### NanoLeap Chemistry Module Nanoscale Materials and Their Properties Teacher Resource Guide

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### NanoLeap Chemistry Module Nanoscale Materials and Their Properties

### **Preface and Overview**

#### Overview

The NanoLeap Chemistry Module is designed to be a three-week *culminating unit* in a high school chemistry course. The module asks students to *apply* concepts and skills learned throughout the year in a traditional curriculum and can serve as an *extension* of those concepts that are of particular relevance in nanoscale science.

Nanoscience and nanotechnology are rapidly expanding fields of science and many of the techniques and scientific concepts involved in the research and development of applications and products require a graduate level background in chemistry, physics, materials science, and technology. Therefore, a deliberate decision was made to include in these NanoLeap materials only those properties and changes in physical and chemical properties observed at the nanoscale that can be explained in terms understood by most first-year secondary chemistry students.

The essential question that students will consider throughout the module is, "How and why do the chemical and physical properties of nanosamples differ from those of macrosamples of the same substance?"

#### Lessons and Timelines:

There are three units in this module in addition to the Poster Assessment. The units are divided into several lessons. Please see the *Student Handbook-Teacher Version* for instructional guidance.

In addition, there is a pre- and post-assessment and a Poster Assessment to complete during the course of the module. A suggested timeline follows:

Estimated Time	Module Component(s):	
45 minutes	Pre-Assessment	
270 minutes	Unit 1: Nanoscience: What is it?	
	Lessons 1.1, 1.2, and 1.3	
55 minutes*	Poster Assessment introduction	
330 minutes	Unit 2: <i>Metallic and Ionic Nanoparticles: Extendable Structures</i>	
	PowerPoint Lessons 2.1, 2.2, and 2.3	
150 minutes	Unit 3: Neat and Discrete Nanoparticles	
	PowerPoint Lessons 3.1 and 3.2	
165 minutes *	Poster Assessment student preparation, research, and peer reviews of	
	drafts	
55 minutes	Poster Assessment Fair	
45 minutes	Post-assessment	

#### Table 1: Module Scope and Sequence

\*You may need to plan additional in-class time for students to choose a topic, research their topic, plan the poster layout with their group, and for peer reviews of drafts and layouts. See Poster Assessment instructions in the Student Handbook-Teacher Version for more information.

The authors propose several unit sequences:

- Unit 1 as a stand alone
- Unit 1–2 only
- Unit 1–3 only
- Units 1, 2, and 3 (complete module)

### **Overview of Instructional Materials**

### **Teacher PowerPoints and Scripts**

The Teacher PowerPoints and Scripts contain background information, suggested procedures, instructional strategies, annotated student handbook, glossary, and appendices. The Teacher Script is formatted in a landscape view and allows the teacher to correlate the PowerPoint slide, corresponding instructional materials, student handbook, and preview upcoming instruction. Each lesson contains the student objectives, a preview of highlights-"at a glance for the teacher," estimated teaching time, materials for activities, demonstrations, and Web site URL addresses. Additionally "Making Connections" questions are provided at the end of each lesson for formative assessment and to foreshadow the upcoming lesson. The "Module Lesson Flow Chart" is provided to let the student review each lesson's essential question. The text of the script is structured such that background information and pedagogy are in *italics* and the suggested teacher script is in **bold**.

The PowerPoint format for each lesson is accompanied with a scripted text that incorporates a teacher directed discussion technique. The questions in the script and <u>possible</u> student answers aid the teacher in facilitating discussion. This is a rather unique application of PowerPoint slides as they are typically used for lecture-type presentations.

Before using this classroom technique, review the guidelines for successful use of Questioning and Whiteboarding as outlined in the Instructional Strategies section. Study the questions in the script carefully to determine whether or not the terminology used is different from that used in your chemistry curriculum and to decide whether or not it will be necessary for you to include additional background material into the script to incorporate or extend your students' classroom experience before posing a particular question. One of the overall goals of the NanoLeap materials is to help high school <u>students</u> learn how their chemistry background applies to the nanoscience world.

The questions themselves have been carefully worded so that they provide students the opportunity to apply their previous chemistry experiences in their answers. Remember, it requires some thought time to formulate meaningful answers to application and synthesis questions, so incorporate enough "wait time" (a minimum of three to five seconds) for this to occur.

The script that accompanies this PowerPoint component is formatted for ease of use. Here is an example:

<u>Slide #</u> Student Journal Page #	<u>Teacher Background Information and Pedagogy</u> <b>Teacher Script</b>
Slide 1 Instructional Strategies: Page 3	<ol> <li>Have students complete the first column of the K-W-L chart for the question, What is Nanoscience? before they watch the video. Then, following the video:</li> <li>You have just watched a video on Nanoscience and Nanotechnology, so let's explore this new field of science further by searching for answers to some questions about it. We have been considering what you know about nanoscience. On the basis of what you saw in NanoSize Me, how would <u>YOU</u> define nanoscience?</li> <li>{Click}</li> <li>Have students revise their notes on the first column and complete the second column</li> </ol>

### Table 2: Sample Teacher Guide

	after they watch the video. Follow instructions found on Teacher Background page 3 of the Instructional Strategies section of the Teacher Handbook.
	Accept student answers, which may include: it is the <u>relatively new field of science</u> that deals with <u>very small particles</u> or the <u>different properties</u> that common chemicals have at the nanoscale level or <u>possible future uses</u> .
	Pilot students said," small, tiny, really small, too small to see." They only mentioned examples from the video.
Slide 2 Fact Sheet 1 – SI Units	3) Have students refer to the Common SI Prefixes table found in the Student Handbook on page 4.
Student Handbook- Teacher	Nanoscience starts with the same prefix as nanometer. 1. What is a nanometer? How large is a nanometer?
Version: Page 5	one billionth of a meter or $10^{-9}$ meter
Student Handbook: Page 3	

### Student Handbook-Teacher Version

The Student Handbook-Teacher Version, is the annotated teacher version with the answer key for the Student Handbook. The teacher version contains exactly the same pages found in the student version and the teacher version of these pages with suggested answers.

### Nanoscale Materials and Their Properties Objectives, Essential Understandings, and Standards Addressed

This module builds upon the big ideas in a general chemistry course. Assessing students on those topics is necessary scaffolding in order to assess them for understanding nanoscience topics.

### Table 3: Big Ideas and Essential Understandings

### **Big Idea/Essential Understanding**

### **EU1: Measurement and Size**

Nanoscience is the study of the fundamental principles of molecules and structures having at least one dimension lying roughly between 1 and 100 nanometers.

### **EU2: Interdisciplinary Nature**

Nanoscience includes the scientific concepts involved in biology, chemistry, and physics

### **EU3: Properties of Matter**

Objects have physical and chemical properties. At the nanoscale level, a large fraction of an object's atoms, ions, or molecules are exposed at its surface; therefore, the object's physical and chemical properties are dominated by surface interactions.

### **EU4: Scientific Instruments**

Scientific instruments can be used to characterize properties of objects, their structure and surfaces, even if the objects cannot be seen.

### **EU5: Applications/ Public Policy**

A sound understanding of nanoscience is required to develop applications of nanotechnology and to inform public policy

Cable 4: Module Objectives a           NSES Content Standards	Big Idea/Essential	Lesson 1/ Objective
Addressed	Understanding	
Physical Science	EU1: Measurement and Size	1. Define nanoscience as the study of the
Structure of Atoms	Nanoscience is the study of the	fundamental principles of structures
Matter is made of minute	fundamental principles of	having at least one dimension lying
particles called atoms, and	molecules and structures having	roughly between 1 and 100 nanometers.
atoms are composed of even	at least one dimension lying	a) Compare and contrast the size
smaller components. These	roughly between 1 and 100	of atoms, ions, and molecules
components have measurable	nanometers.	to the size of nanoparticles.
properties, such as mass and		b) Identify structures that are
electrical charge.		appropriately measured in
8		nanometers.
		c) Compare and contrast
		nanoparticle samples to atomic
		and macro-level samples in
		terms of the particle size,
		number of atoms, and
		operational model.
Science in Personal and	EU5: Applications/ Public	2. Explain the importance of nanoscience
Social Perspectives	Policy	research and technology.
Science and Technology in	A sound understanding of	3. Evaluate the ethical considerations
Local, National, and Global	nanoscience is required to	associated with nanoscience research
Challenges	develop applications of	and nanotechnology.
8	nanotechnology and to inform	and hanoteenhology.
Individuals and society must	public policy.	
decide on proposals involving	I T T T T T T T T T T T T T T T T T T T	
new research and the		
introduction of new		
technologies into society.		
Science and Technology	EU2: Interdisciplinary	4. Recognize the interdisciplinary nature of
Understandings about	Nature	nanoscience.
Science and Technology	Nanoscience includes the	
Scientists in different	scientific concepts involved in	
disciplines ask different	biology, chemistry, and	
questions, and use different	physics.	
methods of investigation.		
Science as Inquiry	<b>EU4: Scientific Instruments</b>	5. Identify the requirements of nanoscience
Understandings about	Scientific instruments can be	and nanotechnology, including:
Scientific Inquiry	used to characterize properties	a) new production methods,
Scientists rely on technology to	of objects, their structure, and	······································
enhance the gathering and	surfaces, even if the objects	b) now moosurement instruction
manipulation of data.	cannot be seen.	b) new measurement instruments,
		and
		c) a cleanroom environment for
		nanoscale research and
		technology.

