Communicating Research to the General Public

At the March 5, 2010 UW-Madison Chemistry Department Colloquium, Prof. Bassam Z. Shakhashiri, the director of the Wisconsin Initiative for Science Literacy (WISL), encouraged all UW-Madison chemistry Ph.D. candidates to include a chapter in their Ph.D. thesis communicating their research to non-specialists. The goal is to explain the candidate's scholarly research and its significance to a wider audience that includes family members, friends, civic groups, newspaper reporters, program officers at appropriate funding agencies, state legislators, and members of the U.S. Congress.

Over 50 Ph.D. degree recipients have successfully completed their theses and included such a chapter.

WISL encourages the inclusion of such chapters in all Ph.D. theses everywhere through the cooperation of Ph.D. candidates and their mentors. WISL is now offering additional awards of $250 for UW-Madison chemistry Ph.D. candidates.

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The dual mission of the Wisconsin Initiative for Science Literacy is to promote literacy in science, mathematics and technology among the general public and to attract future generations to careers in research, teaching and public service.

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Advanced fabrication of toroidal optical microresonators for label-free photothermal imaging and spectroscopy

By

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1. An introduction to using toroidal microresonators for single-molecule absorption experiments for non-specialists

Think about light. First, light serves as an energy source. It delivers heat to the earth from the sun, and through that energy, plants can grow and we can have enjoyable beach vacations. Because of light, we can also perceive the world through sight. Without light, the interpretation of our surroundings would be much different because the way light interacts with objects determines how we view them. When light hits an object, several things can happen, as you can see in Figure 1-1. The light can be reflected, meaning all the light rays bounce back off the surface as when you shine a flashlight at a mirror. The light can be transmitted, with all the light passing through, unimpeded like an untinted window. Finally, the light can be absorbed by the object, allowing less or no light to pass through the object as when you shine a flashlight through a tinted window or a pair of sunglasses. Molecules within the material take in the energy from the light like boiling water takes in heat from the stove. Different molecules absorb light differently because they are made from different atoms that are connected in different ways. These differences help to distinguish molecules from each other, and consequently, light absorption has become a very useful way of identifying molecules. For example, a glass of lemonade absorbs different colors than a glass of tea, because the molecules inside each are absorbing light differently.

However, it takes a lot of molecules (millions!) to tell what colors, and thus which wavelengths, of light have been absorbed. This becomes a problem when you want to know what just *one* molecule is doing. Why would anyone need to know that, you ask? Single molecule insights are important if you want to fundamentally understand how something works. When you shine light on a million molecules at a time, you will see the average value of the light they absorb, which might make you conclude that every molecule in the bunch absorbs light the same way. Each of the million molecules, however, actually absorbs light slightly differently. When you look at all of them in a single measurement you miss the differences, or the heterogeneity, present in the sample. By examining molecules one at a time, we can gain a much richer understanding of the

