Nanoparticle Shape Effects on Sintering Temperatures

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Abstract

This project involved attempting to isolate silver nanoparticle shapes in an attempt to see if the shape of the particle had any effect on sintering temperature. A polyol process was used to synthesize the nanoparticles. Ethylene glycol was used as a solvent, poly(vinyl pyrrilodone) (PVP) was used as a surfactant, and hydrochloric acid was used to prevent twinned seed formation. Isolated particles were synthesized to produce enough material for a DSC analysis.

Introduction

Silver has been used for decoration and jewelry since its discovery. Its use as a precious metal is based on its properties of high ductility, malleability, and its ability to take a high degree of polish. A newer application for silver's use in jewelry making is precious metal clays. These clays consist of nanoparticles of silver mixed with an organic binder that can be shaped and molded like clay. After forming the clay and letting it dry, the clay can be fired to remove the organic binder and you are left with a high purity silver piece. This project examines the particles used in the clay.

The objective for this project was to determine what effects nanoparticle shapes have on the sintering temperatures of silver. Particle shapes examined include: cubes, plates, and rods. All particles involved were created using a polyol synthesis process(1).

Broader Impact

In a broader focus, this research could potentially affect the marketability of precious metal clays. By isolating and determining which particle shape has the biggest effect on the sintering temperature, a synthesis can be refined to produce larger quantities of this shape and minimizing the size of particles. Lowering the sintering temperatures makes precious metal clays more marketable because an expensive furnace would not be needed to fire the clay products. A person could potentially be able to fire the clay products in a conventional oven or a normal household microwave(2).

Experiment

The polyol synthesis used is a very simple process, but it takes between 16 and 24 hours for the reaction to complete. Temperature control is very important in the synthesis of silver nanoparticles. The desired particle shape determines the temperature at which the reaction has to take place. The process uses ethylene glycol as a solvent and uses poly(vinyl pyrrolidone) (PVP) as a surfactant. PVP attaches to the surface of the nanoparticles as they grow. When the PVP has attached to the particle, it inhibits that facet from growing anymore. The PVP attaches itself based on the surface energy of the particle(4). Surface energy is controlled by the temperature of the reaction. The reaction temperature also plays a role in the attachment of PVP to the silver particles. PVP will attach at different surface energies depending on the temperature of the reaction.

Each synthesis has the same basic format; the only variable changed in the process is the temperature. Using a temperature control to heat an oil bath to the desired temperature, 12 mL of ethylene glycol was placed in a flask and then suspended in the oil bath. A hydrochloric acid solution was created by adding one drop of 12.7 M HCl to 5.16 mL of deionized water. One drop of HCl solution was added to the flask. Silver nitrate and PVP were weighed out to .090 g and .098 g, respectively. Each of these samples were then placed into 6.2 mL of ethylene glycol and dissolved on a slightly heated hot plate. The two solutions were then placed in syringes and added to the flask using syringe pumps. After the addition of silver nitrate and PVP, a thermometer was placed in the solution for temperature monitoring. Throughout the entire process the solution was stirred with a magnetic stir bar and vapor was condensed using a condenser placed over the flask.

After about 16 – 24 hours the synthesis was stopped and the flask was flooded with deionized water. The particles then had to be filtered out of the solution using a vacuum pump and a glass nano-sized filter. It is crucial to wash the particles thoroughly as any residual PVP left on the particles will cause them to continue to react which is an undesirable result(3).

After developing a synthesis that isolates the different particle shapes, each synthesis will be conducted to produce enough nanoparticles to be analyzed using a differential scanning calorimeter (DSC). The concentrations of silver nitrate, PVP, and hydrochloric acid were the same as the small scale syntheses. The DSC tests were run on samples that contained the following: rods with a lot of random particle shapes, rods with a small amount of randomly particles, pure rods, and a sample that was a majority of cubes. DSC analysis involved ramping the temperature from 40 degrees C to 400 degrees C at a rate of 10 degrees C per minute. Next, the sample was cooled from 400 degrees C to 40 degrees C at the same rate. Then the temperature was ramped back to 400 degrees C and finally was cooled to 40 degrees C at 20 degrees C per minute.

Results

The synthesis was run at a temperature of 140 degrees C for 16 hours. This synthesis was used to produce silver nano-cubes. The cubes produced were of a very uniform size with a majority of the cubes ranging between 200 – 250 nanometers. There was also a significant amount of particles in the range of 25 – 50 nanometers.

The synthesis was conducted at 125 degrees C for 18 hours. When the product was examined under the scanning electron microscope(SEM), the particles were extremely small and not a very large number were produced. There was no discernable shape pattern or size distribution for the particles. The particles seen were very jagged and not uniform in size.