### Table 4: Module Objectives and Alignment to Standards

NSES Content Standards Addressed	Big Idea/Essential Understanding	Lesson 2/ Objective	
Physical Science Structure of Atoms Matter is made of minute	<b>EU3: Properties of Matter</b> At the nanoscale level, a large fraction of an object's atoms,	Define ext	endable solids.
particles called atoms, and atoms are composed of even smaller components.	ions, or molecules are exposed at its surface; therefore, the object's		dentify elements and compounds at form extendable structures.
These components have measurable properties, such as mass and electrical charge.	physical and chemical properties are dominated by surface interactions.		ompare and contrast extendable olids.
Physical Science Structure and Properties of Matter	<b>EU3: Properties of Matter</b> At the nanoscale level, a large fraction of an object's atoms, ions, or molecules are	nanostruct	that an extendable ure's physical and chemical are dominated by surface us.
Atoms interact with one another by transferring or sharing electrons that are furthest from the nucleus. These outer electrons govern the chemical properties of the	exposed at its surface; therefore, the object's physical and chemical properties are dominated by surface interactions.	sa na su ir	elate the size and properties of a ample (both macro-samples and ano-samples) to the ratio of urface particles to interior particles a the sample.
element. Bonds between atoms are		b) D	Define surface energy.
created when electrons are paired up by being transferred or shared. A substance composed of a single kind of atom is called an element.		aı el b m	Compare and contrast the physical nd chemical properties of metallic lements and ionic compounds at oth the macro and nano scale (i.e., nelting point, electrical
The atoms may be bonded together into molecules or crystalline solids. A compound is formed when two or more kinds of atoms bind together chemically.			onductivity, color, reactivity, atalysis, adsorption).
Science in Personal and Social Perspectives Science and Technology in Local, National, and Global Challenges Individuals and society must decide on proposals involving new research and the	EU5: Applications/ Public Policy A sound understanding of nanoscience is required to develop applications of nanotechnology and to inform public policy		he implications of nanoscale nd technology.
introduction of new technologies into society.			

NSES Content Standards	Big Idea/Essential	Lesson 3/ Objective
Addressed Physical Science Structure and Properties of Matter The physical properties of	Understanding EU3: Properties of Matter At the nanoscale level, a large fraction of an object's atoms, ions, or molecules are exposed	9. Identify elements that can form discrete nanoparticles.
compounds reflect the nature of the interactions among its molecules. These interactions are determined by the structure of the molecule, including the constituent atoms and the distances and angles between them.	at its surface; therefore, the object's physical and chemical properties are dominated by surface interactions.	a) Recognize that discrete nanoparticles are a result of covalent bonding patterns.
Physical Science Structure and Properties of Matter Carbon atoms can bond to one another in chains, rings, and branching networks to form a variety of structures, including synthetic polymers, oils, and the large molecules essential to life.	<b>EU3: Properties of Matter</b> At the nanoscale level, a large fraction of an object's atoms, ions, or molecules are exposed at its surface; therefore, the object's physical and chemical properties are dominated by surface interactions.	<ul> <li>10. Compare and contrast the properties of several allotropes of carbon (i.e., graphite, diamond, fullerenes).</li> <li>a) Analyze the covalent bonding patterns of carbon and the resulting three dimensional shapes of molecules and carbon allotropes.</li> <li>b) Relate the bonding and structure of carbon nanoparticles to their properties (i.e., corannulene, buckyballs, fullerenes, nanotubes).</li> </ul>
Science in Personal and Social Perspectives Science and Technology in Local, National, and Global Challenges Individuals and society must	EU5: Applications/ Public Policy A sound understanding of nanoscience is required to develop applications of nanotechnology and to inform public policy.	<ul> <li>11. Explore the potential applications of carbon nanoparticles and nanotechnology.</li> <li>a) Define nanotechnology as the use of discrete nanoparticles to produce useful products and materials.</li> </ul>
decide on proposals involving new research and the introduction of new technologies into society.		<ul> <li>b) Compare and contrast endohedral (cage) and exohedral fullerene compounds and their applications.</li> <li>c) Describe the properties and potential uses of carbon nanotubes.</li> </ul>

### **Instructional Strategy: K-W-L**

Helping students to construct meaning can also be facilitated with a strategy called K-W-L, which was developed by educator/researcher Donna Ogle<sup>1</sup>. You will lead a K-W-L activity as the students view *NanoSize Me*, the video introduction for lesson 1.1. This will allow you to determine what students already know about nanoscience, find out what they would like to know, and serve as a tool to track their learning as it develops.

Before class, prepare a poster paper, black board, or whiteboard of the K-W-L chart on the following page. K-W-L makes a good bulletin board for students to refer to as they study the module.

The first step in the K-W-L strategy is to ask students what they already know (K) about the topic of the lesson. As students give their ideas (whether right or wrong), write them in the first column of a K-W-L chart.

The second step is to ask students what they want (W) to know about the topic. Write their responses in the second column.

The third step is to present the information, and provide the learning experiences in the module. It is important to remind students to keep in mind what was recorded in the *K* and *W* columns.

Finally, after you have presented the information to students, ask students what they learned (L). As you record their responses, draw arrows to make explicit connections to items listed under K and W. Some of what students learned may validate or correct information listed under K or answer questions under W. This can be done at the end of a class session or at the end of a PowerPoint presentation so students can track their learning.

There are some additional things you can do to make this strategy work for your students:

Under K (what I  $\underline{k}$ now) it is sometimes helpful to ask, "What do you *think* you know?" Then it's okay if students find out later that they were wrong.

Under W (what I want to know) a related question might be, "What do I think I'm going to find out?"

Some teachers add another W (what I want to know *now*) to reinforce the idea that learning is ongoing; it does not stop at the end of the lesson.

Teachers who have used the K-W-L strategy report that they see evidence of students constructing meaning when they use this strategy. For example, during pilot test observations of a K-W-L review, it was noted that students were eager to share examples of what they learned from the *NanoSize Me* video (*small, tiny, really small, too small to see*) and were also able to relate subsequent lesson content to their poster research. However, there are also some predictable glitches: When students are asked, "What do you want to know?" they sometimes reply, "Nothing" or "I don't know enough to know what I want to know," or "so what?" Some students in the pilot test were curious about possible medical applications while others were interested in learning more about how nanoscale science could be a solution to problems (e.g., environmental). Some students in the pilot test were interested in career fields and educational requirements for this field. K-W-L helps students focus on the learning and helps teachers as a formative assessment of student learning and to bring closure to the learning experiences.

<sup>&</sup>lt;sup>1</sup> Ogle., D. (1986, February). The K-W-L: A teaching model that develops active reading of expository text. *The Reading Teacher*, *39*, 564-570.

# K-W-L

What I KNOW	What I <u>WANT</u> to Know	What I <u>LEARNED</u>

### Instructional Strategy: Guidelines for Using Open-Ended Questioning Techniques

How many of the questions you see in the PowerPoint scripts could be answered with a "yes" or a "no"? Not many? Not any? Well, that was by design. Good questioning technique is an essential feature of science classroom instruction. And, you will find that the possible answers to many of these questions result in more questions to be answered. Let us examine some guidelines for developing and using quality, open-ended questions to use with your students.

### We chose the wording for the questions carefully.

It is easy to write questions that can be answered with one or two words or with recall of facts. You will see that a few of these questions have wording

something like:

- What is the definition of \_\_\_\_?
- How is \_\_\_\_ classified?
- When did this occur?

Teacher understanding of this technique is critical to the use of the PowerPoint as a learning experience.

Open-ended questions are more difficult to write without giving away the answers. They usually begin with wording similar to:

- What would you need to know in order to \_\_\_\_?
- What did you find the characteristics of \_\_\_\_\_ to be?
- How would you compare \_\_\_\_?
- How might these observations be different from \_\_\_\_?
- How is this similar to or different from \_\_\_\_?
- In what ways do you agree or disagree with \_\_\_\_?

The wording of a good question is very important. You may choose to edit those given to better reflect the background of your students, but we encourage you to keep the "flavor" and "intent" of the questions. If you choose to use the script as is, <u>print a copy</u> of it so you will be free to concentrate on the student answers and their non-verbal communication.

### Guideline #1

### Wait....wait.... for answers.

Are you uncomfortable with silence in the classroom after you ask a question? Well, learn to take deep breaths and count slowly...to 100...or farther if you have to, but <u>wait silently</u> until the answers start coming. You may want to explain that you are waiting for answers to give students time to think more deeply about an answer so that their answers are more thoughtful and include more analysis of information.

