Name____

Sunscreen and Nanotechnology Lab

Pre-Lab Assignment

- This pre-lab assignment is worth 5 points.
- This part of the pre-lab assignment is due *at the beginning* of the lab period, and must be done individually *before you come to lab!*

I. Background Preparation

- **Read** this **experiment thoughtfully**

Mentally note any procedural questions and plan how you and your partner will complete all experiments efficiently during the three-hour lab period.

II. Safety Hazards/Precautions

1. Complete the following table. Refer to the Safety Data Sheets (SDS) provided by your instructor. You can also search for a SDS by typing in the chemical name into the search box on the Sigma-Aldrich website: http://www.sigmaaldrich.com/united-states.html. After selecting the correct material, click on the SDS link to view.

Materials	GHS Pictograms (Circle all that apply)	Hazard Statements (Check and list all that apply)
dioctyl sulfosuccinate sodium (AOT)		☐ Corrosive ☐ Toxic ___________________ ☐ Flammable ☐ Reactive _________________ ☐ Irritant ☐ Other? __________________
$Zn(Cl)_2$		☐ Corrosive ☐ Toxic ___________________ ☐ Flammable ☐ Reactive _________________ ☐ Irritant ☐ Other? __________________

NaOH		☐ Corrosive ☐ Toxic ____________________ ☐ Flammable ☐ Reactive __________________ ☐ Irritant ☐ Other? ___________________
Heptane		☐ Corrosive ☐ Toxic ____________________ ☐ Flammable ☐ Reactive __________________ ☐ Irritant ☐ Other? ___________________
ZnO		☐ Corrosive ☐ Toxic ____________________ ☐ Flammable ☐ Reactive __________________ ☐ Irritant ☐ Other? ___________________
glycerin		☐ Corrosive ☐ Toxic ____________________ ☐ Flammable ☐ Reactive __________________ ☐ Irritant ☐ Other? ___________________
1-hexadecanol		☐ Corrosive ☐ Toxic ____________________ ☐ Flammable ☐ Reactive __________________ ☐ Irritant ☐ Other? ___________________
sodium dodecyl sulphate		☐ Corrosive ☐ Toxic ____________________ ☐ Flammable ☐ Reactive __________________ ☐ Irritant ☐ Other? ___________________

Waste Disposal	Identify (briefly) how you will dispose of waste materials from this experiment.

2. **Workplace/Personal Cleanup Notes** (indicate what you will do to clean up yourself and your lab space before you leave the lab):

III. Pre-Lab Questions

1. What are the wavelength ranges of UVA and UVB radiation?
   UVA:
   UVB:

2. What is the difference between organic and inorganic filters in terms of their composition?

3. List the two ways that ZnO-based sunscreens work.
   1)
   2)

4. Why are traditional ZnO and TiO_2-based sunscreens white in appearance?

5. Considering the micro-emulsion synthesis used in this experiment, describe how an “inverse” micelle is different in structure from a “regular” micelle studied last week. Use a picture/drawing to illustrate the difference.

Regular micelle	Inverse micelle

6. Write the chemical reaction that will be used to produce $Zn(OH)_2$ in this experiment.

7. Draw the chemical structure of the surfactant used in this experiment, dioctyl sulfosuccinate sodium. Circle and label both the polar head and the nonpolar tail.

8. What is the reason for carrying out the reaction to produce $Zn(OH)_2$ *inside* the micelle “nanoreactors”?

9. To be considered a nanoparticle, what is the approximate maximum diameter of a particle?

IV. Work Plan (Procedural Flow Chart or Numbered List) (You may use additional paper if necessary)

Questions of the Day

1. How does a sunscreen work?
2. What is the difference between organic and inorganic sunscreens?
3. How can micelles be used to synthesize inorganic nanoparticles?
4. Why might nanoparticle-sized inorganic sunscreens be preferable over organic or larger-sized inorganic sunscreens?

Introduction

In this experiment you will investigate how micelles can be used in the synthesis of zinc oxide nanoparticles used in many sunscreens, why nanoparticles are preferred over larger particles in sunscreens and how surfactants and nanoparticles are used to create an emulsion with other ingredients to create a homemade sunscreen lotion that you could use.

Background on sunscreen

I. Recommended Websites to Prepare for this Lab

- http://www.ewg.org/2015sunscreen/report/nanoparticles-in-sunscreen/
- http://www.badgerbalm.com/s-33-zinc-oxide-sunscreen-nanoparticles.aspx
- http://www.webmd.com/beauty/sun/whats-best-sunscreen

II. Why Use Sunscreen?

Unprotected exposure to sunlight is the main cause of skin cancer. Even though sunlight is essential for the human's physical and mental balance, unprotected sunlight exposure should be limited to a minimum. The sun rays that reach our skin can be divided according to decreasing wavelength:

- Infrared (800 nm to 1 mm)
- Visible (400 to 800 nm)
- Ultraviolet (190 to 400 nm)

UV light is further divided into:

- UVA (320 to 400 nm)
- UVB (280 to 320 nm)
- UVC (190 to 280 nm)

Light coming from the sun is filtered when passing through the atmosphere (by ozone, dust particles, smoke, water vapor) and the deadly wavelengths and particles (cosmic radiation, gamma rays, X-rays, UVC radiation) are eliminated. The rest may enter our skin and cause several reactions. Only 10% of the radiation that reaches us is UV light, but these short wavelength photons have a high energy and are very active. The amount of UV light that reaches our skin depends on several factors:

- The season, latitude, and hour of the day: these factors determine the height of the sun above the horizon and the intensity of the light hitting the skin.
- Altitude: there is 20% more UVB radiation at 1500 m (~5000 ft) above sea level.
- The reflection by the earth: snow reflects 85%, sand 17%, water 5% and grass 3% of the light.
- Cloudiness.

The physio-chemical reactions in our skin that are caused by sunlight can be classified as follows:

- The early reactions are generally seen as beneficial:
    - The heat sensation because of the infrared radiation.
    - The production of vitamin D by UVB radiation.
    - For some individuals, suntan caused by UVA and VIS light.

- The delayed reactions are mainly caused by UVB:
    - Sunburn: the significance of the burn is dependent on the intensity and time of exposure and the skin type. UVA radiation worsens this sunburn: the sun rays at the end of the day are mainly UVA and are seen to worsen the sunburn of the day.
    - The delayed pigmentation starts 2 days after the sun exposure and is maximal around the 20^{th} day. It will diminish again if no extra exposure is occurring.
    - The thickening of the upper skin and the suppression of the immune system.

- The late reactions are severe. They are dependent upon the dose and are *cumulative*:
    - Skin aging is mainly caused by UVA radiation, because UVA penetrates the dermis. UVB and IR also play an adverse role (see below).
    - Skin cancer is mainly attributable to UVB radiation, but UVA and IR have an important additive effect. Melanoma is a malignant tumor of melanocytes which are found predominantly in skin. It is one of the rarer types of skin cancer but causes the majority of skin cancer related deaths: according to the World Health Organization about 48,000 melanoma related deaths occur worldwide per year. Around 160,000 new cases of melanoma are diagnosed worldwide each year, and it is more frequent in (but not exclusive to) males and white people.

III. Which Sunscreen Should be Used?

Apart from wearing protective clothes, the use of sunscreen is absolutely necessary to protect yourself from the sun. Which sunscreen should be used is dependent on the skin type.

The sun protection factor (SPF) is one measure for the effectiveness of a sunscreen: the higher the SPF, the more protection the sunscreen offers against UVB radiation. The SPF is related to the inverse of the amount UVB radiation that is passed by the sunscreen.

$$SPF = x\left(1-\frac{1}{x}\right)\cdot 100\%$$; where x = UVB light blocked

SPF Rating	UVB Light Blocked
10	90.0%
20	95.0%
30	96.7%
60	98.3%

SPF <u>used</u> to be thought of as a multiplier that can be applied to the time taken to burn (e.g. when someone would burn after 12 minutes, the person will only burn after 120 minutes when he or she wears sunscreen with SPF = 10), but this is **not** done anymore because there are so many individual differences and other variables that change this equation (skin type, time of day, amount applied, environment, etc.)