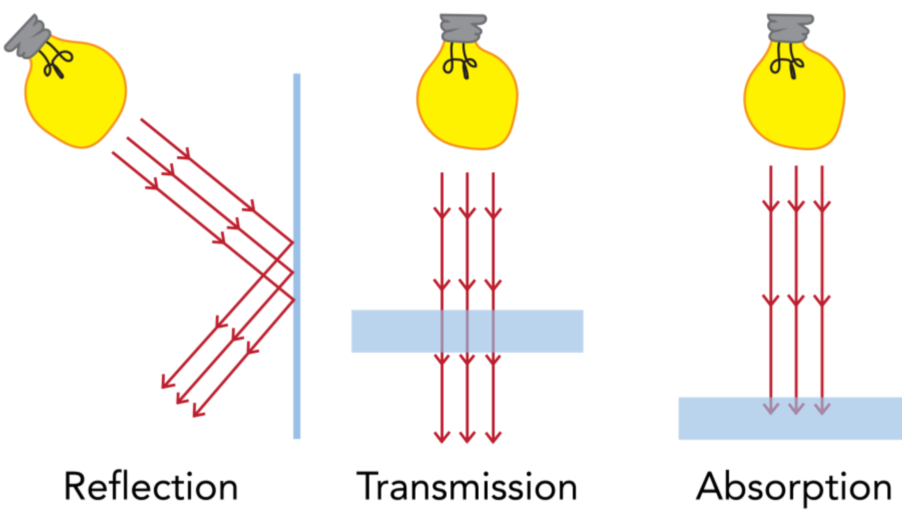

Figure 1-1 Light interacting with objects. Reflection occurs when light bounces off an object. Absorption occurs when the light gets taken in by the object and cannot pass through. Transmission occurs when light passes through the object.

whole system because we can understand what each of the individual parts are. Practically, this could lead to better understanding of diseases and more effective treatments, or even more efficient ways to generate energy.

For example, if we were to look at our brains, there would be many different proteins present. Proteins are the building blocks that make our bodies work, and when they are malfunctioning or damaged, disease can occur. In the brain of a person with Alzheimer's disease, the culprit is thought to be a specific protein called the tau protein, and Alzheimer's can happen even if only some of the tau proteins are misbehaving. To understand the cause of Alzheimer's and develop treatments, you would want to find the specific tau proteins that are misbehaving so that you can fix those and leave the healthy ones alone. If you were to look at all the tau proteins at the same time, it would be hard to distinguish which ones are working and which ones are not. Instead, you would want to observe the behavior of tau proteins one at a time to better understand which proteins are misbehaving, how their behavior is deviating from normal behavior, and what needs to be done to fix them. This kind of analysis—single-molecule analysis—allows scientists to develop more effective treatments that have fewer side effects. In another example, we could

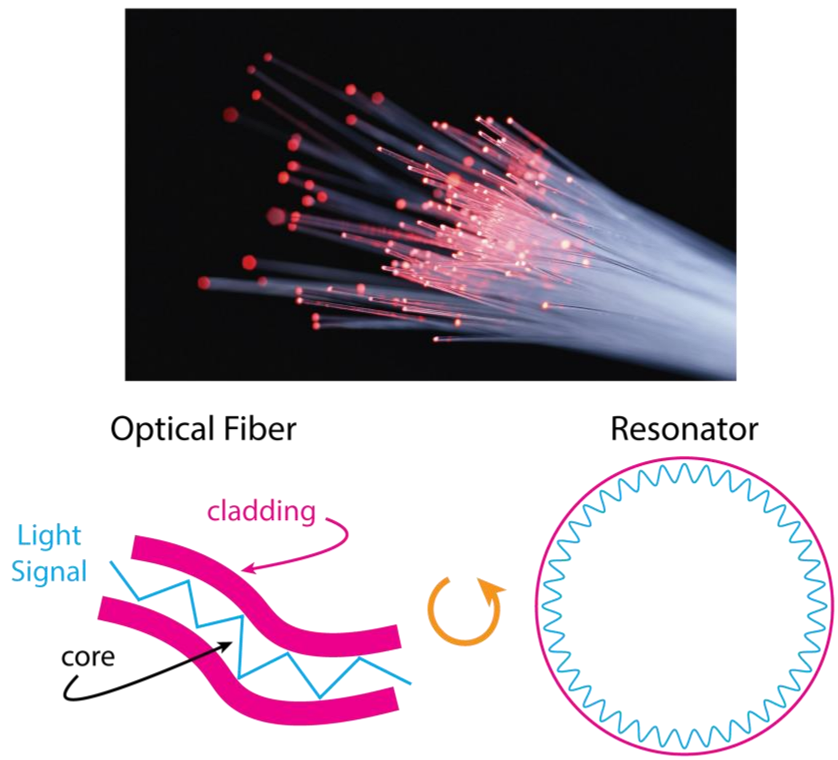

Figure 1-2 Illustrating total internal reflection. Top: a bundle of optical fibers. Photo credit: Tan Aikhong, freeimages.com *Bottom left: Schematic of an optical fiber. The light signal reflects off the boundary between the core and the cladding. Bottom right: Schematic of a resonator. Light propagates around the circumference of the resonator.*