When you are asking for the answers to recall questions, you may want immediate answers. However, when you ask your students higher-level open-ended questions, remember that it takes time for them to think through and formulate the answer to these questions. Often the first answers you get will be rather simplistic. Accept them with a neutral response, such as, "That is one possible answer. Who has another one?" and <u>wait</u> for others that will probably be better.

Use this waiting technique <u>the first time</u> you ask an open-ended question. This sets the precedent for your students. If you, yourself, answer the question prematurely, they will assume that you will give them the answers to all your questions...if they just wait you out.

### Guideline #2

### When repeating the question, use the same wording.

One result of waiting for an answer is that you make students uncomfortable. They are accustomed to teachers *wanting* students to have the answers. Too often, if students don't volunteer answers, the teacher will give them a clue, often by wording the question differently. You may get questions like, "What was the question?" or "Do you mean...?" Students are experts at wording questions so that they sound like they are asking for clarification when they are really asking for the answer.

This is another reason that it is helpful to have a copy of the script. You can read the question to them again...using exactly the same wording the second time. And, <u>wait</u> again.

### Guideline #3

### Acknowledge answers with "neutral" responses.

Accept all answers with a response that is verbally and non-verbally "neutral." If you indicate enthusiastic acceptance of one answer or a negative response to another, even by so much as a non-verbal frown, you will probably discourage other students' responses. In the first case, students will think you "got your answer" so they relax. A negative response, however, often makes students hesitant to risk the rejection of their answers. This takes a lot of practice, so do not be discouraged if you do not accomplish this technique immediately.

In some places in the PowerPoint presentation, you are instructed to paraphrase the answers on the chalkboard, the overhead projector, or on newsprint. This is one way of accepting all student answers impartially, even those that "come from left field." You may want to ask the student if the paraphrase says what he/she meant by the answer.

### Guideline #4

### Listen carefully to the response.

Listening carefully to student responses can "pay off" in many ways. Using a student response as the basis for further class discussion not only gives credibility to the student's answer, but also tells students that you really are listening and their answers are important.

### Use responses as the basis for new questions.

You may wish to couch your questions resulting from student responses in terms such as, "If I understand your answer correctly, how does that relate to, compare with, or explain...?" Another approach may be something like this, "Does your answer take into consideration...?" Again the student will probably need some time to think about his/her answer. In the event that the student successfully defends the answer, your positive response is appropriate. This tells your students that you value the depth to which the student has thought through the answer.

### Listen for misconceptions.

You seldom know what misconceptions students have until you ask. However, once you have heard them, you must deal with them carefully. The best responses to an answer that contains misconceptions are those that give a clue as to the reason for the confusion, such as, "Why do you think so?" or "What did you read or hear that gave you that idea?" This technique requires not only lots of practice but also the ability to multitask. You need to evaluate the level of the student's understanding, to prepare a response to the student, and be planning a next question if the conception is correct.

What if you are not sure how to correct the student's thinking "on the spot"? You may want to say something like, "Let's investigate this idea further," and then <u>do it</u>! Determine the resources from the module (e.g., images, glossary, teacher background) that might be emphasized in order to clear up this

misconception. Again, you will need to do this with a positive attitude so that you are not "putting this student down" but helping to correct his/her thinking. Do not ignore the student's misconception, if you do, it will remain.

### Guideline #5

### Responding to questions with questions.

When responding to students' questions, think of questions to use to help them answer their own questions. For example, if a student asks,

- "Is this the right answer?" you might ask, "Does your answer meet all the criteria required?" or "Why do think it might be the right answer?"
- "How do I do this?" you might ask, "What have you used in the past to solve problems similar to this?" or "What result do you want to achieve?" or "What procedure have you already tried?" These kinds of questions are especially appropriate as students are carrying out the modeling and graphing activities in this unit.

This kind of questioning approach takes more time than just giving the answer. It certainly takes more effort and patience on your part, but it helps the students become more productive problem-solvers. It makes them think in terms of the problem-solving process, rather in terms of just "getting the right answer."

### Guideline #6

### Keep practicing.

Most of us ask lots of questions as children, but they are usually a simple "what?" and "why?" variety. Becoming a good questioner in the classroom takes practice. And practicing requires you to think carefully about the kinds of responses you want to evoke as you phrase your questions.

### **Resources for further study:**

### **Effective Questioning Techniques**

- Hyman, Ronald T. (1987). Discussion Strategies and Tactics: Questions, Questioning, Techniques and Effective Teacher, 135–151, Wilen, William W., ed. Retrieved February 18, 2008, from http://eric.ed.gov/EnRICDocs/data/ericdocs2sql/content\_storage\_01/0000019b/80/1f/4d/ce.pdf
- Wilen. (1986). Effective Techniques of Questioning. Retrieved February 17, 2008, from http://honolulu.hawaii.edu/intranet/committees/FacDevCom/guidebk/teachtip/effquest.htm

### Using Questions in the Classroom

Marzano, R. J., Pickering, D. J., Pollock, J. E. (2001). Cues, Questions, and Advance Organizers. In *Classroom Instruction that Works: Research-Based Strategies for Increasing Student Achievement* (112–117). Alexandria, VA: Association for Supervision and Curriculum Development.

### **Instructional Strategy: Whiteboarding**

Whiteboarding is a teaching strategy that actively engages students in making sense of the science content that they are learning. As students develop an ever increasing understanding of science concepts, whiteboards can serve as a formative assessment. The process is directed by the teacher and probes student preconceptions and helps students construct alternative and more complete understandings. Students use whiteboards to report the results of experimental work or propose a group solution to a problem.

The typical whiteboard is a 32" x 24" piece of white tile board that can be written on with dry erase markers and erased with a paper towel, cloth rag, or whiteboard eraser. One can make six whiteboards from a 4' x 8' sheet of white tile board which can be purchased at a lumber company for \$12 to \$15 each. Some versions of ready made whiteboards can be purchased at discount stores or through school supply catalogues.

In a lab investigation, a lab group would use a whiteboard to illustrate the results of the lab using diagrams, graphs, and mathematical models. The students then present this information to the rest of the

class using the whiteboard to justify their conclusions. Other lab groups can then collaborate or refute the results presented by describing the results of their own lab work.

Students may be asked to show the solution to a problem on a whiteboard. In small groups, students discuss the problem and reach consensus on how the problem is solved. All students in the group are expected to be able to defend the solution, while only one member of the group is selected to present the solution to the rest of the class. The remaining students in the class listen to the presentation and are asked to compare the proposed solution to their own, and ask clarifying questions about the presented solution.



The following tips on using whiteboards are from a PowerPoint presentation by Dan MacIsaac, Department of Physics, SUNY Buffalo State College.

### Why should I use whiteboards?

### Whiteboards:

- Provide a concrete venue to ground student discussion of experiments and problems
- Foster student dialog by providing venue, expectations, and opportunity as regular classroom practice
- Foster alternative representations of problems by sketches, graphs, system maps, motion diagrams, pie charts, equations, etc.
- Greatly increase student dialog; use class time for students to discuss ideas rather than have them presented and to think math and science rather than watch it done
- Engage students in a collaborative learning community
- Practice step-by-step problem solving strategies; to present, explore, critique, and check one another's work during this process
- Promote strongly coherent conceptual understanding while decreasing traditional lecture
- Use collaborative learning opportunities for students to teach one another, practice using the language of the science with one another, and develop personal meaning

- Recognize and elicit student prior knowledge and preconceptions, having students articulate and then explicitly challenging their existing conceptual knowledge structures (and fostering recognition that these structures are being challenged)
- Place exploration before formal presentation
- Engage students in divergent, student-directed discourse with one another and with instructors
- Encourage student conjectures, alternate solution strategies and evidence interpretations

### How can teachers guide Whiteboarding groups as they work? (Socratic interaction)

- Watch group composition (groups of three; mix ability levels; no fewer than two girls); Assign rotating roles (such as manager, scribe, critic); Monitor frustration level (thinking is hard work, but anger impedes learning)
- Invoke advanced student thought by using language to better articulate the problem
  - Tell me what you are doing now.
  - Tell me what have you done so far.
  - Why are we doing it this way?
- Read back student responses without providing an answer, having students confirm, enrich, or paraphrase teacher restatement
  - So you say... Is this correct?
  - *How does this relate to the underlying science (mathematics)?*
  - Where should we go from here?
- Groups will often answer their own questions as they go through the above interaction
- Refer one group to another group that has solved the problem
- Confirm ideas or conjectures from students that have been moving along fruitful paths, with lots of praise for students who have the right idea (e.g., *Listen to Julie. Say that again, Julie.*)
- When dialog changes direction in any group it is time to move on, the teacher should keep dialogue flowing and productive. It is appropriate for students to leave class not knowing the answer yet; lesson closure should focus the days activity without short circuiting the student's thought process.
- Saying the right answer is never enough. Explaining the process completes the answer (e.g., *Why is the accepted answer preferable?*).