The next synthesis temperature was then raised to 130 ^{o}C for 18 hours. This showed the production of two distinct different shapes, cubes and plates. In addition, the filtering process seemed to have separated the two shapes. The cubes were imbedded in the nano-filter as shown in Figure 1, and the plates were removed from the surface of the nano-filter as shown in Figure 2.

Cubes were removed from the filter using the sonicator to dislodge the particles from the filter. Particles embedded in the filter also contained a few scattered octahedrons, but for the most part the overwhelming majority of the particles were extremely well-formed cubes. The cubes ranged in size from about 200 – 300 nanometers. The plates had a size range of about 100 – 300 nanometers and a thickness of around 10 nanometers.

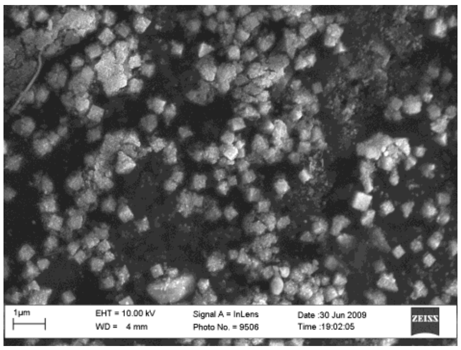


Figure 1. SEM image shows the cubes that had become imbedded in the nano-filter.

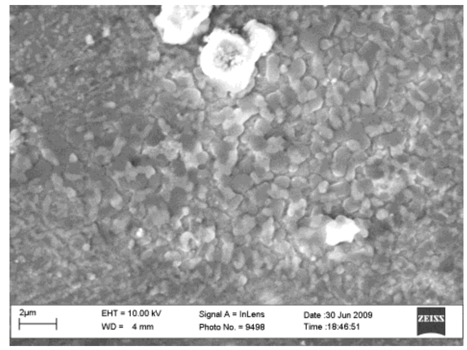


Figure 2. SEM image shows the plates that were scratched off the surface of the nano-filter.

Since the above filtering result was not expected, the synthesis process was run again but this time the process only ran for 14 hours. This had a dramatic effect on the results of the experiment. There was very little product produced and the particles that were produced did not have a narrow size distribution and no discernable shapes were produced.

With the two very different results, the synthesis was run again for 24 hours. This synthesis produced a large amount of product that had a wide size range. The majority of the particles were in the range of 300 – 400 nanometers. Some particles were produced down to the size of less than 20 nanometers. However, no discernable shape patterns were produced. The particles produced were essentially random smooth shapes.

To produce enough material for DSC testing, the synthesis had to be scaled up. Rods were the first nanoparticle produced. The temperature controller was set to 155 degrees C. The same concentrations of silver nitrate, PVP, and hydrochloric acid were used as in the previous synthesis. The first synthesis produced some rods, but it also produced a lot of other undesirable, random particle shapes. The rods that were produced had a diameter range from about 50 – 250 nanometers. These particles are shown below in Figure 3. A second synthesis was conducted to produce rods, and the product can be seen in Figure 4. The material produced was almost pure rods. The rods produced were very uniform in diameter with a range from 75 – 125 nanometers. Both experiments produced enough product for DSC testing.

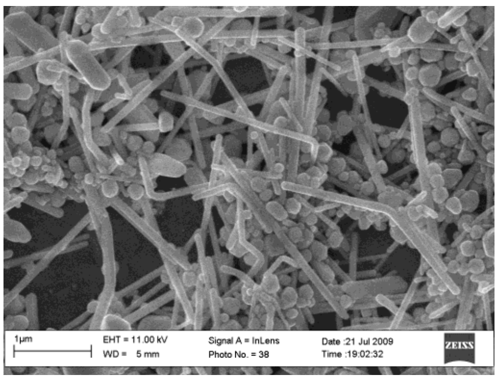


Figure 3. SEM image shows formation of rods with other assorted particle shapes.

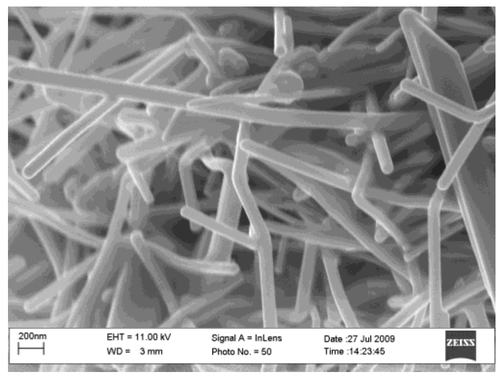


Figure 4. SEM image shows rods that have been isolated.

A large scale synthesis identical to the one used to produce rods was run at 140 ^{o}C, with the desired target shape being cubes. The product from this synthesis was entirely rods. They had a very uniform diameter range of 75 – 125 nanometers. Enough rods were produced for DSC analysis.

