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Exploring Plasmonic-Photonic Coupled Systems Using Microcavity-Based Single-Particle Spectroscopy

By

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A dissertation submitted in partial fulfillment
of the requirements for the degree of

Doctor of Philosophy
(Chemistry)

at the
UNIVERSITY OF WISCONSIN-MADISON
2022

Date of final oral examination: February 16, 2022

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Chapter 8 Mingling a nanoscopic world with a microscopic world

Introduction

This chapter is intended to explain my graduate research to non-scientific audiences and is supported by the Wisconsin Initiative for Science Literacy at UW-Madison. I would like to thank Prof. Bassam Shakhashiri, Elizabeth Reynolds, and Cayce Osborne for their constructive feedback and encouragement. Science should be approachable to everyone. Thus, I hope my research to be both understandable and appealing to a broad readership. In the meantime, it is extremely rewarding that this chapter sparks people's interest in new sciences and passion for exploring interdisciplinary subjects which may revolutionize our understanding about our world from tiny particles to grand universe. My research revolves around plasmonics, photonics, and their interactions. I hope to use this chapter to explain a few critical concepts in these topics. What are plasmons, photons, and the media that host them? How do we understand and control interactions between them?

Plasmons and their media

Let's first get to know plasmons. We can think of a plasmon like a child in a swing moving back and forth (**Figure 8.1A**). But eventually this kiddo will stop at a moment when he is not pushed any more. A plasmon is very like this child but is a cloud of electrons (or negatively charged tiny particles) moving back and forth around an origin. This cloud is moving periodically at a certain frequency when it is driven by light irradiation (an electric field), as seen in **Figure 8.1B**, and will stop soon after this external irradiation ends.

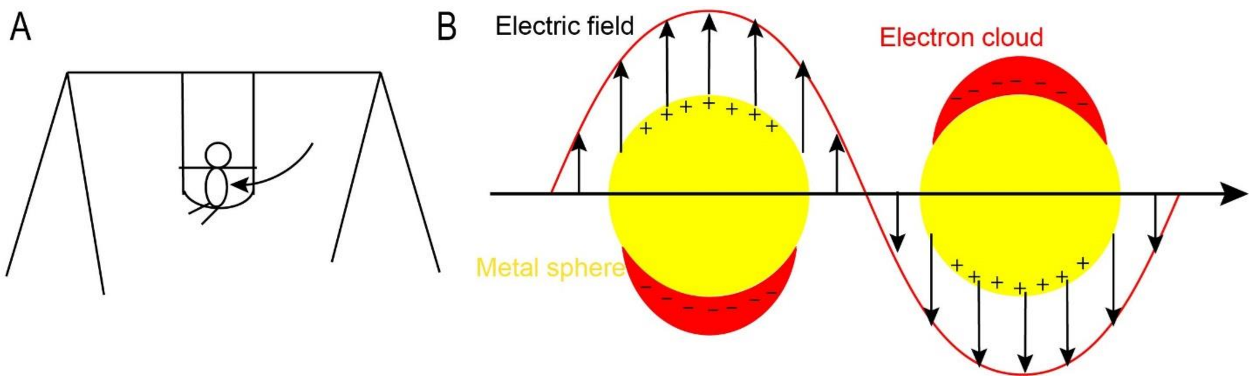

Figure 8.1 Understanding oscillation and plasmon. (**A**) A child is pushed to swing. (**B**) A plasmon (oscillation of electron cloud) in a metal is generated by an electric field.

How do we generate the plasmon? Since it is a cloud of electrons that move periodically, a matter that generates this plasmon must have electrons, specifically, electrons that can move freely with very little friction. Metals, like gold, silver, and aluminum, host such free electrons. However, to have free electrons oscillate back and forth in one of these metals, we must make it extremely small, about a few hundred nanometers (~10^{-7} m), which we cannot see with our eyes. However, when this metal is tiny, plasmons are produced by light of only certain colors (like red light). Since light is also a wave, a formal description for the color of light is frequency or wavelength. We call this condition under which a plasmon is produced a resonant condition. Just like when I want to push a swinging kiddo at a different speed, I would have to fight against the already moving swing. Plasmons must be in harmony with light at a specific frequency.

Now I would like to briefly talk about some important properties of plasmons, which are important to understanding interactions when plasmons mingle with photons in the following discussion. First, the oscillation of free electrons will have a very short lifetime, less than 10^{-13} s. You can think of it this way: after it is generated, a plasmon is already gone before you can blink your eyes. Although it recedes so rapidly, it can be localized in an extremely finite volume, for instance, a few hundred cubic nanometers, due to its tiny physical size.