Additionally, the SPF is an incomplete measure to prevent skin damage: it only takes into account the amount of <u>UVB</u> radiation blocked. Although in the past UVA radiation was considered harmless (because it is less energetic than UVB radiation), recent research has shown that UVA radiation is harmful in the longer term. It is demonstrated that UVA can damage the DNA and can suppress the immune system. Both these effects promote the growth of cancer cells. These effects are mainly observed after intensive exposure on sun beds or to sunlight. However, regular exposure to lower doses of UVA can also have damaging effects.

Figure 1. Types of UV radiation

Type of ultraviolet radiation	Features
UVA 320-400 nm Long wavelength – lowest energy	- Is not filtered by the atmosphere - **Can go through glass** - Causes coloring of the skin - Was once considered harmless, but appears harmful on the long term - Its intensity remains constant throughout the year
UVB 280-320 nm	- Is partly filtered by the ozone layer - **Cannot go through glass** - Causes sunburn, coloring of the skin, skin aging and skin cancer - Highest intensity around noon
UVC 190-280 nm Short wavelength – highest energy	- Is filtered by the ozone layer before it reaches the earth - Burns the skin and causes skin cancer

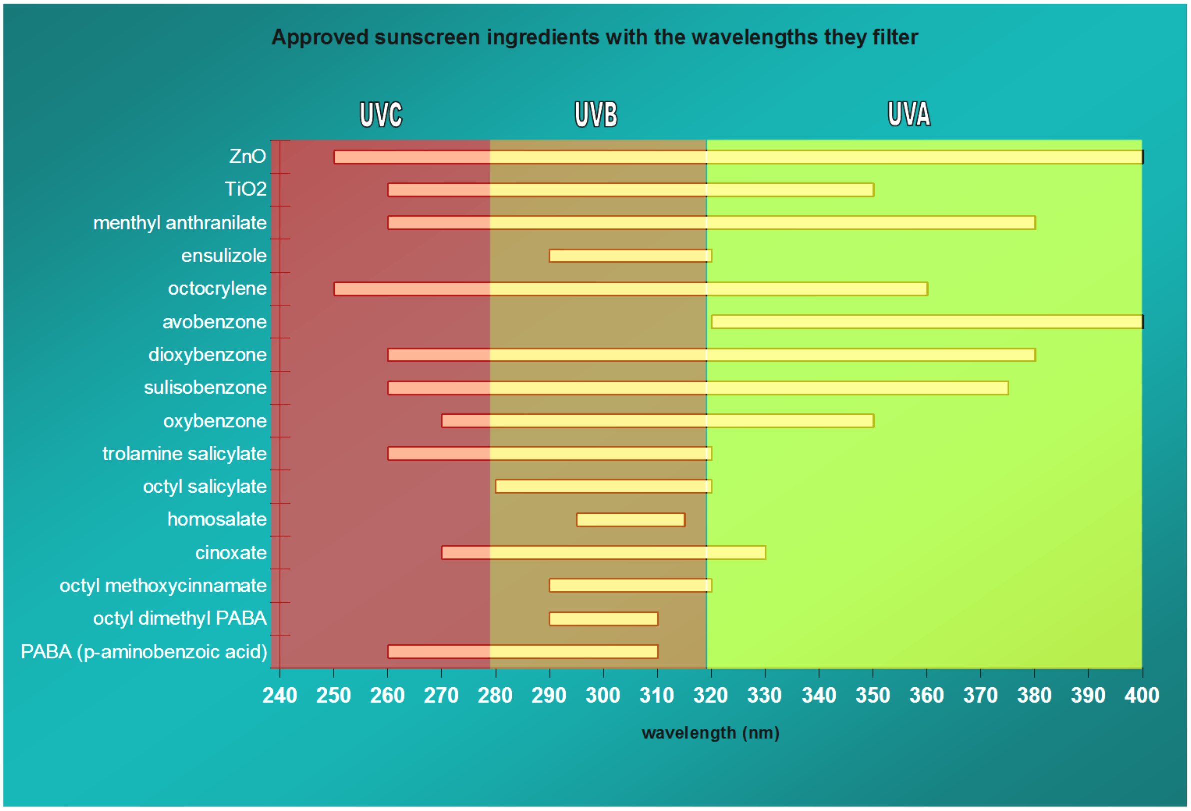
The different additives that are used to block the UV light in a sunscreen have a different ability to protect against UVA and UVB radiation. "Normal" sunscreen does not protect as effectively against UVA as against UVB. *It's important to use a sunscreen that filters both UVB and UVA radiation out of the sunlight; this is a so-called "**broad spectrum sunscreen**".*

The sun protection ingredients in a sunscreen are usually divided into two categories:

- **Organic or chemical filters**: usually these filters consist of molecules containing carbon rings with multiple double bonds and with oxygens bonded to carbons along the backbone of the molecule. An example is the frequently used ingredient *octyl methoxycinnamate*. Organic filters absorb the UV light, causing the double bonded ring system to attain a higher energy. The molecule quickly returns to its stable (lower energy) state by emission of less energetic radiation (VIS or IR). The molecule can then again absorb UV light. Organic sun protection compounds penetrate the skin very easily and *have a reasonable chance of being harmful or causing allergic reactions*.
- **Inorganic or physical filters**: these filters are comprised of ionic solids existing as micro- or nano-particles. The smallest units are crystal extended structures (like those in the "solids" unit of this course). ZnO and TiO_2 powders are very popular because they are efficient, insoluble and are not absorbed by the skin. Inorganic sunscreens are considered the most non-toxic and safe sunscreens to use, and also provide the broadest spectrum protection.

In **Figure 2** an overview is given of some approved ingredients in sunscreens in combination with the wavelength they can filter.

Figure 2. Approved sunscreen ingredients with the wavelengths they filter



As can be clearly seen in this figure, not all sunscreen ingredients are effective in absorbing UVB and UVA light:

- The "older generation" sunscreens contained mainly UVB absorbers like PABA, octyl dimethyl PABA, octylmethoxycinnamate, octyl salicylate etc.
- Although the benzene derivatives (*-benzone*) are mainly used to absorb UVB, they also can absorb some UVA radiation: filters like oxybenzone and dioxybenzone are considered "broad spectrum" filters.
- Avobenzone has recently been added frequently as an UVA absorber.
- Recently also ZnO and TiO_2 are often used as broad spectrum ingredients.

Sunscreens are mostly based on a combination of ingredients, to block a broad as possible spectrum of UV light. Also, the different ingredients are only approved to certain maximum concentrations in the sunscreen to reduce skin irritation.

ZnO-based Sunscreens

A sunscreen that contains ZnO works two different ways:

- Absorption: ZnO particles can absorb UV radiation, both UVA and UVB, and re-emit the absorbed energy as heat.
- Scattering: The ZnO particles mixed in the sunscreen also scatter *some* UV and visible light *away* from the skin.

This last fact is also the reason why traditional ZnO based sunscreens appear white. Although the actual ZnO particles are transparent and colorless, like table salt, the fact that they scatter light in all directions makes them appear white, in the same way that table salt and snow appear white, even though the individual particles are themselves colorless and transparent.

Particle size and scattering

Think about the common image of a lifeguard on a beach with a streak of sunscreen on their nose, Figure 3. This is traditional zinc or titanium oxide sunscreen. Because people tend to apply this white ZnO sunscreen less on their skin (it is not considered attractive), manufacturers developed a type of ZnO (and TiO2) sunscreen that appears clear when applied. But how did they alter the scattering effect of ZnO particles so that they appear clear when applied? The answer is in how particles scatter visible light, which is based on the particle *size*:

- Maximum scattering occurs for wavelengths twice as large as the particle diameter.

