Synthesis and Characterization of Silver Nanostructures and their Application in Surface-Enhanced Raman Spectroscopy

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Abstract

Silver can be used to make elongated nanoparticles that are more flexible, durable, and cost effective than carbon nanotubes. Additionally, these nanowires provide greater emission of light, which potentially allows them to enhance the spectroscopic signals given off by other compounds. Since their size can be manipulated simply by adjusting the reaction time, these nanostructures can be made into controlled shapes in order to study the relationship between their dimensions and optical properties. The purpose of this experiment was to reproduce a simple method for growing silver nanocrystals in controlled structures and use them to amplify the weak scattering signal of a low concentration compound using surface-enhanced Raman spectroscopy. Although it was predicted that the long nanowires would provide the strongest signal, it was actually found that the nanostructures with the 5-minute reaction time generated nearly five times as much signal enhancement as the ones from the 60-minute sample. This is theorized to be due to the increased surface area to volume ratio of the spherical nanoparticles compared to the long nanowires.

Introduction

Silver is one of the oldest and most well-known elements, and its atomic symbol, Ag, is derived from the Latin argentum which means "shiny" or "white". When smoothed and polished, bulk silver reflects about 95% of visible light, and this is what allows you to see your reflection in a mirror. But when you shrink things down to the nanoscale, they can behave much differently, and with silver you start to see some very interesting properties emerge. For example, silver halide nanocrystals are the active ingredient in photographic film, because the silver reacts with the light from the camera flash, causing the film to darken in that spot (and that's why film has negatives that need to be developed).

It turns out that silver can be used to make nanowires that are more flexible, durable, and cost effective than carbon nanotubes (Murphy, Gole, Hunyadi, Orendorff, 2006). Additionally, these nanowires provide

greater emission of light, which is essential for such products as device screens and the photovoltaic cells used in solar panels (Murphy, et al., 2006). Since the size of silver crystals mostly depends on the length of the reaction, and the shape of the crystals can be manipulated by using different reagents (Wiley, Sun, & Xia, 2007), it is possible to produce batches of nanocrystals in controlled structures in order to study the relationship between their dimensions and optical properties.

These silver nanoparticles may have many applications in spectroscopy, which measures the interaction between matter and light to see how much is absorbed or how much energy is emitted as a result. It was predicted that the nanoparticles could be used to increase the intensity of the weak spectroscopic signals given off by other compounds, potentially allowing the detection of chemicals even in very minute amounts (Fantini, et al. 2004). The ultimate purpose of this project was to perform a simple procedure for synthesizing silver nanocrystals in elongated structures, and further use those structures to amplify the signals of a low concentration solution of Rhodamine 6G using surface-enhanced Raman spectroscopy. The long nanowires were expected to provide the strongest possible signal, with the short nanostructures causing a proportionally reduced amount of signal enhancement.

Synthesis

The one-pot method for growing silver nanowires originally designed by Lee, et al. (2015) and refined by Ferraro and Fratini (2018) was reproduced for this experiment. This procedure began with 15 mL of ethylene glycol (EG) in a 50 mL round-bottomed flask, which was placed into a 160°F mineral oil bath with a stir bar and heated for one hour. Then, 120 μL of 4 mM copper chloride (CuCl2) was added, and the solution was stirred and heated for fifteen more minutes.

At this point, 4.5 mL of 0.147 M polyvinylpyrrolidone (PVP) was also added. Finally, 4.5 mL of 0.094 M silver nitrate (AgNO3) solution was slowly injected into the solution dropwise over a fifteen-minute period. For optimal nanowire production, the solution was heated for sixty minutes, but samples were taken incrementally, placed in vials, and quenched in water.

The process of crystallization for silver nanostructures is outlined in Figure 1, below. The first step is the creation of silver seeds in solution, known as nucleation, which comes from the reduction of silver ions from Ag+ to Ag0 by the heated EG solvent. The dissolved silver begins to cluster together into nuclei, and the neutral charge favors the formation of crystal seeds with desired pentagonal structure (Ferraro and Fratini, 2018). Any remaining silver ions are distracted by the chloride ions from the CuCl2 to instead make silver chloride, AgCl. In the second step, crystal growth, the nanocrystals continue to grow into larger structures with different shapes. The dimensions can be controlled by stabilizing different facets of the crystal. The PVP, a polymer with a very large molar mass, accomplishes this by adhering to the long sides of the nanostructures, which concentrates all the growth on the short faces (Ferraro and Fratini, 2018). The copper ions also remove any oxygen from the crystal surface that would normally hinder the growth (Ferraro and Fratini, 2018).
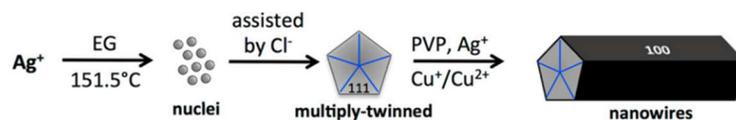

Figure. 1 The primary stages of elongated silver nanocrystal growth from Ferraro and Fratini (2018).

