Nanoparticles And Sunscreen

Center for Nanotechnology Education

This material is based on work supported by the National Science Foundation under Grant No. 0802323 and 1204918. Any opinions, findings and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.

Nanoparticles and Sunscreen

Abstract

In this module, students are introduced to the function of sunscreen and learn how nanoparticles can be used to protect people from ultraviolet radiation. They use photochromic paper as a UV sensor, place samples of different types of sunscreen over this UV sensor, expose their samples to UV light, and determine the level of exposure through each type of sunscreen. Using these tools, students compare the effectiveness of conventional (chemical-based) and nanoparticle-based sunscreens.

Outcomes

After completing this module, students will be able to:

- Define the wavelengths and types of ultraviolet radiation
- Describe the mechanisms of light absorption and light scattering
- Explain the difference in the mechanism of action of chemical sunscreens and inorganic oxide nanoparticle sunscreens
- Compare the efficacy of different sunscreen products by testing them

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Prerequisites

Students should have some exposure to the following physical science concepts typically encountered in eighth grade science:

- the wave nature of light
- basics of chemical bonds
- Familiarity with the SI prefixes. Specifically micro- (10^{-6}) and nano- (10^{-9})

Correlation

Science Concepts

- The electromagnetic spectrum, and where visible light lies in that spectrum
- The relationship between color, wavelength, and energy
- Interactions of light and matter may include absorption and scattering, and are dependent upon light wavelength and material properties

Nanoscience Concepts

- Size dependent properties of matter
- Particles in the nanoscale size range efficiently scatter light of shorter wavelengths compared to larger particles. This property can be exploited in consumer products.

Background Information

When electromagnetic energy strikes matter, the resulting interaction depends strongly on the nature of the material. Interactions of light with matter include reflection, refraction, transmission, absorption, and scattering, as well as a combination of these interactions. Electromagnetic (EM) energy can be described in terms of its wavelength via the equation

$$E = \frac{hc}{\lambda}$$

where h is Plank's constant, c is the speed of light in a vacuum, and λ is the Greek letter lambda which represents the wavelength of the EM energy. Longer wavelengths equate to lower energy, and shorter wavelengths to higher energies. Figure 1 shows the visible portion of the EM spectrum. Visible wavelengths vary from approximately 400 nanometers (nm) (blue light) to 700 nm (red light). Wavelengths longer than red, and thus at a lower energy, are called infrared, while wavelengths shorter than blue (i.e., at higher energy) are termed ultraviolet.

Sunlight contains visible radiation plus shorter wavelength ultraviolet light. Prolonged exposure to sunlight has been shown in to lead to premature aging of the skin and increased risk of skin cancer. These effects are due to the UV present in sunlight; this portion of the sunlight spectrum is also responsible for skin tanning. Solar UV light reaching the Earth's surface is primarily composed of "UV-A" ultraviolet light, with wavelengths from 315 – 400 nanometers and a smaller amount of "UV-B" light, with wavelengths from 280-315 nanometers.

In addition to proper clothing and limiting sunlight exposure, sunscreen products are recommended to reduce the health risk of ultraviolet exposure. Sunscreens work by taking advantage of ways that materials and light interact to reduce the amount of UV reaching the skin. The two types of interaction studied in this activity are *absorption* and *scattering.*

Light absorption. Conventional sunscreens are chemical-based and operate on the principal of

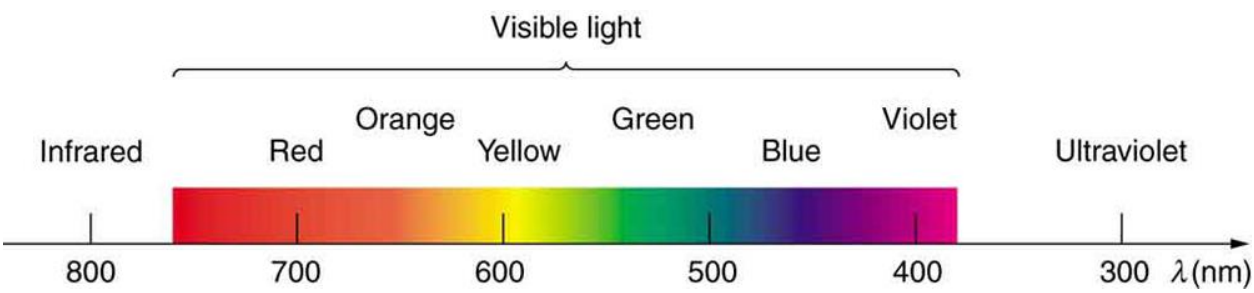


Figure 1: Every color in the visible spectrum has an associated wavelength and energy. Red has the longest wavelength in the visible spectrum, and also the lowest energy. Violet has the shortest wavelength and the longest energy. Wavelength is associated with energy with the equation $E = hc/\lambda$. Image credit: http://cnx.org/content/m42444/1.3/

absorption. These sunscreens use a chemical designed so that each of its molecules can absorb a photon of high-energy UV light and then release that energy as a lower energy photon at a longer wavelength. This lower energy emission is harmless to human skin.