Traditional ZnO and TiO_2 sunscreens have particles that are > 200 nm. Thus, light with a λ > 400 nm is effectively scattered. Light with λ > 400 nm is visible light. Thus, we see traditional sunscreen as white due to the full spectrum of visible light that is scattered. Organic sunscreens do not appear white because the individual molecules are < 10 nm in size and thus are too small to scatter visible light.

To produce ZnO and TiO_2 sunscreens that are clear, it is necessary to reduce the particle size. Manufacturers use ZnO nanoparticles that are 100 nm or less in diameter. Since the nanoparticles are much smaller than the wavelength of visible light, they scatter much less light, and the sunscreen appears transparent. However, even at this small size ZnO absorbs UV light, and therefore is effective as sunscreen. A question remains…are ZnO nanoparticles safe in the environment?

If interested, you can find a brief summary in the Appendix to this lab.

Figure 3. Traditional zinc oxide sunscreen.

Figure 4. Even Spongebob wears ZnO sunscreen on his nose.

Preparation of Nanoparticles

Nanoparticles can be manufactured by a variety of routes, commonly classified as wet chemical, mechanical, form-in-place or gas phase synthesis.

In wet chemical processes, solutions of different ions are mixed in defined ratios under controlled external conditions to prepare a large variety of compounds. This is what many people think of when they think of chemists mixing beakers of chemicals in a lab. Examples of wet chemical methods are sol-gel, hydrothermal and precipitation synthesis. These kinds of routes can be carried out in simple equipment. Moreover, the preparation parameters are easily controllable, allowing a good control over the particle size of the end product.

Mechanical processes like ball-milling of coarse powders, where powders are tumbled in a drum with loose ball bearings to uniformly reduce their particle size, are simple methods utilizing low-cost equipment. However, very small particles cannot be obtained by these methods. Also the end product usually shows a rather broad particle size distribution and is typically contaminated by the milling equipment.

Form-in-place processes like lithography and vacuum deposition are more suitable for the production of nanostructured layers and coatings, and are generally not used for the production of dry nanopowders.

Gas-phase synthesis like laser ablation and plasma synthesis are industrially employed to produce nanoparticles. This process can be expensive.

In summary, nanoparticles can be prepared by different methods, each having its own advantages and disadvantages. The resulting nanomaterials can have different properties depending on the fabrication method used.

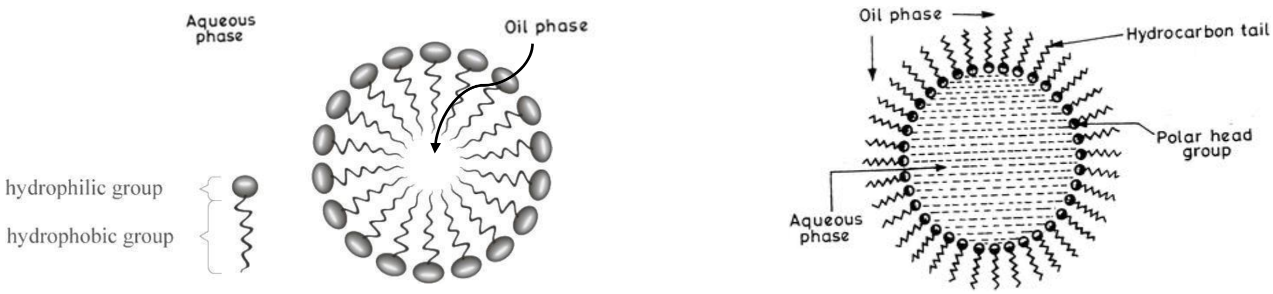
Micro-Emulsion Synthesis – used in this experiment

A method that is becoming much more popular in nanoparticle synthesis is the ***micro-emulsion*** method, which is used in this experiment. It is a way to prepare uniform nanoparticles with a size that can be easily controlled by the micro-emulsion's parameters. A micro-emulsion contains two immiscible liquids like water and an oil phase in which one of the phases is dispersed in the other one as small droplets by using an amphiphilic substance (a soap or surfactant). Similarly, amphiphilic molecules consist of a water-soluble and an oil-soluble part. **At a certain critical concentration,** amphiphilic molecules in an oil phase will spontaneously associate into spherical "micelles", which is known as **critical micelle formation (Figure 5 – left image).**

"Inverse" (Reverse) Micelles

A "water-in-oil" micro-emulsion, in contrast, is formed when *water* micro-droplets are suspended in an "oily" or nonpolar phase. The micro-emulsion requires micelles as well, except this time they must be turned "inside-out". The nonpolar tails must form on the outside of the micelle with the polar heads grouping on the inside, as can be seen in Figure 5, right image.

Figure 5. Illustration of a "regular" micelle (left image) and an "inverse" (reverse) micelle (right image).



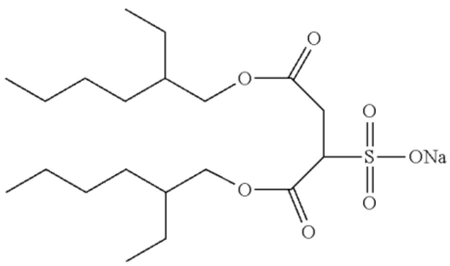
Micelle diameters are generally smaller than 100 nm, making them ideally suitable as "nanoreactors" for the synthesis of nanoparticles. Indeed, chemical reactions (e.g. precipitation, sol- gel) can be performed in the aqueous *cores* of two micelles, *where upon collision,* the micelle droplets containing the different reagents fuse very shortly, and exchange their contents. Think about it. The goal is to create nanoparticles of a certain maximum size. In a beaker for example, the particles could just grow and grow until they become quite large. However, we can limit their maximum growth size by making the reaction occur *inside* a micelle, which generally has a maximum size before it becomes unstable. Thus, we can use micelles to create billions and billions of "nano-reactors" whose nano-scale size limits the ultimate size of the nanoparticles being formed! Cool huh?!

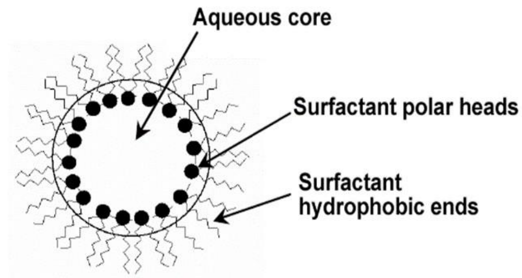
In this laboratory, the reaction of a zinc salt, $ZnCl_2$, with sodium hydroxide NaOH, is chosen as the reaction to be performed in the micro-emulsion environment:

$$ZnCl_2 + 2\ NaOH \rightarrow Zn(OH)_2 + 2\ NaCl$$

The micro-emulsions used in these experiments are created by mixing a surfactant called dioctyl sulfosuccinate sodium (AOT) in heptane (a nonpolar liquid). As can be seen in Figure 6, AOT is a surfactant that has a "double tail".

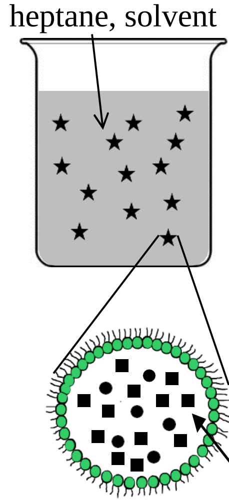
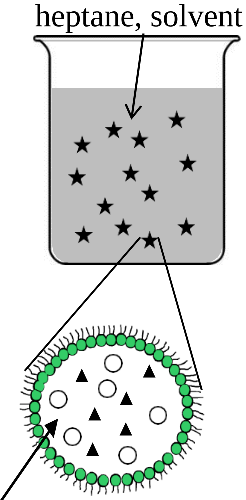
Figure 6. (Left image) Structure of dioctyl sulfosuccinate sodium (AOT). (Right) Inverse micelle of AOT in a nonpolar liquid mixed with water, right.