### How do I grade Whiteboards?

- Coarse scaled group grade (0 5 pts) for quality of board, clarity of presentation, responses to questions; no grade should be given for being right or wrong at this point
- Bonus points for good questions from students
- Small group grade based on percentage; larger individual grade for content understanding on a formal test or exam for student correctness given later
- Extensive discussions of grading rubrics for whiteboards in a high school physics and chemistry class can be found at <a href="http://modeling.la.asu.edu/">http://modeling.la.asu.edu/</a>

### What are the issues arising from Whiteboard use?

- Highly constructivist, national standards (inquiry) driven activity (See National Science Education Standard, on Science as Inquiry)
- Less material is 'covered' in greater depth; greater retention and less review results. Teachers must know the district and state standards, and work them into the activity agenda.
- Students practice valuable critical thinking, collaborative interaction, and presentation skills that are sought by employers, medical colleges, etc. Teacher and students work together to improve understandings, the teacher is not necessarily a subject expert.

- Teachers must have courage to allow students to realize they must ultimately be accountable for their own learning, and let them do so. Whiteboarding classes are nontraditional, inquiry-oriented classes that de-emphasize didactic lecture, fact memorization, and closure; they emphasize student-student and student-teacher discourse and student initiative.
- Some students will resist inquiry teaching; it is easier to memorize and regurgitate facts or plugand-chug formulas than to understand. Thinking is hard work, anticipate some student reaction, and foster student reflection on their own learning to explicitly recognize growth in their reasoning ability.

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### Nanoscience: What Is It?

### **Unit One Background Information**

The introductory video *NanoSize Me* and the three lessons that comprise Unit One are the central components of the NanoLeap: *NanoScale Materials and Their Properties* module. To introduce this module, play the *NanoSize Me* video as part of **Lesson 1.1**, *What is Nanoscience*? This video highlights some current and anticipated applications of nanoscale science and engages students in exploring the counterintuitive properties of some specific nanoparticles. The video can be played from the Web site http://www.mcrel.org/nanoleap/multimedia/index.asp

In this first lesson, students will review measurement unit prefixes to define the relationship between milli, The *NanoSize Me* introductory video highlights some of these counterintuitive properties, including:

- graphite in pencils is brittle and layers rub off, but carbon nanotubes are flexible and have high tensile strength;
- bulk gold and silver are lustrous, malleable, conductors but nanoparticles of these metals transmit red and yellow light in stained glass;
- magnesium oxide is a stable antacid at macrolevel but is a very active neutralizer of acids and other chemicals in nanoparticle size.

micro, and nano prefixes. Then they consider how the size and number of atoms, ions, or molecules in nanoscale samples relate to the interpretation of chemical equations—both at the atomic level and to macroscale samples that they have worked with in their chemistry course. Following that, they are guided to an understanding that nano-sized particles operate under a unique model – one that is neither quantum mechanics nor classical physics.

The <u>size</u> of nanoparticles is a significant, <u>underlying factor</u> in the different chemical and physical properties that some nanoparticles exhibit as described in lesson 1.2. These properties are <u>important</u> because of their <u>cutting-edge applications</u> in the areas of structural materials, environmental cleanup, medical diagnosis and treatment, as well as in optical and electronic materials. Students investigate one of these applications in detail in the poster assessment.

<u>Challenges</u> of nanoscale science and technology are introduced to students in lesson 1.3. The necessity for new synthesis techniques and new instrumentation essential for production and characterization of nanoscale materials and for a cleanroom environment in which to implement this work are presented in lesson 1.3 and the poster assessment. Just when we thought that the periodic table could help us predict the properties of many, if not all, materials, nanoscience presents us with tiny samples of the same substances having very different chemical and physical properties.

<u>Ethical problems</u> associated with nanoscience research and development are considered on the basis of some actual ethical problems that have accompanied past scientific research.

#### Nanoscience Terminology

Introducing some new terminology related to nanoscience presents an opportunity to show students that there are close relationships between some nanoscience terminology and types of solid structures that are part of a first-year chemistry course. Refer to the student handbook for terminology and definitions. If you have been using concept mapping in your course, you could have students use this instructional strategy to classify the terminology into two major headings— Nanotechnology and Nanostructures. They could further divide Nanotechnology into three categories: products, production techniques, and instrumentation.

### Quantum Chemistry and Newtonian Classical Physics

In **Lesson 1.2**, *What makes nanoscience so different?*, we ask students to recall descriptions of an electron's dual wave-matter properties in an atom and to compare and contrast its motion with that of an Earth's satellite, illustrating the regimes of Quantum Chemistry and Classical Laws of Physics (Newtonian), respectively. We then introduce students to a new realm of matter, that of man-made particles whose size is larger than that of the atoms and molecules that make up the world of chemistry, but smaller than the bulk samples of matter that obey the laws of classical physics.

In this new regime, which has not yet been given a name, the size of the particles ranges between 1 and 100 nm in at least one dimension. Chemical and physical properties of these particles, including color, melting points, and chemical reactivity as well as mechanical, electronic, magnetic, and optical properties change with the size and shape of the particles. These counterintuitive properties form the basis for a whole new realm of research and technology.

For additional information regarding electron properties and Newton's Laws of Motion, see: <u>http://en.wikipedia.org/wiki/Atom</u> <u>http://en.wikipedia.org/wiki/Newton%27s\_Laws\_of\_Motion</u>

### Instrumentation

In **Lesson 1.3**, *What makes nanoscience so important?*, the quotes from Professor David Goldhaber-Gordon, Stanford University Physics Department, summarize the challenge of developing instrumentation to further the research and development of nanoscience applications. "We need new instruments in order to be able to advance new technology. We're trying to find new ways to probe small structures...[to] either increase resolution, increase sensitivity or [to find] entirely new ways of probing."

The development of new instrumentation is taking place in university, government, and private research laboratories. This instrumentation, which requires a new set of <u>standards</u> for higher resolution measurements of length, time, force, mass, and chemical composition, is essential to realizing the promises of nanotechnology. Scanning-Probe Instruments are tools for both measuring and preparing nanostructures on surfaces.

The advantages of scanning techniques include:

- the resolution is limited only by the size of probe-sample interaction volume, which can be as small as a few picometers, and
- o interaction can be used to modify the sample to create small structures.

The main disadvantages are the slowness of acquiring images and the small image sizes.

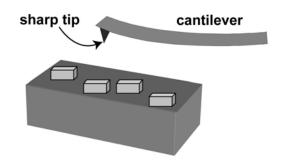
Some technologies are presently used for both analysis and synthesis of nanostructures. These instruments include the various scanning probes, such as the Atomic Force Microscope (AFM), and near-field microscopes (NFM), electron beam (SEM, TEM), ion beam, optical (laser) tweezers, X-ray spectroscopy, and nuclear magnetic resonance (NMR) instruments.

### Imaging and Measurement Tools that Enable

Our unaided eyes can only see objects that are greater than 20 microns (micrometers) in size. To give you some idea of how small that is, consider that a human hair is about 60 microns in diameter. Light microscopes, which are used in many biology laboratories, allow us to see objects that are as small as 1 micron. This includes objects the size of red and white blood cells. In both cases our eyes are actually "seeing" **light** being reflected off the surfaces of the objects. Scanning-Probe instruments use the **interactions between a scanning-tip structure and the nanostructure on the surface**.

The following is a listing of some instrumentation used in analyzing and/or synthesizing nanostructures. As you research specific nanotechnology applications, you may read about other types of newly-developed instruments that are not included.

Atomic-Force Microscope (AFM) – A scanning-probe instrument that maps a non-conducting surface topography by measuring the force (and hence the deflection) acting on a tip, as shown in the graphic below.



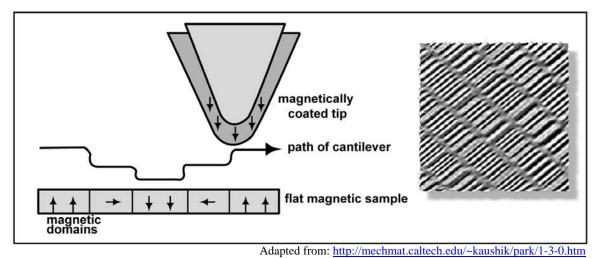
### Figure 1: Atomic Force Microscope

A 3-D image map of the surface is obtained on the atomic (sub-nanometer) scale. An AFM can also be used for the manipulation of matter at the nanoscale. See "A NanoLeap into the Atomic Force Microscope" video located at: <u>http://www.mcrel.org/nanoleap/multimedia/</u> for more about how the AFM is used to image surfaces.

**Differential Scanning Calorimetry (DSC)** – A method used to measure the magnitude of the exo- and endothermic changes that are part of nanoparticle formation.

**High-resolution Transmission Electron Microscopy (HRTEM)** – A technique that images nanoparticle sizes and shapes by passing a high-voltage (100-500 kV) electron beam through a very thin sample. The images formed are of those areas in the sample that do not allow electrons to pass. A resolution in the 0.1 nm range is possible.