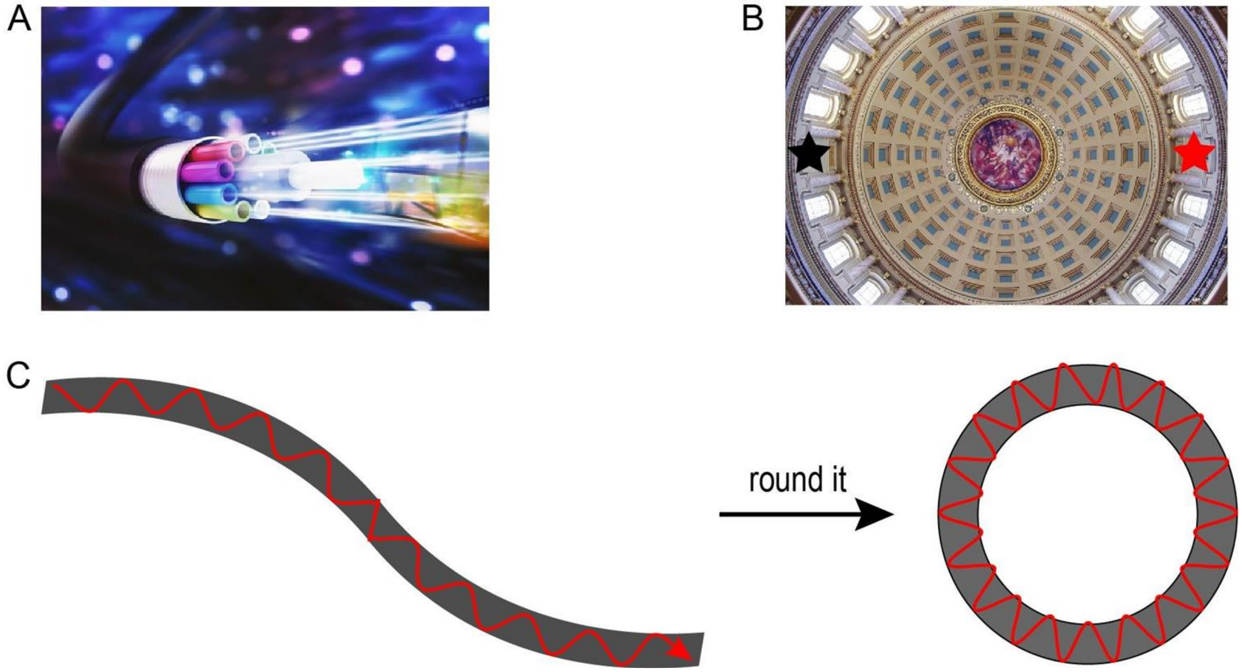

Figure 8.2 Whispering-gallery waves and microcavities. (**A**) The whispering produced at the position of the black star can be heard at the position of the red star. (**B**) Optical fibers. (C). A whispering-gallery cavity is equivalent to a rounded optical fiber.

Photons and whispering-gallery-mode microcavities

Now we have some idea about how a plasmon can act like a particle (a cloud of electrons) and a wave (oscillating behavior). This dual property is exactly like light, or a photon. In daily life, photons are everywhere, for instance, that's why you can read my thesis on a screen. It is because your screen is lighting up and emitted photons are perceived by your eyes. As I just mentioned, a photon is traveling like both a sound wave and a ball. Unlike a sound wave, which must travel in a medium, a photon can travel even in a vacuum where there is no air at all. Also, the photon can travel in a material, for instance, an optical fiber (**Figure 8.2A**), which transmits encoded information at the speed of light. That's the reason why we have internet and are connected to the world.