In this lab, two micro-emulsions will be made. In one, an aqueous solution of $ZnCl_2$ (0.25M) is dissolved into pentane via the AOT micelles, and in a second separate emulsion, NaOH (0.50M) is dissolved into pentane via AOT micelles. When the two emulsions are mixed, the micelle "reactors" can collide and fuse to allow a small-scale reaction of $ZnCl_2$ and NaOH to occur to produce a precipitate of $Zn(OH)_2$ particles. The micro-emulsions' composition is summarized as follows:

Table 1. Micro-emulsion compositions

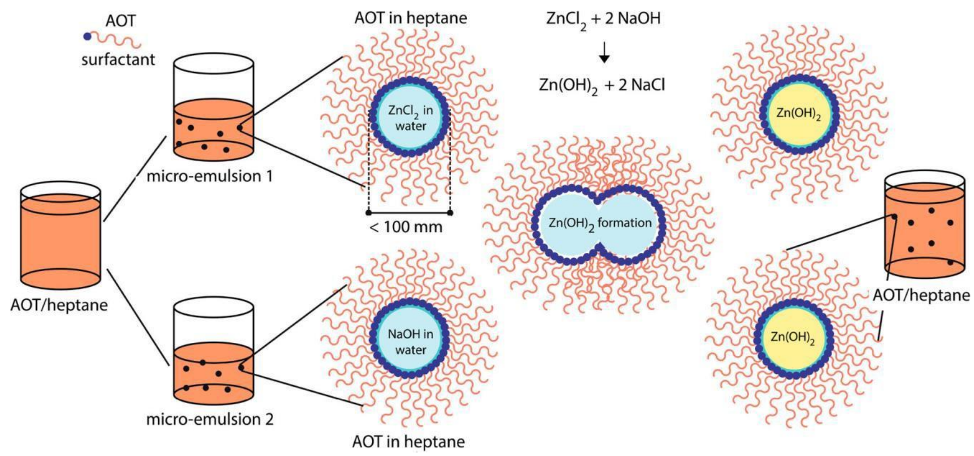
	Micro-emulsion I	***Micro-emulsion II***
Oil phase solvent	Heptane, 25 ml	Heptane, 25 ml
Surfactant	AOT, 1.5 M	AOT, 1.5 M
Aqueous phase	$ZnCl_2$, 0.25 M, 5 ml	NaOH 0.5 M, 5 ml
Schematic image ***Key:*** ★ = ***AOT micelle*** ● = Zn^{2+} ■ = Cl^{-} ▲ = Na^{+} ○ = OH^{-}		

Water inside miscelle (not shown)

After the solutions in the two beakers are mixed, the reaction in the micelles can be represented by the diagram in Figure 7.

Figure 7. Reaction in reverse micelles and synthesis of $Zn(OH)_2$ nanoparticles.

Note that the ions Cl^- and Na^+ are not shown. These ions do not take part in the reaction, and are only present to balance the charge of the original compounds, $ZnCl_2$ and NaOH. (See reference for image source.)



After synthesis of the nanoparticles in the nanodroplets of the micro-emulsion, they generally have to be released from the micro-emulsion environment. This cannot be done by simple filtration or centrifugation, because the micro-emulsion is thermodynamically stable (it won't separate or settle by these methods or by itself). The method you will use in this lab is to break up the micro- emulsion by the addition of a solvent that dissolves the surfactant; *acetone* is frequently used for that purpose. Upon destruction of the nanodroplets, the nanoparticles are released. This is not the exact method used in manufacturing, for reasons that will become clear as you do the experiment.

Summary Table: UV Absorbing Sunscreen Ingredients

	Organic Ingredients	**Inorganic Ingredients (Nano)**	**Inorganic Ingredients (Large)**
Structure	Individual molecule	Cluster ~100 nm in diameter	Cluster > 200 nm in diameter
Interaction with UV light	Absorb specific λ of UV light	Absorb all UV < critical λ	Absorb all UV < critical λ
Absorption Range	Parts of UVA or UVB spectrum	Broad spectrum, both UVA and UVB	Broad spectrum, both UVA and UVB
Interaction with visible light	None	None	Scattering
Appearance	Clear	Clear	White

NOTE: A full list of FDA approved sunscreen ingredients is included in the Appendix at the end of this lab. Look at a bottle of sunscreen sometime…how many of these ingredients do you see?

Experimental Procedures

Waste Disposal Guidelines

- All waste materials MUST be collected in the waste jug in the waste area of the lab. Do not put any zinc-containing materials down the drain or in the trash.
- **Exception**: Hand cream from Part III, if there is NO Zn compound in it, can either be disposed of in the trash or taken home.

Part I. Synthesis of $Zn(OH)_2$ particles in (i) bulk and (ii) a micro-emulsion environment

In this experiment you are going to perform a precipitation reaction both in a "bulk" environment and in a micro-emulsion. Although the same reaction will take place in both cases, you will find out that the properties of the end products are significantly different.

The product you are going to precipitate is zinc hydroxide. It is formed by the following reaction:

$$ZnCl_2 + 2\ NaOH \rightarrow Zn(OH)_2 + 2\ NaCl$$

When the product zinc hydroxide is heated to about 60°C, it is dehydrated and zinc oxide ZnO is formed, the active ingredient in many sunscreens. In Part I we only wish to compare the properties of nanoparticles vs. macroparticles. ***To compare these properties it is not necessary to do this heating step.***

Objectives:

- Synthesize $Zn(OH)_2$ via two different chemical methods (bulk and micro-emulsion).
- Determine if there is any visible difference in the characteristics of the product formed in each method.

(i) Procedure: Synthesis of Zn(OH)2 in Bulk

1. Obtain **two** 10-mL graduated cylinders. **Label** one cylinder as $ZnCl_2$ and the other as NaOH.
2. Obtain 5 mL of $ZnCl_2$ in one graduated cylinder, and 5 mL of NaOH in the other graduated cylinder.
3. Dispense 5 mL of $ZnCl_2$ solution into one beaker.
4. **Report** your observations and answer question 1 in Part I.i of the report sheet.
5. Set the $ZnCl_2$ mixture on a stir plate, add a magnetic stir bar and stir at a medium rate.
6. While stirring, slowly add the 5 ml of NaOH solution.
7. Save your 10-mL solution for part (ii).
8. **Record your observations on the Report Sheet**

(ii) Procedure: Synthesis of Zn(OH)2 in Micro-Emulsion

1. Prepare two micro-emulsions as follows:
   a. Use a 50-mL graduated cylinder to deliver **two** separate 20-mL portions of AOT/heptane emulsions into two 100-mL beakers.
   b. Place each emulsion on a separate stir-plate and add a stir-bar to each.
   c. Stir each solution at medium speed.
   d. Use a 10-mL graduated cylinder to add 2.5 mL of $ZnCl_2$ solution to one of the AOT/heptane solutions to prepare micro-emulsion I. Label the beaker.
   e. Use the other 10-mL graduated cylinder to add 2.5 mL of NaOH to the other AOT/heptane solution to prepare micro-emulsion II. Label the beaker.
   f. Continue the stirring until both mixtures are clear, this may take about 15 minutes. When clear, the micro-emulsions will be formed.
   g. *While you are waiting, you can skip ahead and start working on Part II below.* ***Be sure to watch the time and OBSERVE the micro-emulsions. Return to finish this procedure as soon as the micro-emulsions have formed.***
   h. Mix the two micro-emulsions by **slowly** adding one to the other. At this moment all the reagents are mixed and the formation of $Zn(OH)_2$ can take place.
   i. **Report** your observations upon mixing the two micro-emulsions and answer questions 2-3 in Part I.ii of the Report Sheet.

2. Releasing $Zn(OH)_2$ nanoparticles from the micro-emulsion by adding a solvent, acetone:
   a. Pour 20-mL of the micro-emulsion into a separate 100-mL beaker. Take this beaker to the hood.
   b. **IN THE HOOD** - Destroy the micro-emulsion by adding a sufficient amount (at least 25 mL) of acetone.
   c. Stir with a stir-rod or swirl the beaker to get the reagents to mix.
   d. Compare the results of this step to your observations in Procedure (i).
   e. **Report** your observations and comparisons upon adding acetone, and questions 4-5 in Part I.ii of the Report Sheet.

