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Learning about nanoparticulate ingredients used to block the Sun's ultraviolet rays

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hat are 'nano' ingredients, and how can you tell if your sunscreen has them?" "Why do we need nanosunscreens?" "If a bottle of a well-known sunscreen brand claims that it protects against UVB and UVA rays, should I believe it?" These are just a few of the questions that our "Clear Sunscreen" nanoscience unit has students asking. Students are excited to learn about science that is applicable to their daily lives and because they find the topic interesting, they are motivated to figure out the complex concepts involved.

In this article, we provide a brief overview of the emerging field of nanoscience and why it is an important area for education. We then explain the science behind the new nanoparticulate sunscreens, describe the different elements of the unit, and reflect on some of the opportunities and challenges of teaching nanoscience at the high school level.

Clear Sunscreen

Clear Sunscreen is one of four sets of learning materials collaboratively created by educational researchers, science teachers, and nanoscientists as part of the NanoSense project, aimed at helping high school students learn about science concepts that account for nanoscale phenomena. All of the materials are freely available online and are linked to the National Science Education Standards (NRC 1996) (see "On the web" at the end of this article), as well as related chemistry, physics, biology, and environmental science concepts. Although Clear Sunscreen was designed for chemistry classrooms-introductory, Advanced Placement, or International Baccalaureate, depending on whether the advanced materials are used-it has also been used successfully in 9th-grade biology and 11th-grade biotechnology classrooms. Given the interdisciplinary nature of the content, it could also be used in physics or integrated science classrooms.

Throughout the unit, students explore answers to the questions posed in the introduction through presentations, discussions, readings, hands-on activities, and labs. At its conclusion, students synthesize their learning by creating consumer awareness pamphlets that explain the basics of nanoparticulate zinc oxide: how it can appear clear in sunscreens, but still protect against ultraviolet (UV) light; what its benefits are over traditional ingredients; and any potential dangers that might be associated with its use.

About nanoscience

Nanoscience is the study of matter on the scale of 1–100 nanometers (nm) in at least one dimension. Given that 10 hydrogen atoms lined up are about 1 nm long, we can loosely describe the field as being concerned with molecules and small clusters of molecules in this size range. One well-known example is Buckminsterfullerene, the soccer ball–shaped carbon (C_{60}) molecule often referred to as a "buckyball."

Nanoscience is an important emerging area of research because matter at this size scale has many unique properties. For example, nanosized carbon tubes are 100 times stronger than bulk steel but are also incredibly flexible, and nanosized substances' melting points decrease as they get smaller. Nanosized zinc oxide—a common ingredient in nanosunscreens—in particular, appears clear (transparent) instead of white. While research is ongoing, the unique properties of nanosized materials have already enabled new innovations in areas as diverse as textiles (e.g., stain-resistant clothes), the environment (e.g., paint that "cleans" the air), and personal health care (e.g., clear nanoparticulate sunscreen).

Despite their potential benefits, objects at this size scale still present many mysteries. For instance, they are small enough that many of our models for bulk substances do not accurately predict their properties, but large enough that quantum calculations are prohibitively complicated. Currently, new models and ways of thinking are being developed to better understand their behavior.

Introducing nanoscience ideas to students presents several exciting opportunities. First, it gives them the opportunity to explore applications that are relevant to their lives, which can serve as a "hook" to get them excited about science. It can also introduce an interdisciplinary perspective. Like most nanoscience topics, the science behind clear, nanoparticulate sunscreen brings together concepts from chemistry, biology, and physics, giving students a chance to see the interconnections between traditional scientific domains and the unity in nature (Roco 2003). Finally, teaching cutting-edge science in which many of the answers (and even the questions) have not yet been formulated provides the opportunity for students to experience science in the making (Latour 1987), helping them develop a better understanding of the nature of scientific knowledge.

About nanoparticulate sunscreens

Sunscreens are colloidal suspensions of UV-absorbing agents in a lotion. Two kinds of UV-absorbing agents (or "active ingredients") can be used: organic and inorganic. Organic ingredients are carbon-based, exist as individual molecules, and absorb specific, narrow bands of UV light. Inorganic ingredients are metal-oxides that exist as ionic clusters of various sizes and absorb all UV light whose wavelength is less than a critical value.

Traditional sunscreens often contain "large" inorganic zinc oxide clusters because they effectively absorb the full spectrum of UV light. However, because these clusters also scatter visible light, the cream has an undesirable white color that remains visible on the skin's surface. As a result, people often apply too little sunscreen or choose another, less effective kind (see "Structure and scattering" for more on inorganic versus organic sunscreen ingredients).