Some examples of these absorbing compounds are PABA (para amino benzoic acid) and 4-ethoxycinnamic acid 2-ethylhexyl ester, more commonly known as octinoxate. Figures 2 and 3 present a simplified structure of these two organic molecules. In this type of representation, the carbon atoms are not drawn but lie at each line intersection.

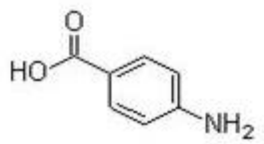


Figure 2. PABA molecule.

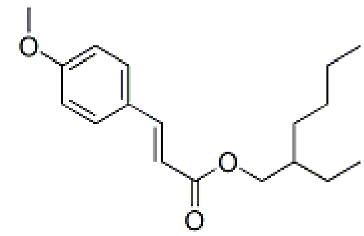


Figure 3. Octinoxate molecule

In both of these compounds, the double bonds are primarily responsible for the UV photon absorption. This absorption may result in a broken bond, rendering it ineffective for continued absorption. After some exposure time, most of the absorbing bonds have been broken, and the sunscreen loses its protective ability. It's time to re-apply.

*Light scattering. S*unscreen manufacturers have looked for other strategies to block UV radiation. One approach uses nanoparticles to scatter the incoming UV radiation away from the skin. Such light scattering requires a material of a size close to that of the wavelength of the light to be scattered (or the material itself may be larger, but it should have features of a size comparable to the target wavelength). Ultraviolet light wavelengths are in the 280 to 400 nanometer range, and small particles at or somewhat below this size are required for effective scattering of UV light. The first products to use light scattering in a sunscreen employed inorganic powders already manufactured for use in the paint industry, such as zinc oxide (ZnO) and titanium dioxide (TiO_2). These materials were finely ground powders with particles of a relatively wide size range; they included particles of the correct size to scatter UV light, but also larger particles effective at scattering visible light (visible light has longer wavelengths and so larger particles are required for effective scattering). As a result, while these products were efficient at reducing UV exposure, they had the undesirable effect of scattering visible light, so they appeared white when applied to the skin.

Nanotechnology. More recently, scientists have been able to make and study particles at the nanometer scale. New methods have been developed to make uniform preparations of particles in the 100 to 200 nanometer range; these particles effectively scatter UV light but do not interact with visible light, making them transparent. Nanoparticle-based sunscreens have gained in popularity in recent years. Figures 4 and 5 contrast the size of the particles used in older sunscreens to that of the nanoparticles used in newer sunscreen.

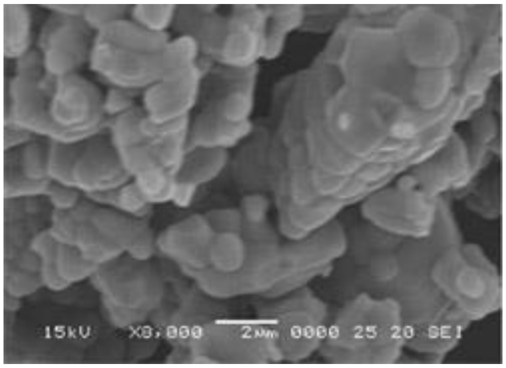


Fig. 4. Commercial zinc particles

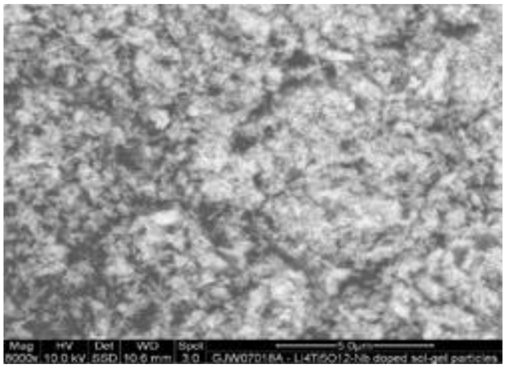


Fig. 5 Zinc nanoparticles

In this activity, students will compare various sunscreens for their ability to scatter UV and visible radiation and evaluate them, much as a lab scientist would study a sunscreen formulation.