Part II. Testing UV absorption ability of micro-powder versus nano-powder of ZnO

In Part II of the lab, you will test the ability of the micro- and nano-powders to absorb UV light. For that purpose you will use a fluorescent dye from a yellow highlighter, as before. This dye absorbs UV light and emits visible light, but it can no longer do that when it is covered by a UV absorbing sunscreen.

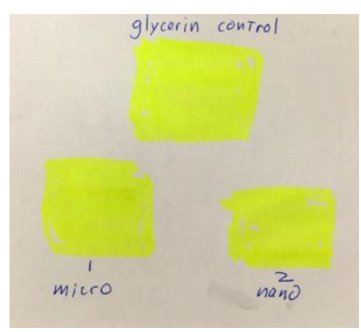
Objective: Your objective is to determine whether there is a difference in the UV-absorbing quality of micro- vs. nano-powders of ZnO.

!

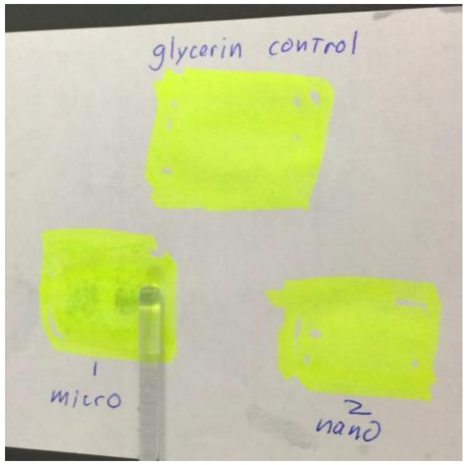
1. Place a petri dish on the weigh pan of the balance. This dish is to catch spills and drippings of glycerin. Be careful not to spill glycerin on the balance.
2. Use two 20-mL beakers to weigh 5 g of glycerin (using a plastic Pasteur pipette) into each beaker.

NOTE: *The next steps can be difficult because the amount of powder you will weigh is very small. Use a microspatula and PRACTICE scooping and weighing out the specified mass until you have a feel for the amount needed. It will be important to get nearly the same amount of each powder.*

3. Label the beakers 1 and 2.
4. Mass 0.025 g of ZnO **micro-**powder into Beaker 1.
5. Wipe the microspatula clean before the next step!
6. Mass 0.025 g ZnO **nano-**powder into Beaker 2.
7. *Note: it is crucial that the same amounts of either micro- and nano-powder are massed out.*
8. Add a magnetic stir bar to both beakers and stir until a homogeneous mixture is obtained.
9. Prepare a piece of paper with 3 yellow squares (~5×5 cm) or circles (diameter about 5 cm) using a yellow highlighter pen and label them "1 micro" and "2 nano" and "glycerin control". See picture at right.
10. Use a stir rod to apply 2 drops of mixture 1 onto square 1-micro, 2 drops of mixture 2 on square 2-nano and 2 drops of glycerin onto square glycerin control.



11. Spread the mixtures out **evenly** over the squares with the side of a stir rod. BE SURE **NOT** TO CONTAMINATE THE SAMPLES – WASH OFF THE STIR ROD!



12. Put the paper under the UV light and observe the ability of each sample to absorb UV radiation.
13. **Report** your observations on the Report Sheet and answer questions 6-9 in Part I.ii.

Part III. Creating and testing the UV absorption ability of a ZnO based sunscreen

In Part III, you are going to prepare a sunscreen based on ZnO as the active, UV absorbing ingredient. The sunscreen's recipe is based on that of a simple hand cream, mixed with ZnO particles as the active ingredients.

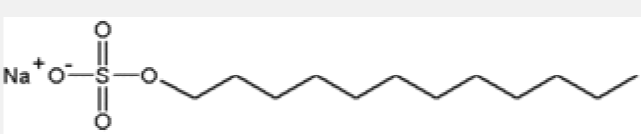
A cream is an emulsion of water and oil, stabilized by an emulsifier. A significant difference with a micro-emulsion, as you prepared in the first experiment, compared to a solution, is that an emulsion does not form spontaneously and requires a lot of energy input to be created, as you will find out during the preparation of the hand cream.

The ingredients for the hand cream are the following:

The oil phase: cetyl alcohol = palmityl alcohol = 1-hexadecanol $CH_3(CH_2)_{14}CH_2OH$

The aqueous phase: water

The emulsifier: sodium lauryl sulphate = sodium dodecyl sulphate $CH_3(CH_2)_{11}OSO_3Na$ (SDS)



Note: The hand cream contains only basic ingredients, no preservatives, and is therefore nonirritating for people with sensitive skin. To obtain a sunscreen, you then mix the cream with ZnO microparticles. *We will not use nanoparticles in the hand cream due to the expense.*

Objectives:

- Create a hand-cream (emulsion) base for a sunscreen lotion.
- Prepare a sunscreen by adding ZnO microparticles to a portion of the hand cream.
- Test the ability of the sunscreen to absorb UV light. For that purpose you will use a fluorescent dye from a yellow highlighter, as before.

(i) Procedure: Preparation of the sunscreen

1. Weigh 7.5 g 1-hexadecanol in a 250 ml beaker.
2. Put the beaker on a hotplate and let the 1-hexadecanol slowly melt at a temperature of about 60-70 °C (SET HOTPLATE AT 5 or medium setting). CAUTION: don't swirl too fast with the melted hexadecanol, because it will freeze again at the walls of the beaker.
3. Weigh 0.8 g sodium dodecyl sulphate in a 50 ml beaker.
4. Add 42 ml of deionized water to the sodium dodecyl sulphate.
5. Dissolve the sodium dodecyl sulphate by gently heating the aqueous mixture on a second hotplate.
6. Remove both beakers from the hotplates, then add **VERY SLOWLY**, under extensive stirring (with a micro-spatula) the sodium dodecyl sulphate solution to the melted 1-hexadecanol. You have to continue the stirring for some **10-15 minutes**, until you see the formation of a gently foaming cream.
7. Essential oils: If you wish to add scent to your handcream, there may be some dropper bottles of essential oils available. You only need 2-3 drops (test first before adding more – you don't want it to be too strong.).

If you want to take the hand cream home, ask your instructor for a container. Remember though that the hand cream does not contain any preservatives and should only be used a short period after its preparation.

8. Place a small part (~1/20) of the hand cream onto a watch glass.
9. Add about 0.25 g ZnO micro-powder to this portion of hand cream.
10. Mix the ZnO powder homogeneously in the hand cream. You now have a small portion of sunscreen.

(ii) Procedure: Testing the UV absorption ability of the sunscreen

1. Take a white paper, draw two squares (5×5 cm) or circles (diameter about 5 cm) and color them using a yellow highlighter pen as before. Mark the two squares/circles as 1 and 2.
2. Take a little bit of hand cream (this is the reference cream) and apply it on square/circle 1. You have to smear it out as if you are applying sunscreen on your skin.
3. Take a little bit of the small portion sunscreen and apply it on square/circle 2. Again you should smear it out as if you are applying sunscreen on your skin.
4. Put the paper with the two squares/circles under the UV light.
5. CAUTION: do not look into the UV light!
6. **Report** your observations on the Report Sheet.

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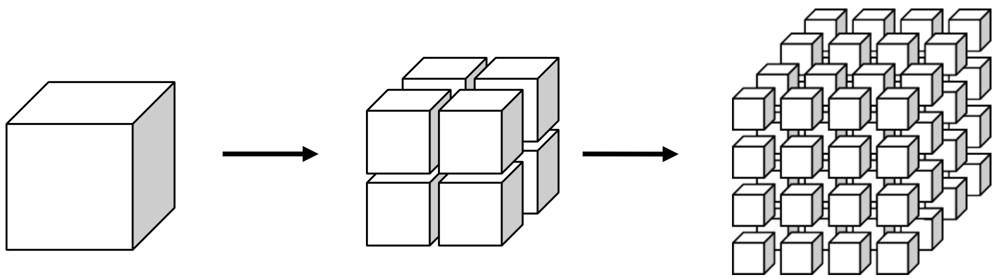
Appendix. What are Nanoparticles and What do We Know of Their Toxicity?

