NNIN
Nanotechnology Education

Name:______________________________ Date:______________ Class:_______________

Student Worksheet

Coffee Break with Nanoscience: Film Formation and "Coffee Rings"

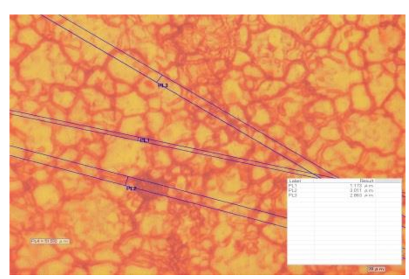
> "The principles of physics, as far as I can see, do not speak against the possibility of maneuvering things atom by atom."
> *Richard Feynman 1959 "There's plenty of Room at the Bottom"*

Introduction

Nano is a prefix meaning "extremely small." Nano comes from the Greek word "nanos" meaning "dwarf". Nanotechnology may be defined as a set of manufacturing technologies that can provide low-cost tools for complete control over the structure of matter. A number of remarkable technological innovations may be enabled by nanotechnology. There are also many everyday technological applications that rely on phenomena at nanoscale. One such technology is the deposition of thin films.

A major tool of nanotechnology products and research is metal or semiconductor nanoparticles. A nanoparticle is any material with at least one dimension of 100 nanometers (nm) or less. Materials at these dimensions may exhibit properties that deviate from the properties of the same material in bulk (that is, at conventional size scales). For example, gold particles less than 100 nm in diameter will have an intense red color, rather than the usual yellow-gold color of macroscopic quantities of gold. Similarly, the electronic properties of materials may change at the nanometer scale.

There are many phenomena that scientists study using nanotechnology. Some of the problems or questions that scientists face when doing nanotechnology research are the same issues that you may observe in everyday life. A good example is the process of coating a surface with a film, like paint or varnish. Paint is a mixture of pigments (colored particles), a vehicle (water or solvents), and a material that dries to form a thin, tough film (usually a polymer of some kind). Once applied to a surface, the paint film protects it from moisture, sun damage, and wear.



Engineers and scientists working with thin films of all kinds must confront two phenomena working against them: cracking and the coffee ring effect. When a liquid film covers a solid substrate and begins to dry, the difference in chemical composition between the substrate and drying film creates mechanical stress, i.e., forces that push and pull on the film. As the film dries, it can no longer stretch or shrink freely, so in many cases this stress causes unwanted cracking of the film.

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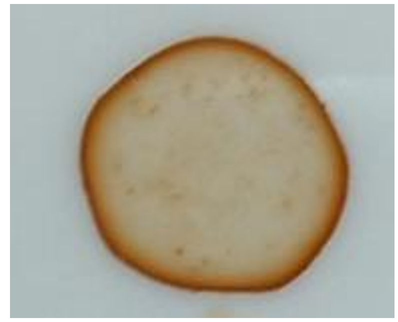
In addition to cracking, another problem encountered with thin films is known as the coffee ring effect. It occurs when a liquid suspension of particles (for example, coffee) is allowed to dry on a flat surface. During the drying process, the particles are not uniformly spread over the surface of the drop, but tend to be transported to the outside edge of the drying droplet. This results in a non-uniform coating with much of the particulate material depositing in an outer ring. This effect must be taken into account, for example, when using conventional inks in ink-jet printers.



Some types of solar cells are made using thin films of particles called nanocrystals suspended in a liquid. When making films from nanocrystals, scientists and engineers must try to solve the problems of film cracking and coffee rings, both of which will destroy solar cell performance. In fact, the real-life problem of peeling paint is being solved by scientists using nanotechnology, too (modern paints contain nanoparticles)!

Equipment

- bubble level
- ruler
- metal binder clips, medium size
- Optical microscope, with 100 to 200X capability
- Small glass bottles or beakers
- Marking pen
- Micropipettes and tips

Materials

- Nanoparticle suspensions, 3 - 5wt% solids
- Instant coffee
- Distilled water
- 12 glass microscope slides
- 12 flat rubber faucet washers
- Gloves
- Safety glasses

This lab will explore the phenomena involved in coating. You will explore the problems that crop up in real- life coating applications, and see how to avoid coffee rings and reduce cracking during the drop-casting deposition of a thin film.

Procedure: Day 1

1. Put on gloves and safety glasses
2. Transfer about 10 mL of the nanoparticle suspension to a small beaker, and label as suspension A
3. Measure 50mg of instant coffee, put in glass beaker, add 5ml of water, and mix well. Label the bottle suspension B.
4. Make twelve sample holders by placing a faucet washer on the front of a microscope slide and clip it with 2-3 binder clips.

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5. On the back of your samples write down the number of your group. For half of your sample holders, also label them as follows: 100, 200, 250, 300, and 350. Add extension A for suspension A.
6. For the other half of your sample holders, label them with 100, 200, 250, 300, and 350, and add extension B for suspension B.
7. Label one plain microscope slide (no washers) as CR-A. Label a second plain microscope slide as CR-B.
8. Place all sample holders on a flat surface that you can move when you are done (like a book or a tray). Use the bubble level to ensure that the surface is level.
9. Use a micropipette to drop 100µl of suspension A on the surface of the sample holder marked 100-A.
10. Use the micropipette to drop 200µl of suspension A on the surface of the sample holder marked 200-A, 250µl of suspension A on the sample holder marked 250-A, etc--repeat for the 300µl and 350µl sample holders.
11. For the sample number CR-A, drop 1-2 drops of suspension A on the surface of the microscope slide. Let the drop spread out, but avoid letting it run off the slide.
12. Repeat steps 9-11 for suspension B, including CR-B.
13. Carefully move the sample holders to a place where they can dry overnight.