**Magnetic Force Microscope (MFM)** – A scanning probe microscope that can map the spatial distribution of magnetism in a nanostructure by measuring the magnetic interaction between a sample and the tip of a scanning probe as shown on the left below. These measurements are then converted into an image similar to that on the right below.



### **Figure 2: Magnetic Force Microscope**

**Scanning Electron Microscope (SEMs)** – SEMs use a focused electron beam to scan a sample surface and cause surface electrons to be emitted. The electrons are collected and used to form an image of objects with resolutions down to nanometer scale. SEM images of objects as small as 1 nanometer have a three-dimensional quality and are used for studying the surface structure of the sample.

**Scanning Tunneling Microscope (STM)** – STMs obtain images of conductive surfaces, like metal surfaces at the atomic scale. Insulators cannot be scanned with STM. The 3-D profile of these surfaces can be used to determine roughness, defects, size, and conformation of molecules. STMs can also be used to alter the observed material by manipulating individual atoms, triggering chemical reactions, and creating ions by removing individual electrons from atoms and replacing the electrons to form new atoms.

**Z-Contrast Tomography** – A non-destructive analytical technique that uses a scanning transmission electron microscope (STEM) with a 0.8 nm diameter electron beam to create 3-D images. It is used to examine crystal shape, size, and faceting of crystals smaller than 100 nm.

#### \_\_\_\_\_

### Ethics

Unit one concludes with a consideration of the ethical problems associated with all types of scientific research and the applications of it. The questions posed relate to the possible economical, political, and social effects of nanoparticle products on a community, national, and international level.

The following are quotes that you may wish to introduce or summarize your discussion of ethics. "[Ethical] integrity without [technical] knowledge is weak and useless, and [technical] knowledge without [ethical] integrity is dangerous and dreadful." Adapted from Samuel Johnson

"Concern for man himself and his fate must always be the chief interest for all technical endeavors; concern for the great unsolved problems of the organization of labor and the just distribution of goods- in

order that the creations of our minds shall be a blessing and not a curse for mankind; never forget this in the midst of your diagrams and equations." Albert Einstein

Nanoparticles are small enough to enter cells, which provides an opportunity to interfere with the cells' biochemical machinery. They can absorb ultraviolet light and trigger chemical reactions. Scientists and engineers want to harness these properties to deliver drugs, clean up pollution, and improve consumer products, like sunscreen. But they also worry that nanoparticles can have unexpected effects on the environment and human health, especially if they're used in medicine. How should we approach the privacy issues that accompany the use of nanoparticles applications? For example, concerns over the implanting of nano sensors, GPS systems, or ID systems in human bodies?

Another ethics consideration is the movement of nanoparticles in groundwater. As fullerenes and other nanoparticles make their way into the environment, there's growing concern about what effect they will have on the water supply. Researchers have conducted laboratory experiments in simulated groundwater conditions on seven different nanomaterials and found that they have widely different transport behaviors, indicating that potential exposure to nanomaterials must be considered on a case by case basis.

For additional background, read: The Double-Edged Sword of Nanomaterials http://www.foley.com/files/tbl\_s31Publications/FileUpload137/2623/Nanomaterials.pdf

### **Applications and Products**

Nanotechnology is an emerging engineering discipline that includes the ability to create and develop new materials, structures, and devices at the nanoscale level. It involves many scientific disciplines in the creation of new properties of metallic and ionic compounds, nonmetallic, ceramic, and composite nanoparticles that have many applications. These are just a few examples<sup>2</sup> of the many nanotechnology products and applications.

### **Structural materials**

With the inclusion of appropriately selected nanoparticles, metals can be made stronger and harder; ceramics can have enhanced toughness and flexibility; and structures containing carbon nanotubes may have 100 times the tensile strength of steel, with only 1/6 the weight.

### **Environmental cleanup**

Nanoparticles of metallic iron and palladium are being used to convert toxic organic chemicals like carbon tetrachloride and trichloroethylene (TCE) as well as chromium-6, the "Erin Brockovich" cancer-causing contaminant, into harmless products.

Nanoparticles of metallic oxides show great promise for absorbing and chemically decomposing a wide range of chlorinated hydrocarbons, phosphorus compounds, alcohols, aldehydes, ketones, and amines on their surfaces.

### Medical diagnosis and treatment

Imagine nanodevices that will be able to repair tissues, clean blood vessels and airways without invasive surgery. Or, a diagnostic tool the size of a pocket calculator with a pencilsized probe that is sensitive to the chemical signatures of specific bacteria and viruses. The probe could be used as a tongue depressor and the diagnosis is displayed on a panel minutes after the probe is removed. Medical diagnostic tools and therapeutic methods ARE becoming

<sup>&</sup>lt;sup>2</sup> The examples provided here are general in nature. For more specific and current examples check out Web sites similar to the following: <u>http://www.forbes.com/2006/01/10/apple-nano-in\_jw\_0109soapbox.inl.html</u>.

smaller and more targeted. Silicon nanoparticles, which are photostable and bright, are being used as markers for "tagging" the targets of medical fluorescent imaging, replacing currentlyused dyes which can break down under room light or higher temperatures.

Shrinking down drugs like Taxol, which is used to treat and prevent cancer from reoccurring, to nano-sized doses will potentially allow more of the drug's active ingredient to be targeted toward affected body tissue and double the response rate to the treatment.

The following Web site contains animation showing medical applications: <u>http://nano.cancer.gov/resource\_center/animation.asp</u>.

### **Optical and electronic materials**

Silicon nanoparticles in discrete particle sizes are already useful in microelectronics and optoelectronics as well as in biomedical applications.

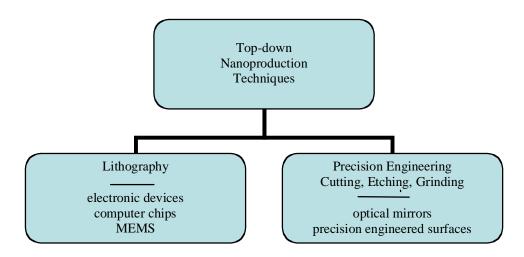
Nanophosphors can convert electricity into visible light with almost 100% efficiency as compared to the 5% efficiency of tungsten-filament bulbs.

Carbon nanotubes conduct electricity better than copper and are excellent conductors of heat; they can be either conductors or semiconductors depending upon the arrangement of atoms.

On the other hand, metallic elements that are good conductors at the macro level become semiconductors or even insulators at the nano level.

### **Nanostructure Production Methods**

There are two basic approaches to manufacturing at the nanoscale – **top-down** and **bottom-up**. The topdown approach builds on silicon fabrication techniques that have been refined for chip manufacturing during the last fifty years; it starts with large bulk material and creates smaller features by removing material using existing larger-scale techniques. The second approach, bottom-up, starts with atoms or molecules and assembles larger units, using synthesis concepts from chemistry.



### Figure 3: Top Down Nanofabrication

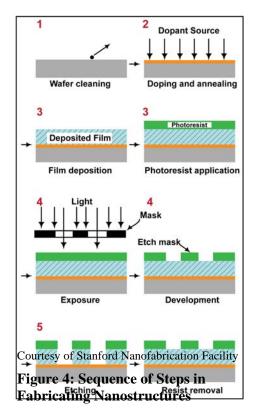
One example of a top-down process is lithography. This technique involves creating a micro or nano sized pattern onto a substrate, such as a thin film. It is used to produce electronic devices, computer chips, and micro electromechanical systems (MEMS) and nanoelectromechanical systems (NEMS).

The image at right shows a typical sequence of basic processing steps used in fabricating micro- or nanostructures. It is based on the methods developed to fabricate silicon semiconductors and integrated circuits.

Step 1- Particles and contamination on the surface of the substrate are removed during the cleaning.

Step 2- Properties of nanostructure materials can be modified by "doping" them with atoms of another element. Diffusion and heating (annealing) may also be used to improve the properties of the structure.

Step 3- A thin film is deposited on the substrate surface using either chemical vapor deposition (CVD) or physical vapor deposition (PVD). In CVD, reactant gases are heated to high enough temperatures to initiate chemical reactions between the reactants and causing a film to be deposited on the surface of the substrate.



Step 4- In optical or "photo" lithography, a film of light-sensitive organic photoresist is deposited on the substrate surface covered by a glass plate mask with a patterned chrome layer that is placed over it. The surface is then exposed to light and either the exposed or the unexposed regions dissolve away in a developer solution, leaving the desired pattern on the surface.

Step 5- Etching with gases or liquids that react with the surface material to remove thin films on the substrate surface or parts of the surface itself. The film is then patterned into the desired shape.

Precision engineered top-down cutting and grinding produces high quality optical mirrors. The main challenges for top-down techniques are the creation of increasingly smaller structures with sufficient accuracy, and producing a large number of them in a cost- and time-efficient manner.