Characterization

It was necessary to confirm not only that the nanocrystals were being formed, but also that they had the structure that the reaction supposed to be controlling for, so a purified

sample of 60-minute nanostructures was sent for microscope imaging. In scanning electron microscopy, an electron beam is aimed onto the sample through a lens, and the excited sample emits secondary electrons. The beam scans across the sample and the instrument registers these electrons, and it generates an image of the sample's surface. (Sawyer, Heineman, & Beebe, 1984). A technique known as ion milling was also applied, using an argon ion laser to cut across a sample of nanowires so that their cross section could be viewed. This imaging, seen in Figure 2, below, verified that the procedure was producing nanocrystals with the intended pentagonal structures.
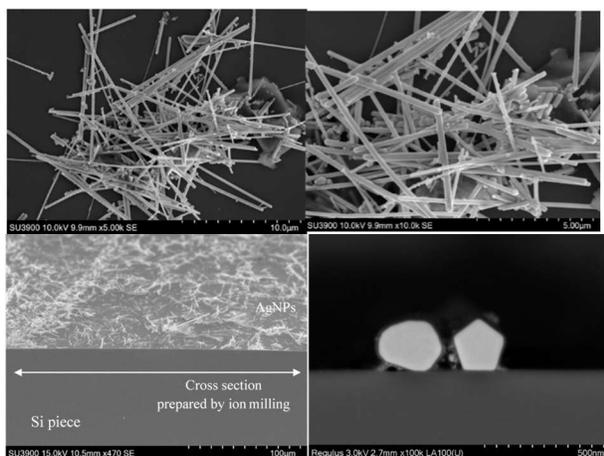
Figure 2. Scanning electron microscope imaging results with the magnification level labeled, courtesy of Atsushi Muto with Hitachi High Technologies America, Nanotechnology Systems Division, Maryland Applications Lab. Based on (b), the nanowires are at least 5 micrometers (or 5,000 nanometers) in length, with (a) showing nanowires as long as 20 micrometers.

Application

Raman spectroscopy relies upon inelastic scattering of photons, known as Raman scattering, to provide a structural fingerprint by which molecules can be identified. In this technique a laser interacts with the molecules, resulting in the energy of the laser photons being shifted. When light is scattered from a molecule, most photons are elastically scattered, meaning they have the same wavelength as the incidence light. However, some of the photons are scattered inelastically (at a different wavelength) instead. This is what is detected by the instrument, and the shift in energy gives information about the functional groups in the molecule. Since Raman scattering signals are very weak, surface-enhanced Raman spectroscopy amplifies the signal by using the electric field of the surface the sample is on, which in this case was the nanostructures (Lombardi & Birke, 2009).

For this application, the molecule being detected was the fluorescent dye Rhodamine 6G. The fluorescence emission is much stronger than the scattering, and there is also an overlap in wavelength, so it just overwhelms the signal. The only way to use Raman spectroscopy on a compound like this is to have it in a very low concentration, and to enhance the weak scattering signal against the background noise using the nanoparticles. It was predicted that the long reaction time sample would provide more signal enhancement due to the long sides and edges of the nanowires. A thin layer of acetaminophen, a known strong scatterer, was also used to calibrate the focal length of the laser, which must be focused directly onto the layer of sample (and not the filter paper or glass slide).

Two separate batches of nanoparticles were produced to ensure the same concentration in each sample. One solution was quenched after five minutes, while the other was reacted for the full sixty minutes. Small samples (~50uL) of the different nanoparticles were dropped onto filter papers and dried, and then the same volume of 1x10-4 M Rhodamine 6G solution was layered on top of them. The filter papers were then taped

to a glass slide and fastened in the sample compartment of the instrument. The laser was focused onto different spots on the filter paper for a minimum of three trials per sample.
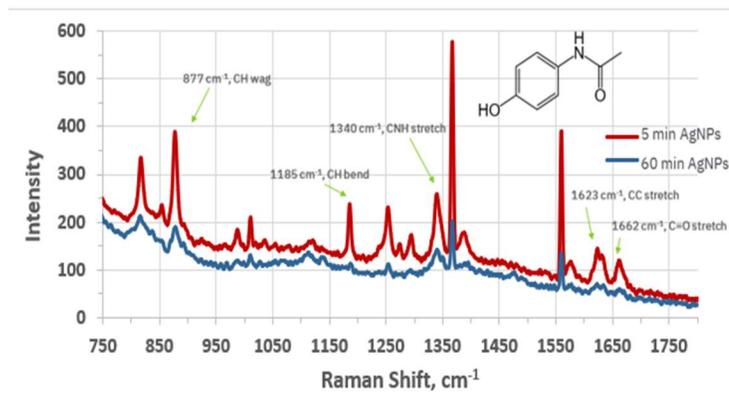

Figure 4: The Raman spectra for a thin layer of acetominaphen. Some of the functional groups of the molecule could be identified by the vibrational frequencies of the peaks.

As you can see, many of the peaks for the 60-minute sample were so weak that they were essentially lost in the background noise.

However, the sample from the 5-minute reaction had a strong enough signal that many of the structural features of the molecule can be identified. By comparing the height of the peak at 1340 cm-1 for all three trials of both samples, it was found that the 5-minute nanoparticles generated about 4.5x more signal enhancement than the 60-minute nanostructures, with a margin of error of about 13%. This is the opposite of what was initially predicted, and is theorized to be due to the increased surface area to volume ratio of the small, spherical nanoparticles compared to the long nanowires. Although this confirms that silver nanostructures are viable for application in surface-enhanced Raman spectroscopy, additional testing is still needed with a low concentration fluorescent dye, since the signal was too weak to positively identify any peaks. Future areas of research could include a similar analysis with shorter reaction time nanoparticles to discover which structures produce the most signal enhancement.

References

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