My research interrogates the behavior of photons propagating in such materials, like silicon oxide, that make the core of optical fibers. We make a unique structure of silicon oxide so that photons can stay inside it for a very long time or have a long lifetime, such as a few tens of microseconds (10^{-5} s). Although it might still sound very short, this lifetime is way longer than that of a plasmon. Now the question is what kind of structure can keep photons traveling so long. Researchers were inspired by sound waves propagating in the whispering gallery of St Paul's Cathedral and invented an optical analog. We can find a similar structure in the State Capitol of Wisconsin (**Figure 8.2B**). Let me use this structure to briefly explain how a sound wave propagates in it. When I stand at a spot along this peripheral ring and then whisper, you can hear my voice at any spot as long as you are still close to this ring, even far from me. We call this type of propagation whispering-gallery waves or whispering-gallery modes. The structure we use for photons is very like this whispering gallery or we think of it like a closed loop of an optical fiber (**Figure 8.2A and Figure 8.2C**). We can imagine that photons are traveling in this loop repeatedly up to millions of round trips under certain circumstances. One condition for keeping my whispering propagating along this ring so that you can hear clearly is that I must whisper at certain frequencies, i.e., my sound must be resonant with this structure. We call this resonant structure a cavity. Likewise, light only at certain frequencies can travel in such a whispering-gallery-mode cavity. If a cavity has a larger size or a larger diameter, then the resonant frequencies would be smaller, or wavelength would be longer. Photons tend to travel a longer distance per period (the interval of time between successive occurrences in a wave) to finish one circulation under this condition. This cavity is not empty but filled with material. Our lab makes a chip of such whispering-gallery-mode cavities whose size is around 50 micrometers ($5*10^{-5}$ m). One such microcavity is presented in **Figure 8.3A**. We can see a disk made of silica sit on top of a pillar made of silicon, or a microscopic "mushroom", as visualized by the scanning electron micrograph. This mushroom is sensitive to humidity, pressure, and temperature because a change in external conditions can affect the frequency of light propagating within this cavity. We can make several sensors out of this mushroom and even transform them into portable devices. Such a device can be incorporated in a mobile phone so that one can obtain information about relative humidity and temperature in a room conveniently.

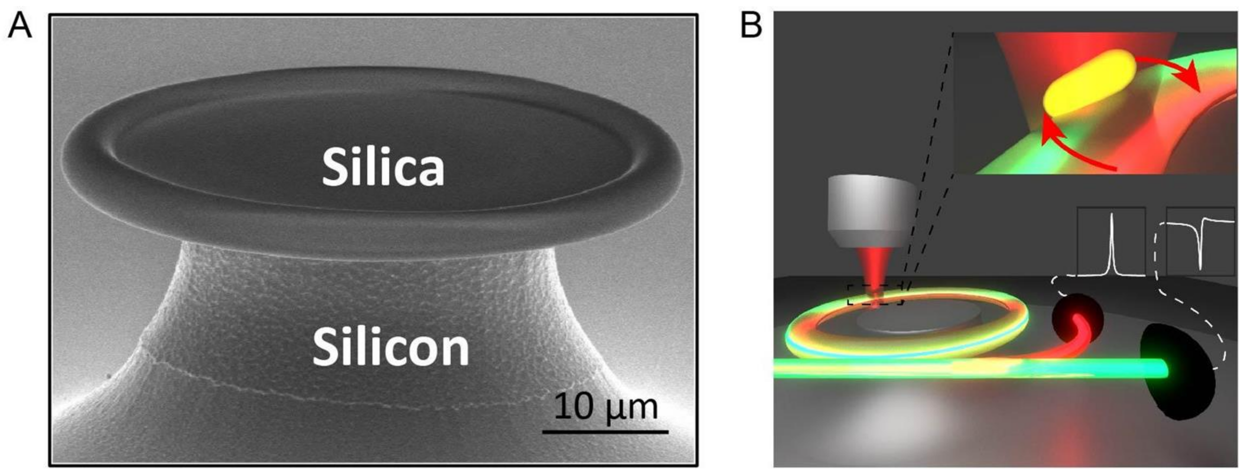

Figure 8.3 A whispering-gallery microcavity and my experimental scheme. (**A**) A scanning electron micrograph of a microtoroid cavity. The scale bar is 10 micrometers (10^{-5} m). (**B**) A mingled system is illuminated by a laser beam (red cone) and energy is redistributed within the system. The whole information about this energy redistribution process is perceived by the two photoreceivers (black hemispheres) as two distinct spectral signatures (white curves in the two boxes). A gold nanorod (yellow glowing rod, inset) is on the surface of the whispering-gallery microcavity shown in **A**.