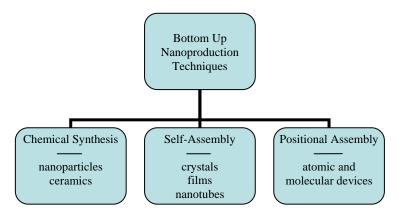


Figure 5: Bottom Up Nanofabrication

Bottom-up synthesis offers the possibility of producing large numbers and arrays of tiny nanostructures. There are three basic types of bottom-up nanostructure processes – chemical synthesis, self-assembly, and positional assembly. Chemical synthesis is the primary method of producing nanoparticles and some nanomolecules, while self-assembly is useful in the production of crystals, films, and tubular structures.

Bottom-up applications include improved ceramics, insulators, and structural material; more efficient catalysts; biotechnology devices and sensors; environmental protection and cleanup and novel electronic devices such as molecular transistors.

**Chemical synthesis** applies both traditional physical and chemical methods to create small-sized particles that exhibit special properties. The following diagram illustrates a generic process that produces nanoparticles or clusters by chemical synthesis.

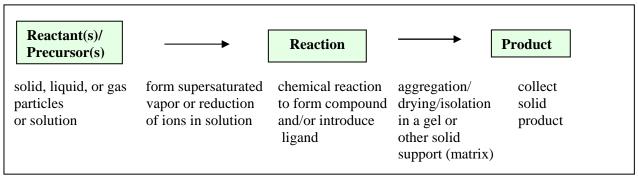
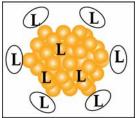


Figure 6: Production of Nanoparticles by Chemical Synthesis



Adapted from Figure 2.23, p. 43, Nanoscale Materials in Chemistry, Kenneth Klabunde. Figure 7: Ligand Stabilized Au<sub>55</sub> Cluster

### Synthesis of metal nanoparticles and structures

In *Gas Phase Synthesis*, metal samples are evaporated by heating or laser irradiation into atoms, which are then passed through slits to focus them into a beam. These particles do not have any protective covering and clump (aggregate) into polycrystalline powders. They are then deposited on a support (matrix) or allowed to react with ligand molecules in solution.

**Chemical Synthesis** of metallic clusters is a multi-step process and there are many variations of the following procedure.

1. Metallic cations are reduced in a solution. The solvent can vary in polarity from water to hydrocarbon solvents depending upon the nature of the metal compound. The reducing agent used also depends upon the compound. Gaseous hydrogen, hydride compounds, and organic reduction agents such as alcohols have been used. Michael Faraday produced gold colloids in the 19<sup>th</sup> century by reducing [AuCl<sub>4</sub>]<sup>-</sup> using phosphorus vapor in aqueous solution.

2. Metallic clusters are generated in the presence of suitable ligands that will cover their surfaces to control the size of the clusters.

### Synthesis of ceramic nanoparticles

Ceramic nanoparticles have been successfully produced using both physical aerosol methods and liquid phase chemistry. Physical aerosol methods include gas condensation processes and thermochemical decomposition of precursors. Liquid phase chemistry procedures include precipitation from solutions.

See "**Nanofabrication**" video located at: <u>http://www.mcrel.org/nanoleap/multimedia/</u> for more information about nanofabrication techniques and the need for a cleanroom.

### Metallic and Ionic Nanoparticles: Extendable Structures

### **Unit Two Background Information**

The questions about physical properties, chemical properties and structural particles of metallic and ionic solids posed in Unit Two provide an opportunity to review concepts previously studied in a typical first year chemistry course. Students will explore extendable nanoparticles and their properties.

The context for this unit is from *Problem Sheet 5– Iron Nanoparticles in YOUR Backyard* of the Student Handbook. The problem will be introduced at the start of **Lesson 2.1**, and then it will be further developed and analyzed by students throughout Unit Two. At the conclusion of **Lesson 2.3**, students will draft responses to ethical questions in response to the proposed problem. You may choose to spend additional time conducting a class discussion on their responses prior to starting Unit Three. Refer to the Student Handbook-Teacher Version for more instructions on *Problem Sheet 5*.

In another student activity embedded in this component, students use spherical objects formed from clay, to make a 13-atom metallic nanoparticle model. They explore the number of surface and interior atoms in the cluster and the number of nearest neighbors for each atom in the model. The simulation of metallic nanoclusters of different sizes allows them to continue this exploration, leading them to discover the increasing ratio of surface particles to interior particles as the size of nanoclusters decreases. The results of this exploration serve as the basis for explaining effects of those changes on physical and chemical properties of metallic and ionic nanoparticles, including increased reaction and adsorption rates as well as changes in melting points, color, and conductivity.

### Science Background for Metallic and Ionic Nanoparticles: Extendable Structures Topics

### **Types of Solids**

*Fact Sheet 2 - Types of Solids* contains a table with descriptive information regarding different types of solids. It also indicates the kind of structure formed by each type and the surface features that determine that structure.

Solids can be either <u>extendable</u> structures, like those formed by metallic, ionic, and some network solids, or <u>discrete or molecular-like</u> structures. Even though the <u>properties</u> exhibited by these solids at the nanoscale may be different, elements and solids (with few exceptions) form the <u>same types of structures</u> at the nanoscale as they form at the macroscale level.

Extendable structures are usually three-dimensional structures whose size depends only upon the number of structural particles–atoms or ions–that are available. Metallic, ionic, and network solids usually form these types of structures at both the macrolevel and the nanolevel. **Identifying the elements and compounds that form these types of solids will help students relate what they have been studying during their chemistry class.** 

The physical and chemical properties of *Metallic and Ionic Nanoparticles*: Extendable Structures is the focus of Unit Two. Unit Three, *Neat and Discrete Carbon Nanoparticles*, spotlights the bonding in carbon allotropes and their many applications at the nanoscale level.

### Surface energy

The atoms in the bulk of a solid are subjected to attraction by atoms all around them, but at the surface they are subjected only to the inward pull of the interior atoms of the solid. Consequently, the surface layer atoms have a higher energy than those in the interior (bulk). **This excess energy is called the** 

**surface energy**. The total surface energy of a given mass or given number of atoms is the number of surface atoms multiplied by the surface energy of each atom.

### What is the relationship between the size of nanoparticles and surface energy?

- As the size of the nanoparticle **decreases**, the ratio of surface atoms to interior atoms **increases**.
- As the size of the nanoparticle **decreases**, the average coordination number of the atoms in the sample **decreases**.
- As the size of an individual nanoparticle decreases, the relative number of surface atoms increases. Hence the total surface energy of a certain mass of nanoparticles will increase as the constituent particles decrease in size.

So, the surface is *where the action is*! The surface is where the interactions that result in changes in physical properties of nanoparticles occur. Chemical processes such as adsorption and oxidation-reduction take place at the surface of the reactants. These chemical processes occur at a high rate and very efficiently at the nanoscale, in part, because of their high surface energy.

In most first-year chemistry curricula, surface energy is alluded to when describing how increasing surface area of reactants or using catalysts can increase rates of reaction. The term itself is seldom used or defined, however. The reason for this is probably related to the higher-level mathematical expressions involved in describing the thermodynamics involved in this complex concept.

However, a basic understanding of the term is essential to students' being able to appreciate the significance of the basic question being addressed in this module; that is, **"How and why do the chemical and physical properties of nanosamples differ from those of macrosamples of a given substance?"** 

Thus, we approach the definition of surface energy from the perspective of coordination numbers. When using models (or simulations) of crystalline solids, students can determine the coordination number for a particular structural particle by counting nearest neighbors and students can visualize the directionality of attractive forces experienced by a particular structural particle. The more directions in which that particle feels an attraction force, the higher the coordination number of a particular structural particle.

This approach leads to a definition of surface energy written at an appropriate level for secondary students, which reads: The atoms in the bulk of a solid are subjected to attraction by atoms all around them, but at the surface they are subjected only to the inward pull of the atoms in the interior of the solid. Consequently the surface layer atoms have a higher energy than those in the bulk. This excess energy is called the **surface energy**.

This definition allows us to directly relate the significance of the increase in ratios of surface particles to interior particles to increases in reactivity of the surfaces of those nanoparticles as they decrease in size. They are introduced to specific examples in which this increased reactivity is quite remarkable. Nanoparticles of magnesium oxide can be used in clothing and masks of first responders involving a hazardous incident. MgO will not only adsorb many toxic chemicals, but, in the nanoscale form, it also decomposes them into products that pose no problems to humans or the environment. Students consider the chemical reactions and the test results of using nanoparticles of iron to clean up trichloroethylene (TCE) from underground water supplies.

This definition of surface energy also helps us introduce surface energy as a "two-edged sword." The high surface energy of nanoparticles increases their chemical reactivity and is a factor in changes in some

physical properties, but it is also the property that makes control of their sizes so difficult during the production process.

### **Surface Electrons and Color Changes**

Except for copper and gold, the only colored metals, all others look "silvery" if they have smooth surfaces. Finely dispersed metals, even copper and gold, are dark brown or black. What we usually consider color is caused by the partial absorption of light by electrons in matter, resulting in the visibility of the complementary part of the light. So the silvery luster of metals is not a color in the true sense, since it is a mirrorlike appearance caused by total reflection of light by a high density of electrons. The dark appearance of finely dispersed metals is caused by total absorption of light.