look at a solar cell. If we measured the efficiency of a solar cell, or how well it converts light into usable energy, we might get a number like 20%. A single solar cell, however, has many different molecules that contribute to its efficiency. So, when you measure 20%, it becomes hard to determine whether all the molecules are converting energy at 20%, or if some are working well and some are working average and some are not working at all. If you can measure the efficiency

of each molecule individually, you can get an answer. Additionally, you would be able to understand the characteristics of the overachieving molecules, which would lead to the design of better solar cell technology.
To make these advances, we need the ability to study individual molecules. To study individual molecules, we employ a toroidal microresonator. A toro micro what? Toroidal is a fancy way to say donut-shaped. A microresonator is a very small waveguide—about twice the width of a human hair—that guides light waves around and around in a circle (the outer edge of the donut) because of the reflection of light. When you look at the top panel of Figure 1-2, it might remind you of one of those toys that kids get at the fair that have lots of colorful, glowing fibers sticking out of the top or the fiber optic network that you may have heard of that carries the internet across countries and oceans. Both examples, like microresonators, contain and guide light through total internal reflection (TIR). TIR occurs when light hits a boundary between two materials and all the light bounces back instead of crossing the boundary (Figure 1-2). Fiber optics, the two cases mentioned earlier, are made from two materials, shown on the left in Figure 1-2: a cladding (on the outside) and a core (on the inside). Light shines into the core of the material, and at a specific angle TIR occurs and the light bounces off the boundary and stays in the core. As the light continues to propagate down the length of the fiber, it bounces back and forth between the edges of the core material. We can take that fiber and wrap it in a circle so that the ends meet and the light never reaches an end. Now we have TIR occurring around a circle, as seen on the right half of Figure 1-2. The circumference of the circle is equal to a multiple of certain wavelengths, or colors, of light. At these wavelengths, the beginning of one wave perfectly meets at the end of the next, allowing the light to travel around the circle. This is a resonator. If we shrink it down so that it is very small, we have a *micro*resonator.

Light propagates around the circumference of the donut-shaped toroid. Because the light must take a full number of wavelengths to get around, only very specific wavelengths of light can exist in this resonator. We call these wavelengths resonant wavelengths or resonances. Resonant wavelengths are very sensitive to the properties of the toroid like the temperature of the glass that