Whispering-gallery-mode microcavity as a tiny thermometer

We can use this whispering-gallery-mode microcavity as a tiny thermometer in an experiment and then determine absorption ability of molecules or how many photons are absorbed per second by a molecule, like any dye molecule you can imagine. To understand how this temperature sensor works, let's recall the resonant condition. Only photons (light) at certain frequencies can travel in this microcavity. Fortunately, we can change this resonant condition by tweaking the local temperature because one of the optical properties in this microcavity, refractive index (the ratio of the velocity of light in a vacuum to its velocity in a specific medium, here the microcavity), linearly depends on temperature. When the local temperature increases, the refractive index will increase and only photons at a shorter wavelength (or higher frequency) can travel in the microcavity now. I track the change in wavelength in my experiments when the refractive index changes. Thus, I can use this microcavity as a tiny thermometer to sense a change in temperature. The temperature change I can measure here is very minute, even below 10^{-6} K. This capability allows me to determine how many photons are absorbed by a single molecule per second. When I shine light upon a single molecule, the molecule absorbs a certain amount of light and eventually converts this energy into heat, which results in a change in the local temperature. I finally obtain the number of photons being absorbed by this molecule per second by measuring the change in temperature. If a gold nanorod that hosts a plasmon sits on the microcavity, I can certainly determine the number of photons being absorbed by this nanorod per second while a plasmon is generated. I use this powerful tool to glean important information about how energy is redistributed and dumped upon light irradiation in a mingled system that hosts plasmons and photons in its components.

What we learn from a mingled system

I lay out a foundation for understanding plasmons, photons, and cavities as well as how to determine absorption ability in a gold nanorod in the previous sections. Now let's see what will happen when we mingle plasmons and photons together. We can consider that plasmons exist in a nanoscopic cavity (in a length scale of 10^{-7} m) while photons are in a microscopic cavity (in a length scale of 10^{-5} m). When we bring them together, it is interesting to see how plasmons and photons communicate with each other and whether their own behavior will be influenced by this communication. This understanding has significant implications for creating highly sensitive assessment tools even better than the whispering-gallery-mode microcavity itself for biological applications and building optical networks for communication and information storage. In my research, I attach a single gold nanorod that can host a plasmon to the surface of a whispering-gallery-mode microcavity that can host photons. The photons in this microcavity can either come from energy conversion between plasmons and photons due to the communication between the two worlds or be launched into the system through an optical fiber. I use the whispering-gallery-mode microcavity for two purposes, one as a tiny thermometer for measuring photons absorbed by the mingled system per second, the other as a component microcavity for mingling with the gold nanorod (**Figure 8.3B**). Note that these two purposes are not interfering with each other. I tightly focus a laser beam through an objective lens to a very small area (10^{-12} m^2), as represented by the red cone shown in **Figure 8.3B**, which illuminates the gold nanorod (yellow glowing rod, inset) on top of the whispering-gallery microcavity (**Figure 8.3A**). This illumination generates plasmons in the gold nanorod and then plasmons may convert into photons propagating in the microcavity. An optical fiber that is brought close to this mingled system captures photons leaking out from the system. I use photon receivers (black hemispheres in **Figure 8.3B**) to measure these leaking photons and convert them into an electrical signal that I can read on my computer, like how our retinas perceive incoming light and converts it into an electrical signal sensed by our nerves and then finally processed by our brains. Ultimately, by analyzing the spectral signatures (white curves) shown in **Figure 8.3B,** I paint a full picture of energy flow in both the nanoscopic and microscopic world. I find that although energy is exchanged between these two worlds, the exchange rate is slower than the rates that plasmons and photons dump energy to their local environment. These two worlds primarily operate on their own but occasionally communicate with each other.