### What properties of electrons affect color at the macrolevel?

The short answer to this question is the specific wavelengths of light that surface electrons can absorb, transmit, or reflect.

In metallic macrosamples, very mobile surface electrons can <u>absorb electromagnetic radiation of any</u> <u>energy (including visible light)</u> and, in samples with smooth surfaces, the high density of <u>electrons at the</u> <u>surface reflect most</u> visible light, producing a metallic luster in metals like silver. In metallic gold, some blue light is absorbed, thus more red and yellow light is reflected.

### What properties of surface electrons change in nanoparticles?

In the smallest nanoparticles, random, mobile *surface electrons* are *confined* in a very small space—between 1 and 5 nanometers across.

As photons of light interact with the sea of electrons at the nanoparticle surface, the <u>electrons start</u> <u>moving in unison</u>, forming waves having the same wavelength as the photons of light. <u>These waves of</u> <u>electrons then behave as if they were a single charged particle</u>, rather than individual mobile electrons with random motion. The electrons absorb, reflect (or transmit) <u>only the specific frequencies</u> of electromagnetic radiation (light) associated with a specific nanoparticle. These frequencies are dependent on the particle's size, shape, and material composition.

### How do these surface electron properties affect color changes in nanoparticles of the same metal?

At the nanoscale, the color of gold nanoparticles changes depending upon the relative particle size. Gold nanoparticles that measure 25 nm in diameter appear red. The electrons at the surface of these nanoparticles absorb blue and yellow light, and reflect (or transmit) red light. Larger samples of gold nanoparticles are orange or green-brown.

These differences in colors of nanoparticles of the same metal can be attributed to changes in energy of surface electrons. We can visualize a nanoparticle containing only a few thousand atoms to be a "**super atom**" that <u>forms it own discrete energy levels</u>. Its highest-energy surface electrons absorb, reflect (or transmit) <u>only specific wavelengths</u> of electromagnetic radiation. As the size of the nanoparticles decreases,

- the <u>number of atoms</u> forming the "super atom" <u>decreases</u>. This, in turn,
- <u>changes the energy levels</u> of the outermost electrons, which
- <u>changes the absorbed wavelengths</u> of electromagnetic radiation.

Remembering that visible light ranges in wavelength from only 400 nm to 770 nm, it doesn't take much of a difference in electrons' absorption energy to change the color of light reflected from nanoparticles.

For students who select a nano application that involves the detection or reflection of light for their poster assignment, you might want them to know that the motion of electro-magnetic waves in the surface of the metal are called the **surface plasmons (SP)** so they can search on these keywords.

Surface plasmons (SP) are essentially light waves that are trapped on the surface as they interact with free electrons confined in a nanoparticle. In the interaction, the free electrons respond by collectively oscillating in resonance with the light wave. Plasmons are composed of many electrons, but behave as if they were single charged particles. Part of their energy is expressed as oscillation in the plane of the metal surface. Their movement, like the movement of any electrically-charged particle, generates an electrical field which extends about 100 nanometers perpendicularly above and below the metal surface. It is this resonant interaction between the surface charge oscillation and the electromagnetic field of the light that gives rise to the unique color properties of nanoparticles.

For more background reading on surface plasmons:

http://scienceweek.com/2004/sc040109-1.htm includes a bibliography for further information http://www.voyle.net/Future%20Technology/Future%202004-0009%20.htm

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http://chem.ch.huji.ac.il/~eugeneiik/spr.htm

### **Band Theory**

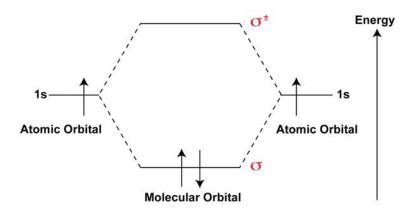
An early model of metals envisioned a metallic crystal as a lattice of positive ions anchored in a "sea" of mobile electrons. The electrons are regarded not as tethered to any particular cation, but free to meander throughout the entire crystal. This simple electron-sea model found qualitative success in explaining many of the characteristics of metals such as electrical and thermal conductivity. Nevertheless it failed to provide much of the necessary information required for a complete understanding of metals and related materials such as semi-conductors.

A refinement called "band theory" that grew out of molecular theory provides a more satisfactory picture. The following background information is included for your review as you prepare to present the last topics in Unit Two.

<u>Molecular Orbitals</u>. The formation of covalent bonds from the overlap of atomic orbitals (valence bond theory), hybridization of atomic orbitals (to force a fit to experimentally determined geometry), and the concept of resonance (where necessary) permit one to derive a useful and pictorial understanding of molecules. Nevertheless this approach has many shortcomings. A higher level and more successful approach is "molecular orbital theory" (MO theory). To apply this approach, atomic orbitals of the constituent atoms of a molecule are combined to provide entirely new orbitals that are characteristic of the molecular orbitals formed is equal to the number of atomic orbitals combined. For example, when two hydrogen atoms combine to make a hydrogen molecule, two *s* atomic orbitals (one from each atom) yield two new molecular orbitals. Once the molecular orbitals are formed, they are arranged in order of increasing energy, as determined from experiment or highly sophisticated calculations, and then the valence electrons of the constituent atoms are "fed" into the system of molecular orbitals, the electrons being placed in the lowest energy orbital available. As is the case with atomic orbitals, each molecular orbital available. As is the case with atomic orbitals, each molecular orbital can hold a maximum of two electrons and Hund's rule applies.

Stemming from these considerations is a "molecular orbital diagram" that, in its simplest form, shows the constituent atomic orbitals, the molecular orbitals created, the relative orbital energies, and where desired,

the electronic population of the derived molecular orbitals. Thus, for a hydrogen molecule we would have:



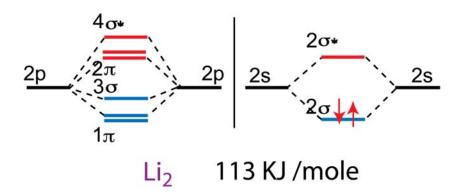
### Figure 8: Molecular Orbital Diagram for Hydrogen

The lower of the two levels is called the "bonding" level since it has an energy lower than that of the constituent atomic orbitals and the upper level is referred to as the "antibonding" level because the region of high electron density is outside the region between the bonded atoms. Any electrons entering into the latter orbital are unstable because of their high energy.

<u>Band Theory and Metals.</u> Band theory is an extension of MO theory to metals. It also permits a qualitative understanding of semiconductors and insulators. In MO theory a metallic crystal is considered to be <u>one</u> huge molecule composed of <u>all</u> of the constituent atoms. As was the case with the hydrogen molecule, the <u>entire</u> collection of valence atomic orbitals is combined to make molecular orbitals. If we remember that there is a one-to-one match between the number of atomic orbitals combined and the number of molecular orbitals formed, it is immediately clear that within a collection of atoms constituting a metallic crystal, there will be an enormous number of molecular orbitals.

For example, consider a one-gram sample of lithium, which would contain approximately  $10^{23}$  atoms. Each lithium atom possesses a single electron in its half-filled atomic 2*s* valence orbital. In the one-gram sample these  $10^{23}$  2*s* orbitals would combine to form  $10^{23}$  molecular orbitals. The energy levels of the resultant molecular orbitals, while distinct in principle, are packed together incredibly closely. So close that individual molecular orbital energy levels cannot be distinguished. The whole collection is therefore referred to as a "band" of energy levels and the valence electrons are said to be "delocalized" throughout the crystal. [Specifically, the orbital energies are spread over an energy band that is about 100 kJ/mol wide, providing a spacing between adjacent molecular orbitals of about  $10^{-21}$  kJ/mole. Clearly, the individual orbital energy levels within the band cannot be identified.]

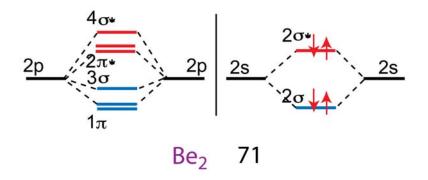
Since each lithium atom contributes one electron to the picture and each molecular orbital in the band can hold two electrons, it follows that the band is half filled, as shown in the picture below.



### Figure 9: Molecular Orbital Diagram for Lithium

The upper half of the band is empty and electrons near the top of the filled molecular orbitals can jump to empty orbitals located at an infinitesimal distance above them in the empty region. The ability of these delocalized electrons to move about within the band accounts for the electrical conductivity of the metal.

The situation in other metals is more complex. Consider beryllium, for example. Here the band formed from the valence 2s orbitals is filled since beryllium possesses two valence electrons. One might conclude that beryllium would not show the same electrical conductivity as lithium since there does not appear to be any "wiggle room" for the electrons. However, we know that beryllium is an electrical conductor just like lithium. More detailed, but not necessarily obvious, considerations provide an escape from this dilemma. It turns out that the molecular orbitals (band) formed from the empty beryllium 2p atomic orbitals overlap in energy with the band formed from the 2s orbitals. Electrons in the filled 2s band can "spill over" into the empty 2p band and create the necessary conduction band for electron movement and electrical conductivity. Other metals can be understood within this framework as well.