If, however, nanosized clusters of zinc oxide are used instead of the larger clusters, the sunscreen is transparent because the diameter of each nanoparticle is much smaller than the wavelength of visible light, and thus does not scatter it. The protection remains the same because reducing the particle size does not change its absorptive properties.

students' current science knowledge. In chemistry classes, this usually means asking students to share what they know about using and choosing a sunscreen, and then to examine the kinds of chemicals that are used as active ingredients in the sunscreens they have at home. The "Sunscreen Label Ingredients" activity asks students to compare the different combinations of ingredients found in sunscreens and look for patterns. We have found that students are excited to recognize some terms on the labels, and a discussion of chemical names usually ensues. This can then segue into a class discussion of consumer chemistry issues, such as why the same chemicals show up repeatedly-the reason is that a limited number are approved by the Food and Drug Administration-and raises important questions about how sunscreen ingredients protect us from UV light (e.g., "Why do most sunscreens have more than one active ingredient?" and "Why is it that sunscreen makers cannot just put in more of the 'best' ingredient?")

In biology classes, we take a slightly different approach and often begin with a discussion of what students know about the dangers of skin cancer and the need for sun protection. In a physics class, the electromagnetic spectrum and the energy of different wavelengths of UV light can serve as anchors.

Regardless of the entry point, to help students think about the different kinds of sun rays that reach Earth and how

Given our increased awareness of the dangers of long-wave ultraviolet (UVA) light-which many organic ingredients used in sunscreens do not block-a full spectrum sunscreen that people are willing to apply in sufficient quantities is an important tool for preventing skin cancer. Sunscreens that use nanosized inorganic ingredients can provide this protection. However, there are some concerns about using nanosized ingredients in sunscreens since they more easily cross membrane barriers, though no adverse effects have been found to date.

Nanosunscreens in the classroom Sun protection basics

Our Clear Sunscreen materials are designed to be modular and adaptable to a variety of classroom levels and orientations. We begin by connecting with Graph of spectrometer data collected for three sunscreens.

The diffuse reflectance from the film surface due to scattering is measured using an integrating hemisphere, an optical device that allows measurement of the total light reflected back in all directions.



Light Back-Scattered (Reflected) by Three Sunscreens

they interact with our bodies, we use the information, images, and embedded discussion questions in the interactive "Sun Protection: Understanding the Danger" PowerPoint. These slides are best used to support the development of understanding after students have participated in an activity, such as Sunscreen Label Ingredients, which cultivates a "need to know."

FIGURE 2

We have consistently found that students (at all levels) are fascinated by the issues related to protecting their bodies and invariably have a lot of questions and personal experiences to share. Interestingly, we have also found that while most students are familiar with the terms *UVA* and *UVB*, few actually understand what they refer to: that they are wavelengths of light falling within certain ranges along the continuum of the electromagnetic spectrum (UVB

Answers to	o three sunscree	n spectrometer g	graph questions.
	Sunscreen 1 (contains organic ingredients)	Sunscreen 2 (contains nanosized inorganic ingredi- ents)	Sunscreen 3 (contains traditional inorganic ingredi- ents)
Appearance	No scattering in the visible range. Sun- screen appears clear on the skin.	Very limited scat- tering in the visible range. Sunscreen appears clear on the skin.	Significant scattering in the visible range. Sunscreen appears white on the skin.
Size	Since no scattering is seen, it is not pos- sible to estimate the size of the molecule from the informa- tion in the graph.	The sharp drop in the curve at 380 nm (and the low scatter- ing below 380 nm) is actually due to UV absorption (if light is absorbed, it can- not be scattered). Therefore, we can- not know the exact size of the cluster, only that the curve would have peaked below 380 nm. So the cluster size is smaller than 190 nm.	Because the graph peaks around 450 nm, we would esti- mate the cluster size to be about 225 nm (well above nano- scale dimensions).
UV blocking	The graph shows very little scattering in the UV range; however, this does not tell us anything because absorption is the main blocking mechanism for UV. Because the UV light is not scattered, we know that it must either be absorbed or transmitted, but we do not know which. We would need an absorption or transmission graph in order to determine the UV blocking ability of the sunscreens $(T + R + A = 1)$.		
Identity	Virtually no scat- tering in the visible range indicates organic ingredients. This sunscreen con- tains the organic in- gredients octinoxate and oxybenzone.	Low amounts of scattering in the vis- ible range indicate inorganic ingredients with nanosized clus- ters. This sunscreen contains nanosized zinc oxide.	Significant amounts of scattering in the visible range indicate inorganic ingredients with large clusters size. This sunscreen contains traditional zinc dioxide.