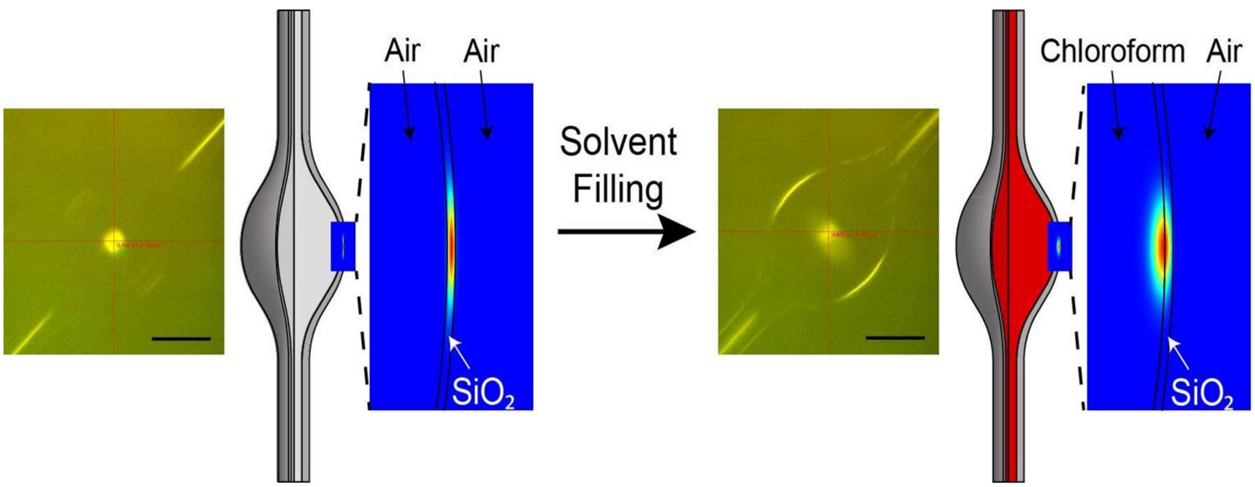

Figure 8.4 Optical difference between a bubble-shape microcavity filled with air and an organic solvent. Optical image, microbubble geometry, and false color image for electromagnetic field are shown in sequence under each filling condition. The black scale bar is 50 micrometers.

To make them connect more closely, I then invented a new method to manipulate the interaction between plasmons and photons. Instead of using the mushroom-shaped microcavity shown in **Figure 8.3A**, I choose a bubble-shaped microcavity like an extremely small soap bubble (~10^{-4} m), another member of the whispering-gallery-mode microcavity family. This microcavity has a hollow structure so that I can flow a variety of liquids through the microcavity to modify the refractive index inside the microcavity. This property governs how photons travel in this microcavity, just like that a chopstick looks bent in a glass bottle filled with water. When the microcavity is just filled with air, photons primarily propagate inside the thin glass (SiO_2) wall, as shown in the false color image of the electromagnetic field on the left (**Figure 8.4**). Note that when a photon travels in a vacuum or specific medium, it results in a specific pattern of electromagnetic field distribution. If we look at the air-filled microbubble in a microscope (optical images in **Figure 8.4**), we barely see the profile of the microbubble. When illuminating light is reflecting at the air-glass interface many times due to the high contrast in refractive indices between air (1.0) and glass (1.45), we will see the image get blurred. By contrast, when a liquid, for instance, chloroform, fills the microbubble, there is a striking difference. First, we can see the profile of the microbubble much more clearly in the optical image. The reason is that there is a very small contrast between the filling medium (1.43) and glass (1.45) and reflection at the interface is largely eliminated. We can experiment with this behavior by watching the difference before and after filling a glass bottle with water. In the meantime, the electromagnetic field also populates the filling medium, acting like there is no difference between the glass and the liquid (**Figure 8.4**).

How does this filling enhance the communication between plasmons and photons? When a gold nanorod is sitting on the surface of an interior glass wall and we then fill the microbubble with a liquid (chloroform), we will see that the liquid totally immerses the gold nanorod. As I show the electromagnetic field in the liquid-filled microbubble in **Figure 8.4**, we observe the most intense electromagnetic field at the interface, which is exactly where the gold nanorod may sit. When photons are traveling in such a microbubble, plasmons are more likely to interact strongly with photons because they are closer to each other. When we flow a different liquid which has an even higher refractive index than glass, we will see that the electromagnetic field favors the liquid now and plasmons will interact less with photons again. Basically, by changing the refractive index inside the microbubble, we can control the communication between plasmons and photons. The control of this interaction will provide insight into the rational design of new sensors that can better harness the advantages of plasmons and photons.

Understanding this mingled system provides the knowledge about which knob we need to tweak for getting an even better system. For instance, like the communication between plasmons and photons I presented above, we can tweak this parameter to create a strongly interacted system so that the transformation between plasmons and photons is easier to occur. In the meantime, an elegant control over the mingled system leads to a more sensitive tool for studying molecules and materials. One application might be to create new sensors and imaging tools for detection and measurement of single molecules. Researchers might use this diagnostic tool to determine the size of different viruses or tiny particles and even identify different proteins in solutions. Also, when we anchor a substrate (a molecule that can attract specific proteins) onto this mingled system, we can examine binding behavior of proteins to the substrate at the single-molecule level. This knowledge is important to design new drugs for curing diseases. One day we may transform this mingled system into a portable device for field experiments to sense air quality because our mingled system responds very sensitively to low-concentration particulates in the air.