Light Sources. This activity will use several different types of ultraviolet light sources. Direct unfiltered sunlight at midday has a high UV intensity and offers the fastest exposure times. A 48” light fixture with two black light fluorescent tubes will also expose the photo paper quickly (in about 5 minutes). Standard fluorescent lamps of the same size will take about 20 minutes for an exposure. Compact fluorescent bulbs of at least 25 watts may also work, but will take longer to expose the paper. Incandescent bulbs are poor sources of UV light.

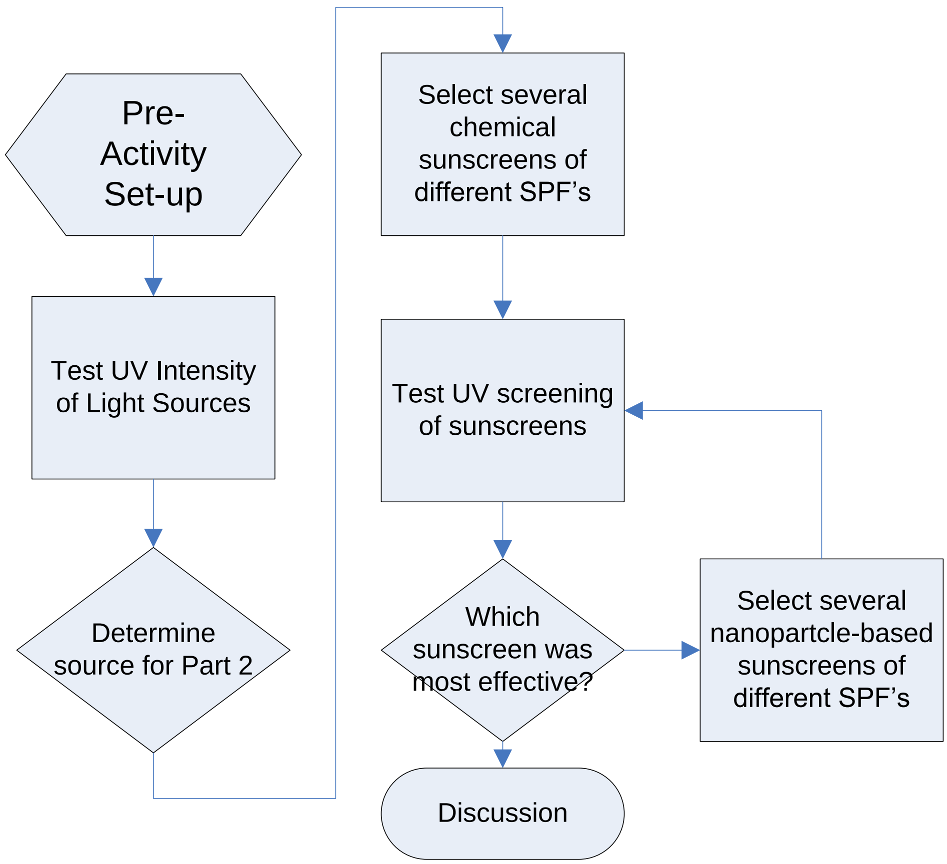
Current and Future Applications

Applications of nanoparticles are many and growing. In addition to sunscreens, nanoparticles of different materials are being used in many products, including cosmetics and personal care items, foods, paints and coatings, pharmaceuticals, and sporting goods. To be well-informed consumers, we need to be able to recognize the presence of nanomaterials in products and have a general idea of their function.

Sunscreens containing zinc oxide and titanium dioxide nanoparticles are one of the first widespread uses of nanotechnology at the consumer level. Many, but not all modern sunscreens contain these nanoparticles. Today, researchers are focusing on reducing the production of free radicals from these nanoparticles in UV light. They have found it is possible to reduce the production of free radicals by coating the nanoparticles with a thin layer of silica or alumina.