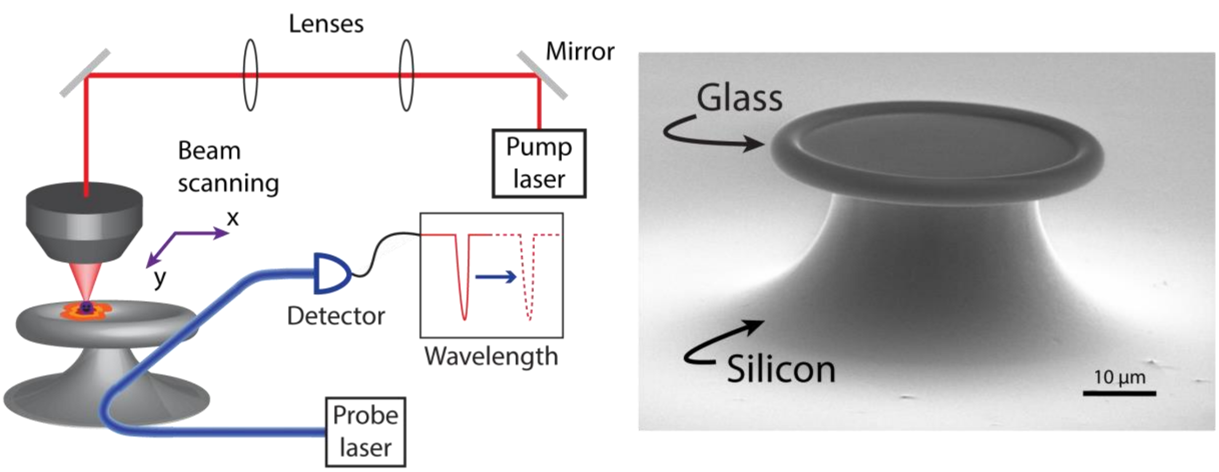

Figure 1-3 Toroidal microresonators for measuring absorption. The pump beam (red) is absorbed by molecules on the surface of the toroid. When a molecule relaxes, it emits heat. The resonator heats up and the resonant wavelength shifts. We change the wavelength of the probe beam (blue) until we find what the new resonant wavelength is. The picture on the right shows a toroid that has a glass resonator sitting on a silicon pillar. The toroid is about 40 µm in diameter, which is approximately twice the width of a human hair.

forms the toroid, or the air around the toroid. This means that if we *change* the temperature of the glass or the air by heating it up, the wavelength that can exist in the resonator must also change. The change in the resonance as a result of a temperature change is shown in the wavelength chart in Figure 1-3; the solid line is the original resonant wavelength and the dotted line is the resonant wavelength after the toroid has been heated up. We can calculate how much the temperature increased based on how much the resonance shifted to use the resonator as a thermometer.

Our experiment, which you can see in Figure 1-3, takes advantage of the thermometer capabilities of toroids. Toroids are exceptionally good waveguides, which allows them to be exceptionally sensitive thermometers. In fact, they are so sensitive that they can detect the heat that is generated by a single molecule! This is great news for our experiment! We can relate the resonance shift from a single molecule to the amount of energy that it absorbed, giving us a way to measure the absorption of a single molecule. To do this we use a light beam, which we call the pump beam (shown in red in Figure 1-3). Another light beam, which we call the probe beam, is circulating in the toroid and reports the resonance shift as a function of temperature (shown in blue in Figure 1-3). We can move the pump beam around with mirrors and focus it to a small spot on the toroid. The goal of this beam is to excite single molecules that we put on the toroid, like sprinkles on a donut. We move the pump beam around, and when it overlaps with a molecule, the molecule absorbs the energy from the light and becomes excited. When the molecule releases that energy, or relaxes, it emits heat and raises the temperature on the toroid. The resonance shifts, and based on how much it shifts, we can calculate how much the molecule absorbed. People have studied single molecules using toroids before us. Our method, however, allows us to map out where the molecules are on the toroid (you can see examples in Figure 1-5), something that other methods are incapable of doing. Using a pump beam that can change wavelength, we can identify unknown molecules based on what color light they absorb, where other methods must place a priming agent on the toroid first so that only specific molecules stick. These two characteristics of our technique make it a powerful tool for single molecule analysis.

Unfortunately, there is a problem with our thermometer. Our thermometer contains silicon. Silicon is a prominent material in microtechnology development and has allowed for big advances in the miniaturization of electronics. You may have heard of Silicon Valley as it is a hub for microtechnology development and industry. And now you may be wondering where this is going. Toroids contain silicon because they are made by the same processes that are used to make microchips in cell phones and computers. Borrowing this technology means that toroids are very easy to make, and we can make a lot of them at one time. However, silicon absorbs light very well and it takes up the whole center of the toroid (Figure 1-3, right). When it relaxes, it emits more heat than a single molecule, which effectively makes the single molecule invisible. Think about trying to hear your friend whispering while you are attending a rock concert. There is no way you would be able to hear what they are saying because the sound from the concert would completely drown out the small sound of the whisper. The same thing happens to the heat signal of the single molecule. The only way you would be able to hear your friend whispering is if you left the concert and went to a quieter place, removing yourself from the overwhelming sound. Similarly, to see the single molecule, the single molecule signal needs to be separated from the overwhelming silicon signal. We have a few options to do this. First, we pump our molecule at a wavelength that silicon does not absorb. Unfortunately, when we move to these wavelengths, we lose the ability to study systems that absorb at visible wavelengths, which are

