutes before dryness at 7 minutes.*	*Golden brown with some bubbles/foam*	*Blue, dim*
Juice 2	*Light yellow, translulcent*	*Started boling at 3 minutes. Spitting and popping a lot. Turning darker at the edges first. Dry at 8 minutes.*	*Light orange, lots of small bubbles.*	*Blue-green, dim*

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Analyze the Results:

Because ……*the lemon juice I am using is more acidic than orange juice*…. We predicted…. Lemon will give brighter fluorescence than orange. (this example may not be true). Our results show….. they were very similar in brightness, but had slightly different colors.

1. Was your prediction correct based on the results and observations? Should you keep or discard your "because" idea?

   No. Lemon and orange had the same brightness but the lemon juice fluoresced blue green versus the orange's hue of pale blue.

2. Is there another "because idea that might predict results better?

   Because the acidity affects the color, more acidic juices like lemon will make greener fluorescing quantum dots. (this may not be true)

3. How would you change the experiment to investigate whether your "because" hypothesis works in a different situation?

   Add extra citric acid or sodium bicarbonate to lemon juice at the start to see if it changes the color of the product.

4. Why might quantum dots from fruit juice be useful. Be inventive but give your reasons for each use.

   Homemade invisible ink because it would only be visible with black light.
   Fluorescent tattoos that glow in the dark (like a nightclub) because it would be sage to put on the body. Graphene is conductive so perhaps there is a way to get the fluorescence to switch on and off with electricity so that it could be used in screens.

Grading Rubric for each question

1 pt.	2 pt.	3 pt.	4 pt.
Answer is readable	Student makes statements that are appropriate to a science class	Student gives reasons for their statements. The explanations are connected to some observations	Student gives a reason for each of his/her claims and includes details from what they already know. The explanations are not contrary to observations

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Next Generation Science Standards (Grades 9-12)

HS-PS4-3 Evaluate the claims, evidence and reasoning behind the idea that electromagnetic radiation can be described either as a wave model or a particle model, and that for some situations one model is more useful than the other.
HS-PS3-2 Develop and use models to illustrate that energy at the macroscopic scale can be accounted for as either motions of particles or energy stored in fields.
Cross-cutting concept 2: Cause and effect
Cross-cutting concept 6: Structure and function
Engineering and Design Practice 2: Developing Models.

- Develop, revise and use a model based on evidence to predict relationships between components of a system

Engineering and Design Practice 3: Planning investigations.

- Make directional hypotheses that specify what happens when the independent variable is manipulated.

Engineering and Design Practice 4: Analyzing and interpreting data.

- Evaluate the impact of new data on a working explanation of a proposed system.

Engineering and Design Practice 6: Constructing Explanations.

- Make a qualitative claim regarding the relationship between dependent and independent variables.
- Link evidence with claims to support explanations or conclusions.

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