Learning Activity

Activity Flow Chart



Activity Set-up (prior to doing the activity)

1. **Gather materials**
    a. Photochromic paper, available at art and craft stores
    b. Clear plastic sheets (e.g., overhead transparency sheets)
    c. 1-2 shallow rinse trays – at least 15 cm x 25cm x 2cm deep. Food storage containers may be used.
    d. White vinegar or lemon juice solution
    e. Light sources: a 48 inch fluorescent tube fixture with black light or conventional lighting tubes works best. You can also try compact UV source like an LED-based UV flashlight or multiple compact fluorescent bulbs. Unfiltered midday sunlight through an open window will work as well.
    f. Glass or plastic microscope slides
    g. Several samples of conventional (chemical-based) sunscreen, with different SPF values (typically the cheapest sunscreens are entirely chemical)
    h. At least one sample of a nanoparticle-based sunscreen (will contain a component labeled as titania, titanium dioxide, and/or zinc oxide).

2. **Cut three to four 5 cm x 5 cm pieces of photo paper for each student or team.** Keep these in a dark place until they are ready to use.

3. **Cut the transparent plastic into 5 cm x 5 cm pieces; one or two per student or team.** These will be used as the surface to which the sunscreen will be applied. These sheets can be reused by the students after careful washing and drying.

4. **Set up the light sources.** A single 48 inch 40 watt black light tube held 8 cm above the surface of the photochromic paper usually gives an acceptable image in a 5 minute exposure. Two 40 watt conventional fluorescent tubes at the same distance from the paper gives a less well-developed image in a 20 minute exposure, but is still useful if a black light is impractical. Sunlight is very effective and a few minutes exposure to full sun in the summer is ample. If you want to quickly evaluate light sources, put a couple of coins on a piece of photochromic paper so you can have something to compare against and expose to your light source . When the paper fades to a very pale blue, exposure is complete.

5. **Set up rinse trays and prepare the developer solution**. This is water containing a small amount of vinegar or lemon juice (approx. 1 Tbs. per qt.). The acid solution will help develop the photo paper faster.

6. **Set up warm water bath (*optional*).** A warm water bath, at about 30 C, may be used to warm up the sunscreen if necessary. The bath can be set up on a hot plate or warmed in a microwave oven.

Instructor Notes.

Students working in teams. For Part I of the activity, break the class up into teams of 4-5 students, and let each group use a different light source. When done with Part 1, students can compare results and come to a consensus about the best procedure for the next experiment; measuring the efficacy of various sunscreens.

Setting initial conditions. For the students' results to be comparable, all must use the same exposure time and distance.

The exposure step in Part 1 should be done for

- 5 minutes (if using a 40 watt black light)
- 20 minutes (if using white fluorescent bulbs)
- 3 minutes (if using sunlight)

Place the photochromic paper 8 cm beneath the light sources. If there is time, have students experiment with variations on these initial conditions.

Sunscreen thickness. If you choose, you or your students can prepare applicators with more than one layer of foil to investigate the effect of thickness of application on sunblock efficacy (see below).

Nanoparticles and Sunscreen

This activity explores the absorption and scattering of light energy by matter in three parts. In Part 1, you will use photochromic paper as a light absorption sensor to determine which light source produces the most energetic light. Part 2 uses the light source found to be most energetic to test the absorbance of chemical sunscreens. In Part 3, you will compare the performance of chemical versus nanoparticle-based sunscreens in preventing UV light from passing.

Materials and Equipment (master list for all parts)

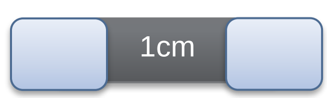
1. Photochromic paper. This is a paper coated with a chemical that will react with light and/or acidic solutions.
2. Transparent plastic sheets
3. Light sources. These can be unfiltered sunlight (i.e., through an open window), a ‘blacklight’ fluorescent tube, standard fluorescent lamps, or incandescent lamps (at least 100 Watt). Incandescent lamps are weak emitters of UV energy.
4. Solution rinse trays with acidic developing solution. This is water containing a small amount of vinegar or lemon juice (approx. 1 Tbs. per qt.). The acid solution will help develop the photo paper faster.
5. Glass or plastic microscope slides
6. Several samples of conventional (chemical-based) sunscreen, with different SPF values
7. At least one sample of a nanoparticle-based sunscreen
8. A warm water bath – approx. $30^{o}C$ – to warm up the sunscreen if necessary

Activity

Procedure –Part 1

1. **Prepare the microscope slide applicators.** Wrap a small piece of aluminum foil around the end of the slide, so that it covers about 1/3 of the slide at one end, and secure the foil to the slide with tape. Do this on both ends, leaving an approximately 1 cm gap between the two foil sections. Be careful to ensure that there are no wrinkles in the foil/plastic along the bottom edge of the slide. You can gently smooth this area with your finger. Typical aluminum foil is about .016 mm thick.

Figure 5. Example of the slide applicator.