≈ 280–320 nm, UVA ≈ 320–400). Instead, students often talk out them as singular entities t can be blocked (or not) in a ary fashion, and a surprisingly ge number mistakenly believe t they are actually two types protective ingredients that be put into sunscreens. Our roduction to the unit helps dents reveal and remedy these as; supports them in making nections between traditional mistry, physics, and biology ics; and lays the foundation understanding the chemistry nind new nanoparticulate screens.

At the end of the introductory section, we pose three essential questions to help students monitor their learning throughout the rest of the unit:

- 1. What are the most important factors to consider in choosing a sunscreen?
- 2. How do you know if a sunscreen has "nano" ingredients?
- 3. How do "nano" sunscreen ingredients differ from most other ingredients currently used in sunscreens?

We ask students to consider their initial ideas about these questions, emphasizing that this is not a test of what they know and encouraging them to make guesses that they can later reevaluate based on what they learn in the unit. Time allowing, we have students share their answers reminding them that there are no "bad" ideas at this stage—and discuss as a group which statements they think are true and the rationale or evidence supporting their assertions.

Appearance and UV blocking

In the second part of the unit, the focus is on chemical and physical properties of sunscreens and their interactions with light. The core activity is the "UV Protection Lab," which invites students to investigate whether or not there is a correlation between a sunscreen's appearance-its degree of transparency-and its UV-blocking ability. (Note: They later find that there is no relationship, since one depends on interactions with wavelengths of light in the visible range [which determines appearance] and the other depends on interactions in the UV range [which determines blocking ability]. Thus, while there are some materials that are opaque and block UV light, there are also examples of materials that appear clear, but are equally good or better blockers.) The exploration of the counterintuitive nonrelationship between opacity and UV blocking differentiates this lab from many sunscreen labs, which simply have students test the blocking ability of different substances.

In the UV Protection Lab, students select a variety of protective agents (e.g., different sunscreens; t-shirts; inexpensive, clear UV-blocking glass) to test using beads that change color when exposed to UV light. Using a color guide, students compare the color change of a bead covered by a protective agent to that of an uncovered bead. (**Note:** UV-sensitive beads and color-change guides are readily available from several commercial suppliers.) Students also evaluate the appearance of the substances using an opacity guide that we print on a sheet of transparent acetate (available online in Lesson 1 of the Clear Sunscreen unit).

Using the opacity and UV-protection ratings for each substance tested, students create a scatter plot to determine whether or not there is a relationship between protection and opacity. Assuming students select a wide enough variety of substances to test, the plot should have points in all quadrants, indicating no relationship. If some groups test a restricted range of substances, we use it as an opportunity to talk about sampling issues and then combine the whole class's results to create a more complete data set.

The main safety consideration in this lab is to remind students not to put the sunscreen on their bodies in case of an allergic reaction. Additionally, although no adverse effects attributed to nanoparticles in commercially available sunscreens have been reported, because nanoparticles are still being studied, it is better not to apply them to our bodies in situations where they are not needed.

Structure and scattering

We follow up the lab with the "All About Sunscreens" interactive PowerPoint. (**Note:** For advanced classes, there are two additional interactive PowerPoints that go into greater depth on absorption and scattering mechanisms, which are freely available on the website). The information, images, discussion questions, and activities embedded in the slides help students explore the different structure and UV-absorption patterns of organic and inorganic sunscreen ingredients.

Their understanding of the different absorption patterns can then be used to explain one of the findings from the Sunscreen Label Ingredients activity: When sunscreens use organic chemicals as UV blockers, they are always formulated with multiple active ingredients; but when they use inorganic chemicals as UV blockers, they can be formulated with just a single one. This occurs because although these inorganic compounds absorb strongly across almost the entire UVB and UVA spectrum, the organic molecules have narrow UVabsorption ranges, thus different ingredients are needed to provide full spectrum coverage.