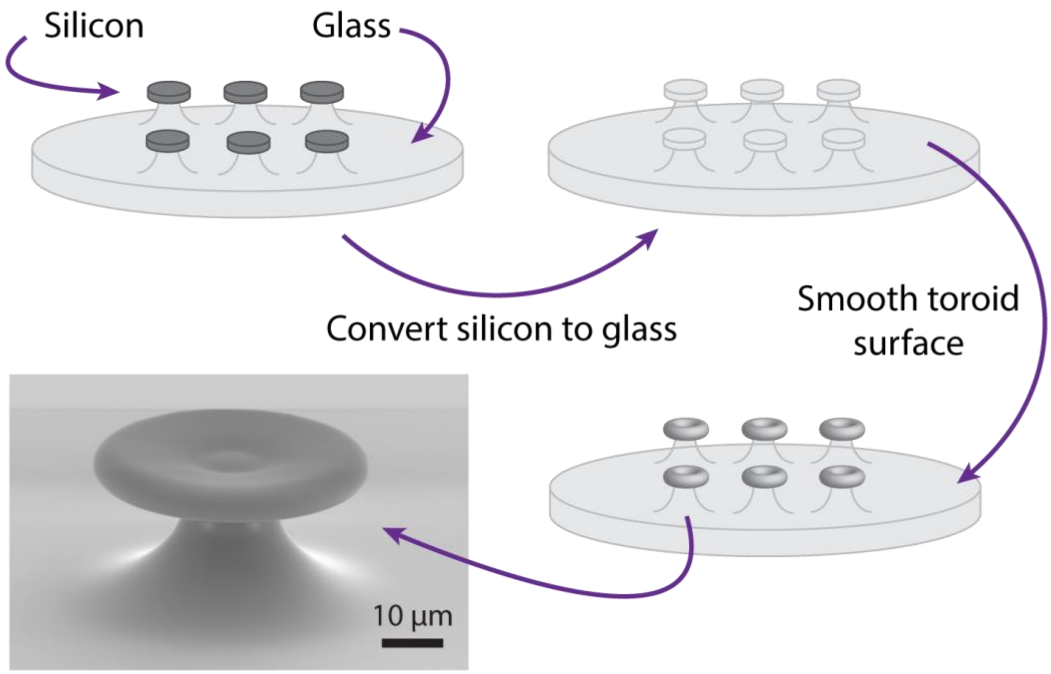

Figure 1-4 All-glass toroids. We start by making silicon-on-glass toroids. By adding heat and oxygen, we convert the silicon to glass. Finally, we smooth out the surface of the toroids by melting the edges at a high temperature to end up with an all-glass structure.

the colors we can see. Although this solution works, it eliminates many interesting systems—like the parts in plants that carry out photosynthesis, proteins in our bodies that keep us from getting sick, and important components in solar cells—and is not ideal. The second, and more ideal solution, is to remove silicon from the toroid, leaving us with a transparent all-glass toroid and keeping systems with visible absorption in our grasp.

We make all-glass toroids in the same way that we normally would, except we flip the materials—instead of starting with glass on silicon, we start with silicon on glass. Hold up now! I thought we were getting rid of silicon? That is correct. We make the toroid out of silicon initially, which you can see in Figure 1-4, but then we can convert the silicon into glass at the end by heating it up and adding oxygen. Also, instead of blasting them with a laser to make the edges of the toroid smooth like we do with toroids that have a silicon pillar (important for making a good waveguide and making sure this whole thing works), we heat them up in a high-temperature furnace. This is gentler and a lot more controllable, which is important since the silicon is gone. Once the toroids are made, we can scan our pump beam around and check to make sure the silicon is gone. If it is, no heat will be generated by the pump beam. And it works! When we scan the beam around, there is no sign of any silicon, which you can see in Figure 1-5.