What are nanoparticles?

Nanoparticles are conventionally defined as materials with at least one dimension smaller than 100 nm (one nanometer being one billionth of a meter). Nanoparticles are at the interface between bulk materials and atomic or molecular structures. In contrast with bulk materials, a nanomaterial frequently shows size dependent properties, such as quantum confinement in semiconductor quantum dots or as in ZnO nanoparticles. Moreover, when the size of a material is diminished to the nanoscale, the percentage of atoms at the surface of the materials becomes significant. Surface properties are then dominating the material's properties instead of bulk properties, frequently leading to new and unexpected properties when the material is nano-sized. Because of their small size, nanoparticles are characterized by a very high surface area to volume ratio, which is highly desirable for a number of applications, for example in catalysis. See Figure A1 below.

Figure A1. The increase in surface area when a cube (representative of a micro-sized particle) is subdivided into smaller cubes (representative of nanoparticles), having in total the same mass and number of atoms as the original micro particle.



Although nanoparticles are only being systematically studied the last decades, nanoparticles are not new. Even in ancient times nanoparticles were used, for example, by Roman glassmakers who added metal nano-sized particles (although they did not realize it at the time, of course) to glass for creating specific coloring effects. At the beginning of the 20th century, colloid science was working with nanoparticles. Typical colloids are representative of nanoparticles stabilized in solution by the creation of repulsive electric charges on the surface of the particles. Nanoparticles also play a role in many processes in nature. However, the synthesis of nanoparticles with the aim to obtain and study their new and innovative properties only emerged at the end of the 20th century. Since then nanoscience has become a key discipline with fundamental and applied research topics in diverse areas ranging from chemistry and physics to biology, medicine, and earth sciences. The development of nanoscience was further catalyzed by the development of advanced characterization techniques for nanomaterials, such as electron microscopy (TEM, SEM), atomic force microscopy (AFM), dynamic light scattering (DLS). A diverse range of applications of nanoparticles already established or under development can be identified, for example automotive catalysts, MRI contrast agents, metal powder inks, stain-repellent textiles, ferrofluids, electrodes in solar cells and fuel cells, (bio)sensors, self-cleaning glass, among others.

Toxicity of Nanoparticles

Recently the toxicity of nanoparticles towards the environment and human health is under intense public focus, leading some organizations to call for bans on the research, development and sales of these systems. Indeed, at this time the safety assessment of nanoparticles is still in an early phase; with an increasing number of studies observed in recent years.

Concerning nano-ZnO containing sunscreens, the main toxicity concern for humans is free radical generation in the presence of light (photocatalytic activity), damaging DNA. There is indeed evidence from *isolated* cell experiments that ZnO (and TiO_2) can induce free radical formation and that this may damage these cells. However, this would only be of concern in people using sunscreens *if the ZnO could penetrate into skin cells*. Most of the current evidence points out that they are not absorbed through healthy skin. Moreover, coatings are applied on ZnO nanoparticles used in sunscreen to decrease the photocatalytic activity.

Oral intake is another potential concern for nanoparticles in sunscreens, because they get washed off consumers in swimming pools. The few studies that have investigated gut absorption of nanoparticles generally found low uptake.

The most harmful of all potential human exposures appears to be the inhalation of nanoparticles. Pulmonary toxicity studies in rats demonstrate that lung exposures to nanoparticles produce greater adverse inflammatory responses compared with larger particles of identical composition at equivalent mass concentrations. However, inhalation of the nanoparticles of a sunscreen is only of concern for industry workers formulating the sunscreen, but not for consumers.

Although at this time not enough systematic research is done on the adverse effects of nanoparticles, particularly in sunscreens, it is recommended to use sunscreen that contain ZnO (or TiO_2), nanosized or not. For these compounds are among the only chemicals capable of shielding both UVA and UVB rays and they can, therefore, prevent potentially deadly skin cancer. Moreover, studies show that sunscreens containing alternative organic chemicals such as oxybenzone and octinoxate can definitely percolate into healthy skin, even in large amounts according to some studies. In the body they sometimes behave like the hormone estrogen (estrogen mimics), leading to abnormal activity in the human reproductive system, raising risks for breast cancer, and showing effects like hormone-driven uterine damage. Therefore, consumers who use sunscreens without ZnO (or TiO_2) are likely exposed to more UV radiation and greater numbers of hazardous ingredients than consumers relying on ZnO (or TiO_2) products for sun protection.

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Summary of FDA Approved Sunscreen Ingredients

	λ range (nm)	Protection Against		Possible Allergies	Other Issues
		UVB 280-320 nm	UVA 320-400 nm		
Organic Ingredients					
PABA derivatives					
Padimate O (Octyl dimethyl PABA)	295-340	Good	Little	Yes	-
PABA (p-aminobenzoic acid)	200-320	Good	Little	Yes	Greasy, Stains
Cinnamates					
Octinoxate (Octyl methoxycinnamate) (OMC) (Parasol MCX)	295-350	Good	Little	Yes	-
Cinoxate	280-310	Good	Little	Yes	-
Salicylates					
Homosalate	295-340	Good	Little	Yes	-
Octisalate (Octyl salicylate)	295-330	Good	Little	Yes	-
Trolamin salicylate	260-355	Good	Little	Yes	-
Benzophenones					
Oxybenzone (Benzophenone-3)	295-375	Good	Some	Yes	-
Sulisobenzone (Benzophenone-4)	260-375	Good	Some	Yes	Hard to solubilize
Dioxybenzone (Benzophenone-8)	250-390	Good	Some	Yes	Hard to solubilize
Other Organics					
Ensulizole	290-340	Good	Little	Yes	-
Octocrylene	295-375	Good	Little	Yes	-
Menthyl anthranilate (Meradimate)	295-380	Good	Some	Yes	-
Avobezone (Parsol 1789) (Butyl methoxydibenzoyl methane)	295-395	Good	Good	Yes	If not well formulated, loses potency
****NEW**** Ecamsule (Mexoryl SX)	310-370	Some	Good	Yes	Water- soluble
Inorganic Ingredients					
Titanium Dioxide	up to 365	Good	Good	No	-
Zinc Oxide	up to 380	Good	Good	No	-

Name:____

Partner's Name:____

Nanotechnology and Sunscreens Lab Report Sheet

Part I. Synthesis of $Zn(OH)_2$ particles in (i) bulk and (ii) a micro- emulsion environment

Data and Results

(i) Procedure: Synthesis of $Zn(OH)_2$ in Bulk

1. **Observations** – Report and discuss your observations as you prepared Zn(OH)2 in the bulk. A picture may be helpful.

2. If you can see a substance, and it is not transparent, it must be either scattering or absorbing visible light or both. You should be able to observe the product of the bulk reaction. Do the Zn(OH)2 particles formed in this synthesis scatter visible light?

3. What must be the minimum size of the Zn(OH)2 particles formed in this synthesis if they have the ability to scatter light? *(Hint: In the pre-lab reading it was discussed when maximum scattering occurs based on particle diameter.)*

(ii) Procedure: Synthesis of $Zn(OH)_2$ in Micro-Emulsion

1. **Observations** – Report and discuss your observations as you prepared $Zn(OH)_2$ in a micro-emulsion. A picture may be helpful.

2. Are you able to visibly see the product $Zn(OH)_2$ formed as a result of this micro- emulsion synthesis?

3. Do the particles of $Zn(OH)_2$ formed as a result of this micro-emulsion synthesis scatter visible light?

4. If the $Zn(OH)_2$ particles formed in the micro-emulsion synthesis do not scatter light, what must be the maximum size of these particles? *(Hint: In the pre-lab reading it was discussed when maximum scattering occurs based on particle diameter.)*

5. Does it seem reasonable to call the $Zn(OH)_2$ particles formed in the micro-emulsion synthesis *nanoparticles*? Why or why not?