### Figure 10: Molecular Orbital Diagram for Beryllium

**What properties of electrons affect electrical conductivity at the macrolevel?** The short answer to this question is mobility and the ability to interact with light and electrical energy.

### How are valence electrons in metallic elements described?

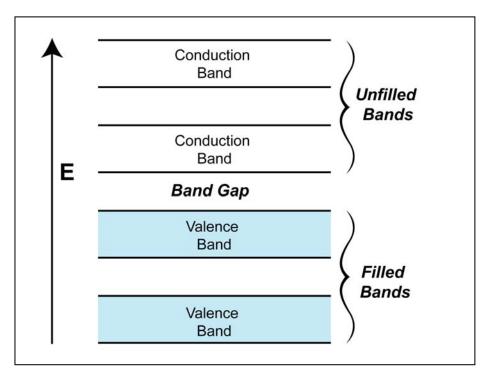
It is difficult to describe all the properties of electrons using one simple model. We use one model to indicate the electrons as occupying s, p, d, or f orbitals surrounding a specific atom. We use this **atomic** 

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**orbital model** when we write electron configurations of atoms of certain elements, such as  $1s^2$ ,  $2s^2$  for the element beryllium.

Now visualize what happens when we move two metallic atoms close together. Their **atomic** orbitals overlap to form **molecular orbitals**, which have different energy levels than the *s*, *p*, *d*, *and f* atomic orbitals from which they were formed. As more atoms join the metallic crystal these molecular orbitals can be spread over many atoms and *metallic crystals can be thought of as "supermolecules.*" The larger the number of atoms in a crystal, the more atomic orbitals there are to form "molecular orbitals." Just like atomic orbitals, these **molecular orbitals can hold only two electrons of opposite spin**.

In macro samples of metals, the energy differences among these molecular orbitals are so small that we can think of them as **bands** of very closely spaced energy levels. **In the ground state, the valence bands are usually filled and the conduction bands are either partially filled or empty**. The delocalized or mobile electrons are found in the **conduction band** because <u>these are the electrons that are free to</u> <u>conduct electricity.</u>



### Figure 11: Band Gap

In **conductors**, electrons in the valence band are easily promoted to the conduction band because the energy of the valence band electrons is just slightly below the energy of the conduction band or partially overlies it.

- In some conducting metals, the valence band is full but electrons can easily move into the empty higher conduction band that overlaps the valence band. Examples include Be, Zn, and Fe. Diagram A in Figure 12 corresponds to this type of conducting metal.
- In other metals, like Li, Al, Cu, Au, and Ag the valence band is only partially full of electrons, so the valence band can also serve as the conduction band. Diagram B in Figure 12 corresponds to this type of conducting metal.

In **semi-conductors**, the energy gap between the full valence band and the empty conduction band is small enough that some electrons can move up to the conduction band by acquiring energy from an external source, such as, electrical, thermal, or electromagnetic radiation (light). Examples include  $C_{(gr)}$ , Si, Ge, and As. See Diagram C in Figure 12.

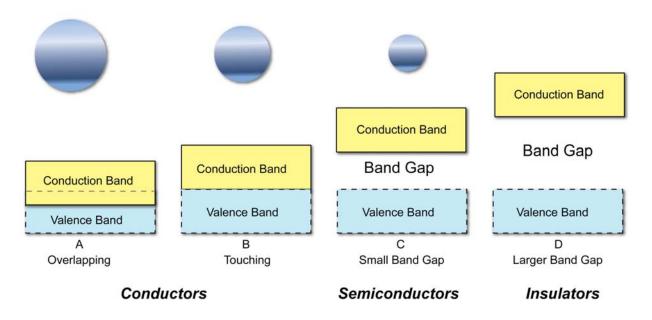
In **insulators**, shown in Diagram D in Figure 12, the energy gap between the valence and the conduction band is so large that few, if any, electrons can absorb enough energy to make the transfer from valence band to the conduction band. An example is  $C_{(diamond)}$ .

### **Properties of Electrons at the Nanolevel**

In the smallest nanoparticles, like ones that your students modeled, these random, mobile electrons are confined in a very small space—between 1 and 5 nanometers. As the size of nanoparticles decrease and shapes change to include more edge and corner sites, the <u>energy</u> and <u>motion</u> of valence electrons change. These changes in electron motion appear to affect the <u>conductivity</u> of these metallic nanoscale particles.

On the nanometer scale, the band gap is a characteristic and unchangeable property. In semiconductor materials, at the macro level, the band gap widens as the particle size decreases.

### As particle size decreases, band energy increases



### Figure 12: As Particle Size Decreases, Band Energy Increases

As a result, the energy required to move electrons from the valence band to the conduction band increases. However, in cases such as gold, as the nanoparticle size decreases, the band gap widens, resulting in a decrease in conductivity. The results of various studies show that this transition from conductor to semiconductor usually occurs in metal nanocrystals ranging between 1-2 nm in diameter; that is, in nanoparticles containing between 200 and 400 atoms.

### Are only metallic nanoparticles affected by band gap changes?

Band gap energies in CdS were observed to go from 2.4 eV in bulk samples to 4.5 eV in 2 nm nanoparticles, so the same change appears to hold for at least selected compounds with some ionic character. For semiconductor nanocrystals, the band gaps decrease to almost macrosample values at about 5 nm. How does this compare with what you discovered about nanoparticle melting points? At what size did the melting points of gold nanoparticles come very close to being that of gold macro samples?

### Is conductivity the only property of nanoparticles that change with band gap energy?

We found that color changes in metals, which are good conductors, are dependent upon the energy of the surface electrons. <u>Color changes in nano semiconductors</u>, like those made of silicon, gallium arsenide, cadmium sulfide, and cadmium telleride are more <u>dependent upon size of band gap energies</u>. Since the band gap increases as nanoparticles decrease in size, the frequency of light that it takes to energize an electron from the valence band to the conduction band increases and changes the color of reflected light.

### The Gold Standard

You and your students may wonder why there are so many references to gold nanoparticles in these materials. You may wish to share with students these short paragraphs from two sources so that they can appreciate that the same properties that make gold so appreciated at the macro level make for a new "gold standard" at the nano level.

### Gold is indispensable

A review of publications on nanotechnology related research and applications reveal the widespread use of gold in nanotechnology. One might ask what characteristics make gold an ideal material for such wideranging applications. The nobility of gold and its resistance to surface oxidation (which would hinder the operation of nanoscale technologies and devices based on other metals) is one important material characteristic. The optical properties of gold at the nanoscale are also exciting, because gold nanoparticles have a color varying from red to purple depending on particle size, a property that can be successfully exploited in a range of applications. Additionally, gold nanoparticles are now known to be catalytically active for a range of commercially important reactions and they also have a surface chemistry particularly suited to the attachment of sulfur-containing molecules, such as thiols, which permits the 'bottom-up' assembly of interesting and useful structures.

See <u>http://www.gold.org/discover/sci\_indu/indust\_app/nanotech\_intro.html</u>.

### Synthesis of Colloidal Gold

The formation of gold nanoparticles can be observed by a change in color since small nanoparticles of gold are red. A layer of absorbed citrate anions on the surface of the nanoparticles keep the nanoparticles separated. The presence of this colloidal suspension can be detected by the reflection of a laser beam from the particles. Switching to a smaller anion allows the particles to approach more closely and another color change is observed.

The site <u>http://mrsec.wisc.edu/Edetc/nanolab/gold/index.html</u> contains the experimental procedure for producing gold colloid nanoparticles. You may wish to incorporate this experience in the module.

### Neat and Discrete Nanoparticles

### **Unit Three Background Information**

Another category of structures might be called "**discrete**" or **molecular-like.** In this category, the predominant mode of bonding between atoms is covalent and the structures formed are more or less self-contained. That is, the structures cannot be extended simply by adding more and more building blocks to a three-dimensional lattice. In a sense, these materials are like large, discrete molecules and, in fact, at the nanolevel it is often a matter of semantic choice as to whether they are referred to as gigantic molecules or nanoparticles. Buckyballs, the first of these unusual materials to be discovered were treated as particles because of their unique nanoscale sized soccer ball shapes.

Students will review covalent bonding patterns, carbon chemistry, and VSEPR thee-dimensional shapes. This unit will also address the discovery of the buckyball, fullerene chemistry and applications, and the structure, properties, and applications of carbon nanotubes. The proposed space elevator, with cables made of nanotubes, provides an intriguing context for students.

For more information on fullerenes, carbon nanotubes, and the space elevator: <a href="http://www.pbs.org/wgbh/nova/sciencenow/3401/02.html">http://www.pbs.org/wgbh/nova/sciencenow/3401/02.html</a>