Procedure: Day 2

1. Gently remove the metal binder clips.
2. Measure the diameter of the inside of the faucet washers. This is your drop diameter, unless the liquid leaked under the washer.
3. Enter your measurements in scientific notation format in Table 1 for Suspension A and in Table 2 for Suspension B.
4. Now we need to determine how thick the films are, but they are far too thin to measure with a ruler. Instead, we will calculate the thickness based on things we can measure.
5. Calculation procedure for suspension A (titanium dioxide or zinc oxide suspension):

   a. Convert the volume of particle suspension to mass.

   $$mass\ of\ suspension\ = \frac{volume\ of\ suspension}{suspension\ density}$$

   The volumes you used were 100µl, 200µl, 250µl, 300µl, and 350µl. Convert these volumes from µl to cm^3 (hint: convert them first to ml, which is the same unit as cm^3). Use 1.02 g/cm^3 as the density of the titanium dioxide suspension and 1.04 g/cm^3 as the density of the zinc oxide suspension. Your answer should be in grams--remember to convert the volume units as needed!

   b. Use the result in part (a) to calculate the total mass of particles in each dried film. The mass of the particles in the dried film is given by

   $$mass\ of\ particles\ = mass\ of\ suspension\ \times particle\ fraction\ of\ suspension$$

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The particle fraction of the titanium dioxide suspension was 3.5 wt% (multiply by 0.035) and the zinc oxide suspension was 5 wt% (multiply by 0.05).

c. Use the result in part (b) to calculate the total volume of particles in each film.

$$volume\ of\ particles = \frac{mass\ of\ particles}{particle\ density}$$

Use 4.23 g/cm^3 as the density of the titanium dioxide particles and 5.6 g/cm^3 as the density of the zinc oxide particles.

d. Calculate film thickness. Treat the films you made as very thin cylinders with area *A* and thickness *T*. The volume of a cylinder *V* is given by $V = A \times T$.

Using algebra, we can get the film thickness *T*: $T = \frac{V}{A} = \frac{volume\ of\ particles}{measured\ area}$

So the film thickness is calculated by taking the particle volume (from part (c)) and dividing by the area of the film. Since the film is (or should be) circular, its area is given by

$area = \pi\frac{D^2}{4}$ where *D* is the measured diameter of the circle.

6. Do this for each of your nanoparticle films made with suspension A, and enter the results in Table 1. Convert the thickness of your film from centimeters to micrometers.

7. Repeat step 5 for your nanoparticle films made with suspension B, and enter the results in Table 2. The values you will need for suspension B (the coffee) are:

   Density of liquid coffee = 1.0 g/cm^3

   Density of solid coffee particles = 0.40 g/cm^3

   Particle fraction of coffee = 1% (=0.01).

Observations and measurements:

1. Under a microscope, examine the films for cracking, as follows: pick three places on each sample, focus in on each spot at a higher power (50 - 100X), and count the number of individual cracks visible. Enter this number in Table 3 for samples with extension A and in Table 4 for samples with extension B.
2. If you microscope has digital imaging, save some pictures of your deposited layers.
3. Draw a graph using data from Table 1 and Table 3 showing the relation between the thickness and the number of the cracks in the film.

Observations and measurements: coffee rings

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1. Observe the coffee ring pattern made by both the nanoparticle suspension (CR-A) and the dried coffee (CR-B).
2. Do you see a non-uniform distribution of the particles?
3. How do the CR-A and CR-B patterns differ?

Cleanup:

1. Put the rest of your Suspensions (A&B) into a container designed for inorganic waste.
2. The rest of the coffee can be poured down a sink.
3. The microscope slides may be washed and reused.
4. Clean your experiment table.

Table 1—Suspension A

	Diameter (cm)	Area $(cm)^2$	Liquid Volume (μl)	Liquid Volume (cm^3)	Particle Volume (cm^3)	Film thickness (cm)	Film thickness (μm)
Sample #1B							
Sample #2B							
Sample #3B							
Sample #4B							
Sample #5B							

Table 2—suspension B (Coffee)

	Diameter (cm)	Area $(cm)^2$	Liquid Volume (μl)	Liquid Volume (cm^3)	Particle Volume (cm^3)	Film thickness (cm)	Film thickness (μm)
Sample #1A							
Sample #2A							
Sample #3A							
Sample #4A							
Sample #5A							

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Table 3. Cracks in films made with suspension A.

	No. of Cracks	No. of Cracks	No. of Cracks	Average No. of Cracks
Sample #1A				
Sample #2A				
Sample #3A				
Sample #4A				
Sample #5A				

Table 4. Cracks in films made with suspension B

	No. of Cracks	No. of Cracks	No. of Cracks	Average No. of Cracks
Sample #1B				
Sample #2B				
Sample #3B				
Sample #4B				
Sample #5B				

Draw Conclusions

1. Did you observe what you expected?

   ____

   If not, how were your observations different from your prediction?

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2. What natural effects make the thin films non-uniform?

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3. How did Suspension A and Suspension B differ in their cracking behavior?

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4. From your observation, how can you prevent the coffee ring effect during deposition of the suspension?

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5. From your experiment what parameters can reduce the cracks during the deposition?

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6. Why is it convenient to use an optical microscope to analyze thin films?

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7. Please describe the result of the experiment in one paragraph and how it relates to nanotechnology. Give your opinion of your experience.

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