6. In both experiments (bulk vs. micro-emulsion) the same reaction is taking place and still you observe something different. Explain this observation.

7. **Observations** – Report and discuss your observations when you added *acetone* to the $Zn(OH)_2$ prepared in a micro-emulsion. A picture may be helpful.

8. Do you see nanoparticles or macroparticles after adding acetone? **Explain how you know this.**

9. Recall that an objective of a sunscreen manufacturer is to develop a ZnO sunscreen that is transparent when applied to the skin. Based on your observations of the results of producing $Zn(OH)_2$ particles in the bulk and in a micro-emulsion, which method would be preferable for a sunscreen producer if they were concerned about the appearance of the sunscreen when it is applied? Why?

Nanotechnology and Sunscreen Lab - Report Sheet

Part II. Testing UV absorption ability of micro-powder versus nano-powder of ZnO

1. **Observations** – Use the diagram below to report and discuss your observations when placing the paper with the samples under UV light.

glycerin control | beaker 1 – micro | beaker 2 - nano

2. Do both the micro- and nano-sized ZnO act as UV absorbers?

3. The same mass of ZnO powder, micro- or nano-, was mixed with an equal amount of glycerin. Which sample do you think contained the larger number of particles? Or do they both contain the same? Explain how you know this.

4. The same mass of ZnO powder, micro- or nano-, was mixed with an equal amount of glycerin. Which sample do you think contained the larger number of ZnO *formula units*? Or do they both contain the same? Explain how you know this.

5. Based on your observations, are you able to determine which sample acts as the better sunscreen – the nano- or micro-sized ZnO particles? If so, which one? Explain why you chose your answer.

Part III. Creating and testing the UV absorption ability of a ZnO based sunscreen

1. **Observations** – Use the diagram below to report and discuss your observations when placing the paper with the samples under UV light.

hand cream	sunscreen

Data Analysis

1. Why are some sunscreen manufactures developing inorganic sunscreens that contain nanoparticles as opposed to the older (and cheaper) technique using micro-sized particles?

2. Scattering (not absorption) of light is the reason for the difference in visible appearance of micro-particles (white) vs. nanoparticles and organic molecules (clear) in sunscreen formulations. Briefly explain why nanoparticles and organic molecules do not *scatter* visible light while microparticles do.

3. Suppose the surfactant AOT was used in a different nanoparticle synthesis, but this time water was the solvent and the interior of the “microdroplets” (micelles) were to contain hexane, a common non-polar solvent. In the box at the right, draw a diagram of what a micelle of this system would look like. Be sure to label all the phases and show how the AOT molecules would be arranged. The water phase is already labeled for you.

water

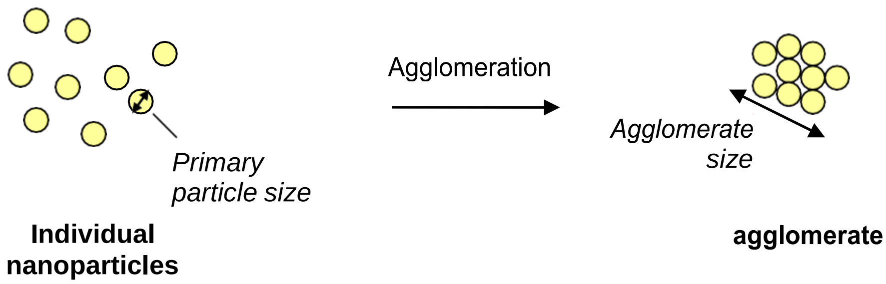
4. Heptane is less environmentally friendly and is more expensive than water. Why did the synthesis of $Zn(OH)_2$ nanoparticles in this lab require inverse micelles in a heptane solvent as opposed to a regular micelle in water? *Hint: Think carefully about this question and consider what you observed when preparing $Zn(OH)_2$ particles in the bulk (Experiment (i)). What type of substance is generally contained in the interior of regular micelles suspended in water?*

5. After adding acetone to the microemulsion that contained $Zn(OH)_2$ nanoparticles, you should have observed the formation of a somewhat gelatinous white precipitate that resembled that formed in the bulk. **Propose a hypothesis for this result**.

   Hints to consider: The gelatinous precipitate formed in the bulk was $Zn(OH)_2$, but it was not *individual formula units. What was it? Why would adding acetone to the microemulsion cause the formation of the same substance? Why was acetone added?)*

6. Nanoparticles have a large tendency to agglomerate (see Figure 1 below) because of the van der Waals attraction force.

Figure 1. Agglomeration of nanoparticles



Most applications, such as the sunscreen considered in this experiment, require unagglomerated or separate nanoparticles. If agglomeration occurs, the properties of the end product are dominated by the size of the agglomerates that can be a hundred times bigger than the original particles. In the sunscreen however, the nanoparticles should remain unagglomerated if we want the sunscreen to appear clear when applied to the skin. Recall how the particles from this experiment were prevented from agglomerating and answer the questions below.

a) In what part of this experiment did you observe the agglomeration of nanoparticles to form micro-sized particles?

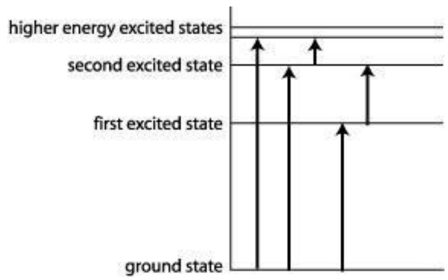
b) You should have observed that both micro- and nanoparticles of ZnO act as UV absorbers. With regard to their use as in a sunscreen, what is the undesirable aspect of the formation of agglomerated nanoparticles that is trying to be avoided? Observe your results of the agglomeration step to help answer this.

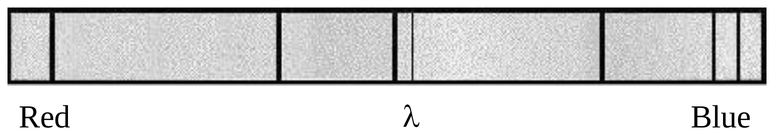
c) Suggest an additional step that would have to be included in the synthesis of ZnO nanoparticles if they were to be used by a sunscreen manufacturer. What type of chemical would be needed in this step?

Additional Writing Assignment

The mechanisms by which organic sunscreens and inorganic sunscreens, such as ZnO or TiO_2, work to absorb UV light seem different at first but are mostly based on the same idea. Ignoring the effect of scattering by inorganic particles, both types of sunscreens work by absorbing photons of UV light. Molecules or inorganic compound absorb photons that correspond to specific electron energy levels *jumps*. Study the figures below representing the absorption mechanism for individual atoms, molecules, and inorganic extended structure solids (like the ZnO nanoparticles).

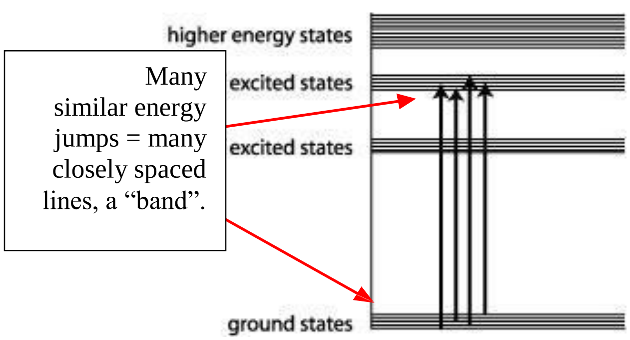
Figure 2. Electron energy levels and absorption possibilities of a hypothetical **atom**.