With a non-absorbing, all-glass toroid in hand, we can start our journey towards investigating single molecules in the visible region. To demonstrate our new toroid's capabilities, we started by looking at gold nanorods. Gold nanorods, though they are very small, are much bigger than molecules, so the amount of heat they release when they relax is greater. This makes them easier to see, which is a step in the right direction and a good demonstration. When we scan the pump laser, we see heat dissipating from single particles! To confirm that these are single particles, we

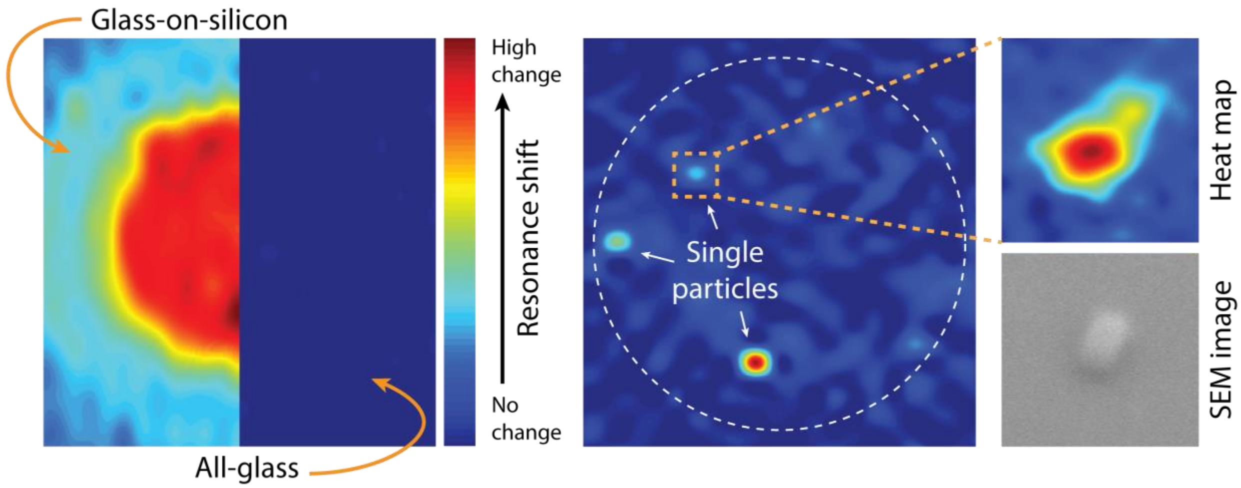

Figure 1-5 Measuring single molecules with all-glass toroids. Left: Heat maps of a glass-on-silicon toroid (left half). The bright red spot in the middle indicates that the silicon pillar is generating a lot of heat because the resonance shift is large. All-glass toroid (right half) does not contain silicon and does not have any heat signal. Center: A heat map of an all-glass toroid with several single molecules on the surface (heat spots). The dotted white circle indicates the rim of the toroid. Right: Zoomed-in images of a single gold nanorod. The top shows a heat map of a gold nanorod and the bottom shows the same nanorod imaged by SEM.

recruit an alternative method of characterization: scanning electron microscopy (SEM). SEM uses electrons, instead of light to make images. Because electrons are smaller than the wavelength of light, we can easily obtain images of nanoparticles. We can match the positions of the single nanorods that we find in our heat maps to the nanorods that we find in the SEM images (Figure 1-5), indicating that we are imaging single nanoparticles!

With all-glass toroids as a tool, we can investigate single molecules through absorption. One of the most common ways of studying single molecules is through fluorescence, when excited molecules emit light instead of heat. However, few molecules are fluorescent and can be easily studied this way. Adding an absorption method to the single molecule toolkit opens the door to learning about molecules in a way that we could not before. With this extra information, there will be many new possibilities for improving healthcare, technology, and industry.

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