The area on the bottom edge of the microscope slide between the two pieces of foil or plastic is the working portion of the applicator.

2. Select a light source. Place a piece of photopaper eight cm under the light source and place an object on the paper (a coin, a comb, a key, or other small object works well).
3. Turn on the light source and expose the photopaper for the amount of time given by your instructor.
4. After exposure, develop your photo paper by placing it in the acidic solution. Swish around for about 1 minute, and watch for a color change.
5. After exposing and developing your paper samples, dry them on paper towels.
6. Compare your exposed photo papers to those of other groups who used other light sources.

Potential questions for the class after Part 1.

- Which light source resulted in the greatest and the least exposure?
- What other factors might influence the exposure?

Procedure-Part 2. Using the light source found in Part 1 to produce the most UV energy, you will expose the photochromic paper the test conventional (chemical–based) sunscreens with different SPF's.

1. Select a chemical sunscreen. Note the brand and the SPF rating.
2. If needed, warm sunscreen bottles in the warm water bath to make the liquid easier to spread.
3. Place a small amount of sunscreen on a piece of transparent plastic.
4. Using the slide applicator, spread the sunscreen out thinly across a 1 cm x 1 cm region of the plastic sheet. Do this by slowly drawing the applicator across the drop of the sunscreen. This should leave a uniform layer of sunscreen behind. The thickness of the sunscreen layer is dependent on the thickness of the flanking pieces of foil or plastic. The goal is to have a 1x1cm patch of uniformly applied sunscreen.
5. Place the sheet of plastic covered in sunscreen on top of a piece of photochromic paper, with sunscreen facing up.
6. Immediately expose this to the light source. Use an exposure time that was determined to be effective in Part 1.
7. Remove the paper from underneath the plastic.
8. Develop the photopaper in the acid developing water.
9. Take the paper out and lay on a paper towel, letting it dry a bit (image should be visible).
10. Compare your results with those of other students using sunscreens of different SPF values.

Potential questions for the class after Part 2.

- Which sunscreen seemed to block the light the best? (consider that the result of areas that received the least UV light exposure will appear the lightest).
- Do you see a difference in the ability of two different products to block UV light? Is this difference related to the stated SPF factor on the label?
- How do you think a thicker layer of sunscreen would affect the results? Why?

Procedure-Part 3. Repeat the Part 2 procedure, now using samples of nanoparticle-based sunscreen. Try to get results from sunscreens with SPF's similar to those used in Part 2. Compare the UV exposure that resulted with conventional (chemical-based) and nano-article-based sunscreen products.

Optional: Compare the durability of the two types of sunscreens by preparing plastic samples coated with chemical and nanoparticle-based sunscreens. Do not place these on photopaper yet; instead, leave both types of sunscreen under UV radiation for a substantial amount of time (>2 hours). Then repeat the exposure testing as described in Part 2. Can you show that nanoparticle sunscreen lasts longer than chemical sunscreen?

Potential questions for the class after Part 3.

- Was there a noticeable difference in the ability of the two different products to block UV light?
- Did the nanoparticle-based sunscreen perform as well/better/not as well as the chemical sunscreen?

Discussion Questions *(Answers in red)*

1. How does the wavelength of light relate to its energy?
   The shorter the wavelength of light, the higher its energy.

2. What light source did you find to be highest in UV intensity?
   Sunlight and the full size (48") black light will have the most UV intensity. White fluorescent lamps will have somewhat less. Tungsten lamps offer the least amount of UV light in their spectrum, which is predominantly in the red and infrared wavelengths.

3. How could UV rays be harmful to human skin?
   The high energy photons making up UV light are capable of damaging human skin cell components, including DNA in the cell nuclei. This may eventuall manifest as skin cancer.

4. How does chemical sunscreen protect the wearer? Explain in detail.
   The double bonds of the active ingredient in chemical sunscreen absorbs the high energy UV light. They release this energy in the form of longer wavelength, lower energy light which is harmless to skin cells.

5. Why does sunscreen with micro-sized zinc oxide particles appear opaque, and sunscreen containing zinc oxide nanoparticles appear clear?
   The larger particles tend to scatter all visible wavelengths back to ur eyes, resulting in a white color.

6. How does the action of nanoparticle-based sunscreen differ from that of chemical sunscreen?
   Nanoparticles scatter the incoming light away from the skin.

7. Did you find evidence that sunscreen of different SPF absorbed different amounts of UV light?
   Answers will vary.

8. Did you find evidence that nanoparticle-based sunscreen was as effective as conventional sunscreen in blocking UV light?
   Answers will vary..