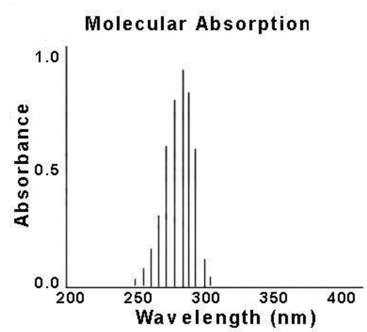




Example: Absorption lines in the spectrum of helium

Figure 3. Electron energy levels and absorption possibilities of a hypothetical **molecule**. Molecules have multiple atoms which can vibrate and rotate in relation to each other. Each kind of vibration/rotation = different energy state. Thus many more energy transitions possible.





Notice that because of vibrations/ rotations, each electron energy state is split into a series of closely-spaced sub-states. As a result, for each electron transition between energy states, there will be a spread of absorptions near that wavelength, as shown above. Thus instead of sharp lines in the spectrum, we see narrow absorbance *bands* for molecules

Absorption range for a new sunscreen molecule under testing.

Absorbance Band Range: 255 – 345 nm

Peak Absorption: 310 nm

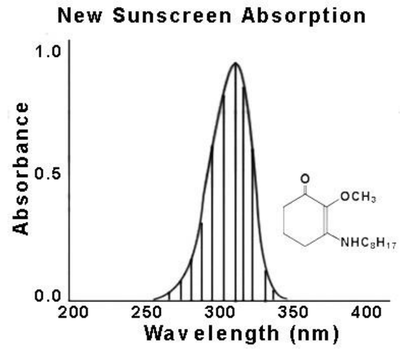


Figure 4. Peak absorption and absorption range vary by molecule. Molecules are usually strong UVB or UVA absorbers *but not both*.

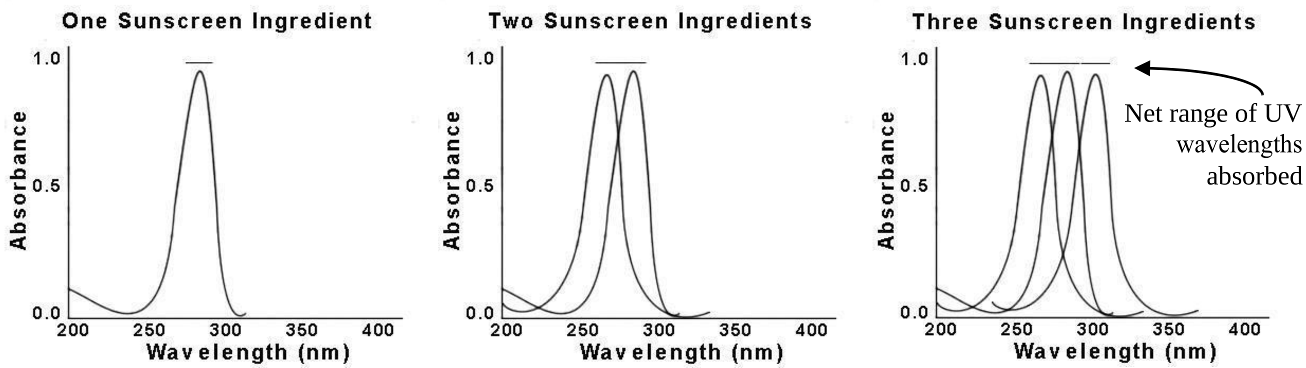
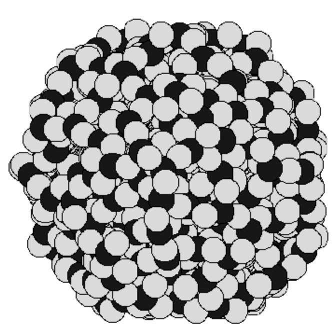
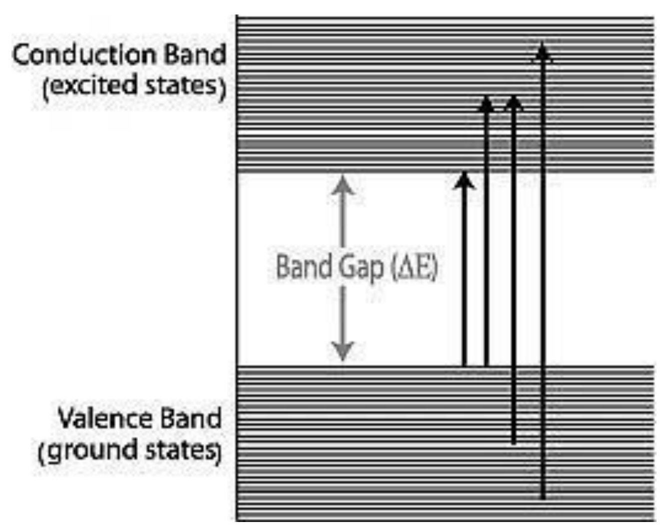


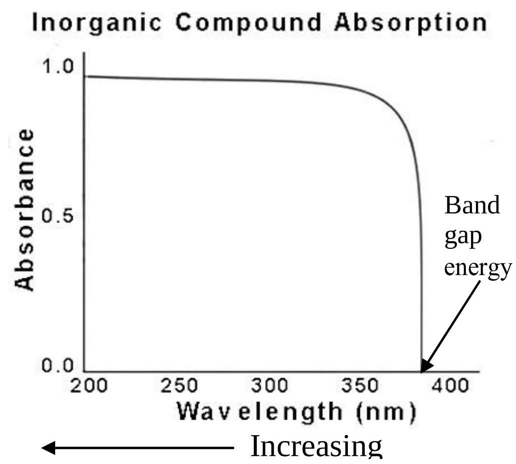
Figure 5. Energy (light) absorption by nanoparticles is based on the same mechanism you studied in the previous unit on solids, *band theory*. Even small nanoclusters are clusters of millions upon millions of atoms/ions.



~100 nm ZnO nanoparticle



Notice that there is a *minimum energy* that a photon must have if it is to cause an electron to jump from the valence band to **the conduction band. This minimum energy is the *band gap energy (Eg)*.**



However, unlike individual atoms and molecules, **all** energies above this minimum (i.e. shorter λ's) are allowed. Thus, solids like ZnO and TiO_2 are *broad-band absorbers*. They absorb all light above the cut-off energy (Eg).

What happens to the absorbed energy? Molecules and many solid inorganic extended structure particles re-emit this energy as lower-energy infrared (IR) radiation; this is not the same wavelength which was absorbed, as in LEDs. You would feel this emitted IR radiation as heat.

Summary Writing

In what ways are "nano" sunscreen ingredients (i.e. nanosized ZnO) similar and different from other ingredients currently used in sunscreens? For each of the four categories below, **circle** the term (*not*, *slightly*, *fairly*, or *very*) that best describes the differences (if any) between "nano" sunscreen ingredients and organic and large inorganic ingredients and explain how.

	Organic Ingredients (e.g. PABA)	**Large Inorganic Ingredients (e.g. classic white zinc oxide used by lifeguards)**
Chemical Structure (Diagrams may help)	Nano sunscreen ingredients are *not* *slightly* *fairly* *very* different compared to organic ingredients How:	Nano sunscreen ingredients are *not* *slightly* *fairly* *very* different compared to large inorganic ingredients How:

Ranges of Light Spectrum Absorbed	Nano sunscreen ingredients are *not* *slightly* *fairly* *very* different compared to organic ingredients How:	Nano sunscreen ingredients are *not* *slightly* *fairly* *very* different compared to large inorganic ingredients How:
The Mechanism by Which Light is Absorbed	Nano sunscreen ingredients are *not* *slightly* *fairly* *very* different compared to organic ingredients How:	Nano sunscreen ingredients are *not* *slightly* *fairly* *very* different compared to large inorganic ingredients How:
Appearance on the Skin	Nano sunscreen ingredients are *not* *slightly* *fairly* *very* different compared to organic ingredients How:	Nano sunscreen ingredients are *not* *slightly* *fairly* *very* different compared to organic ingredients How:

Nanotechnology and Sunscreen Lab- Report Sheet – Final Page