One concept we have found that students consistently have difficulty with is the difference between molecules and ionic compounds. (**Editor's note:** For strategies to help students understand and visualize the difference between substances that exist as true molecules and those that exist as ionic crystals, see Smithenry on p. xx of this issue.) While our students were familiar with the difference between molecular formulas and formula units, when it came time to use these concepts in practice, they often confused the two. We would encourage other teachers to dedicate extra time and attention to this issue, since it relates to concepts that are fundamental to chemistry.

The second half of the All About Sunscreen slides addresses interactions with visible light, helping students understand that traditional inorganic sunscreen ingredients appear white on the skin because of the way the larger zinc oxide clusters scatter light. Students can explore the scattering mechanism in more depth through the "Sunscreens and Sunlight Animations" activity. This activity has two variations. Students can use the ChemSense Animator tool, which is freely available online (see "On the web"), to create their own animations of how visible light interacts with different kinds of sunscreen ingredients. Or, if time is limited, they can explore a premade interactive animation of visible light interacting with different kinds of sunscreen ingredients using a guiding worksheet.

The interactive All About Sunscreens PowerPoint also allows us to introduce the size-dependence of light scattering—the central principle of nanoparticulate sunscreens. Maximum scattering of light occurs for clusters whose diameter is half as large as the wavelength of the light (scatter_{MAX} of λ occurs when $d = \frac{1}{2}\lambda$) Thus, zinc oxide clusters whose diameter is less than 100 nm are too small to scatter visible light. These concepts are further explored through the interpretation of spectrometer data we have collected on three kinds of sunscreens containing organic ingredients, nanosized inorganic ingredients, and traditional inorganic ingredients, respectively (Figure 1, p. 38). We ask students to think about four questions for each sunscreen (answers provided in Figure 2, p. 39):

- 1. Will it appear white or clear on your skin?
- 2. What size (approximately) are the molecules or clusters?
- 3. Can we tell how good a UV blocker it is from this graph? Why or why not?
- 4. Which one of the sunscreens is it? How do you know?

Finally, we raise the question of the potential health risks of nanoparticulate sunscreens, including both scientific aspects (e.g., very small clusters are more likely to cross membranes and get into unintended parts of the body) and socially situated ones (e.g., as new substances, nanoparticulate sunscreen ingredients are not yet fully studied and thus possible harmful effects may still be unknown).

Pulling it all together

At the end of the unit, students solidify their understanding by creating a consumer awareness pamphlet that explains the benefits of nanoparticulate ingredients—the combination of good UVA and UVB protection with clear appearance—and potential dangers associated with their use. The required scientific information we ask for in the pamphlet and a rubric we have created for judging its completeness, depth, and accuracy allow us to use it as a performance assessment tool. We find that this task gives students a meaningful opportunity to show what they have learned, and that situating this task in the context of social awareness helps students to see science as something that is relevant to their lives.

Opportunities and challenges

The teachers we have worked with to implement the Clear Sunscreen unit have been extremely pleased with the results. In our own estimation, students seem genuinely interested and concerned about sunscreen issues. It is apparent that the issues hit home in that students ask real-life questions (e.g., "How am I going to get something that protects me?") and quickly realize that there is a lot they do not know.

Despite high levels of student enthusiasm, we encountered several challenges in teaching the unit. One set of challenges relates to the specific content involved, and we have consistently found these issues—such as the definitions of UVA and UVB as wavelength ranges along the electromagnetic spectrum and the distinction between molecules and ionic compounds—across all grade levels.

The other set of challenges we have encountered is pedagogical in nature. Nanoscience is on the cutting edge of interdisciplinary scientific research and is expanding the limits of our collective scientific knowledge. Existing models do not always apply, and there are still many unanswered questions. This provides an exciting opportunity to help students experience science in the making, but also requires us to firmly embrace an inquiry approach to science learning. In support, we have created a guide to help other teachers use these challenges as opportunities to model the scientific process (see "On the web").

Conclusion

The high levels of student interest and engagement we observe with the Clear Sunscreen unit leads us to believe that teaching the science behind nanoscience can be a useful hook to get students excited about learning chemistry. While challenges exist, addressing them provides opportunities to reinforce core chemistry concepts and help students gain a deeper understanding of the nature of science.

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On the web

Nanoscience Project materials: http://nanosense.org/activities.html Alignment with National Science Education Standards: www.nsta. org/highschool/connections.aspx

ChemSense tool: www.chemsense.org

Premade interactive animation: http://nanosense.org/activities/clearsun screen/sunscreenanimation.html

Teacher guide to challenges and opportunities: www.nsta.org/high school/connections.aspx

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