Going further (requires additional research):

9. What happens when high energy UV light interacts with human skin cells? Describe the results at the cellular level, and indicate why this is a health problem.
10. What are the health effects of chemical or nanoparticle sunscreens?

Contributors

- This activity was originally developed by Dr. Thomas Deitz of Lansing Community College, Lansing, MI.

- The manuscript was edited and rewritten by Dr. James Marti of the University of Minnesota, Minneapolis, MN.

- Additional contributions by Christopher Kumm, Dakota County Technical College, Rosemount MN.

Multimedia Resources

Videos

- PowerPoint and background from NanoSense: http://nanosense.sri.com/activities/clearsunscreen/oneday/CS_OneDayPPT.ppt
- "Five things worth knowing about nanoparticles and sunscreens" from the Risk Science Center at the University of Michigan: https://www.youtube.com/watch?v=VV0cCg4clMw

Simulations

- Sunscreen visualization: http://nanosense.sri.com/activities/clearsunscreen/sunscreenanimation.html

- A simulation from PhET at the University of Colorado Boulder demonstrating the photoelectric effect. This demonstration shows how energy relates to wavelength through the formula $E = hv/\lambda$.

  http://phet.colorado.edu/en/simulation/photoelectric

Articles

- A comprehensive review of the safety and effectiveness of titanium dioxide and zinc oxide nanoparticles in sunscreens from the Dove Medical Press: http://www.dovepress.com/titanium-dioxide-and-zinc-oxide-nanoparticles-in-sunscreens-focus-on-t-peer-reviewed-article-NSA
- An article from Scientific American outlining the potential risks and benefits of sunscreens containing zinc oxide nanoparticles: http://www.scientificamerican.com/article/do-nanoparticles-and-sunscreen-mix/
- NISE Net program on nanoparticles in sunscreen http://www.nisenet.org/catalog/programs/exploring_products_-_sunblock_nanodays_2011_2012
- FDA: Nanotechnology press release: http://www.fda.gov/NewsEvents/Newsroom/PressAnnouncements/ucm301125.htm
- Zinc oxide and nanoparticles: http://www.badgerbalm.com/s-33-sunscreen-zinc-nanoparticles.aspx

Alignment to the Next Generation Science Standards

Table 1 clarifies the nature of the alignments by Scientific and Engineering Practice (Practice), Disciplinary Core Idea (DCI), and Crosscutting Concept as related to a Performance Expectation.

TABLE 1. ALIGNED PRACTICES, DISCIPLINARY CORE IDEAS, AND CROSSCUTTING CONCEPTS

PRACTICE	***DCI***	***CROSSCUTTING CONCEPT***
HS. Analyzing and interpreting data: Analyze data using tools, technologies, and/or models (e.g., computational, mathematical) in order to make valid and reliable scientific claims or determine an optimal design solution. *Partial in student materials*	*MS-PS4.B: Electromagnetic Radiation:* When light shines on an object, it is reflected, absorbed, or transmitted through the object, depending on the object's material and the frequency (color) of the light. *Strong in teacher and student materials*	*HS. Structure and function:* Investigating or designing new systems or structures requires a detailed examination of the properties of different materials, the structures of different components, and connections of components to reveal its function and/or solve a problem. *Partial in teacher and student materials*
		CROSSCUTTING CONCEPT *HS. Influence of Science, Engineering, and Technology on Society and the Natural World:* New technologies can have deep impacts on society and the environment, including some that were not anticipated. Analysis of costs and benefits is a critical aspect of decisions about technology. *Partial in teacher and student materials*

Alignment to the Common Core State Standards for English Language Arts/Literacy and Mathematics

Alignments in Table 2 were made to the Anchor Standards, unless a more specific version of the standard was a closer fit to the skills in the module.

TABLE 2. ALIGNED COMMON CORE STANDARDS FOR ENGLISH LANGUAGE ARTS & LITERACY
CCR.L.6: Acquire and use accurately a range of general academic and domain-specific words and phrases sufficient for reading, writing, speaking, and listening at the college and career readiness level; demonstrate independence in gathering vocabulary knowledge when encountering an unknown term important to comprehension or expression. *Partial in teacher and student materials*
RST.11–12.3: Follow precisely a complex multistep procedure when carrying out experiments, taking measurements, or performing technical tasks; analyze the specific results based on explanations in the text. *Partial in teacher and student materials*

No alignments to mathematics were found.