Discussion

Some synthesis product was affected by improper rinsing. Figure 5 shows an example of a thin ethylene glycol and PVP layer still on the particles. If you examine Figure 6, these particles were originally cubes, but most of them have formed into tetrahedrons or octahedrons. This is due to the particles desire to reach its most stable form, a perfect sphere. The fewer defined edges a particle has the more stable it becomes. This explains why the cubes will form into more stable particles if improperly rinsed.

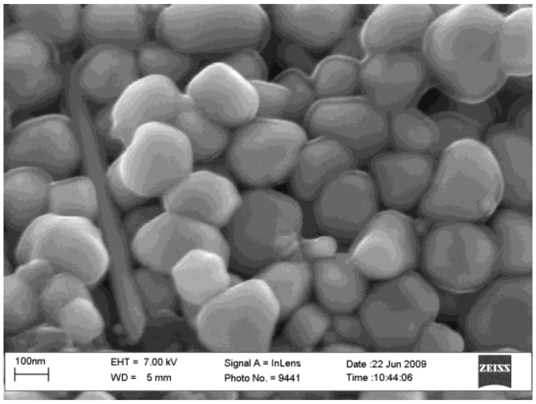


Figure 5. SEM image shows thin layer of ethylene glycol and PVP still on the particles

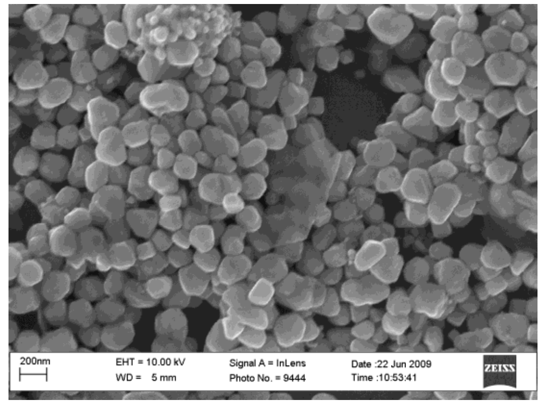


Figure 6. SEM image shows formation of cubes, tetrahedrons, octahedrons, pyramids, and plates.

The synthesis conducted at 125 ^{o}C showed that at that particular temperature the kinetics of the reaction are not fast enough for the nanoparticles to completely form, or there was simply just not enough heat available to make the reaction proceed at all. The length of the reaction was not varied with this temperature because the SEM results did not show any desirable particles.

The syntheses conducted at 130 ^{o}C had the most varied results. The first result showed the formation of both cubes and plates, and the filtering process separated the two nano-shapes extremely well. However, these results were never duplicated in either of the two subsequent syntheses conducted at 130 ^{o}C. The second synthesis showed almost no particle formation and this was due completely to the length of the reaction being too short. The third synthesis ran for about 20 hours and it produced an adequate amount of nanoparticles. The problem with these particles was that they did not seem to have any defined shape patterns. It is speculated that the ill-defined shapes were the result from letting the reaction run for too long of a time period or not keeping the reaction temperature near the 130 ^{o}C target.

The synthesis that was conducted at 140 ^{o}C produced mostly cubes and the lower energy particles that cubes react to become. Cubes seem to be the most temperature sensitive because the syntheses that were conducted to produce them had such varied contents of cubes in the product. Thus, it appears that isolating cubes for DSC analysis is very difficult because cubes seem to be very unstable.

Overall, the syntheses at 155 ^{o}C were the most successful. A side from the first experiment, these syntheses produced product that was in large majority rods, as shown in Figure 7. The first experiment was conducted without adequate temperature control which explains the formation of the undesirable particle shapes. The second synthesis produced significantly less random shapes because the temperature was controlled well.

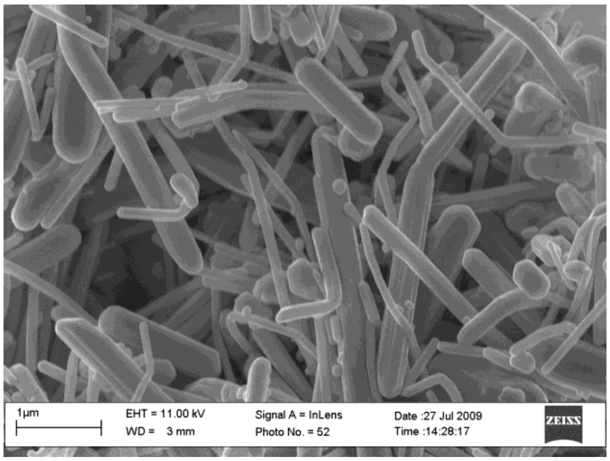


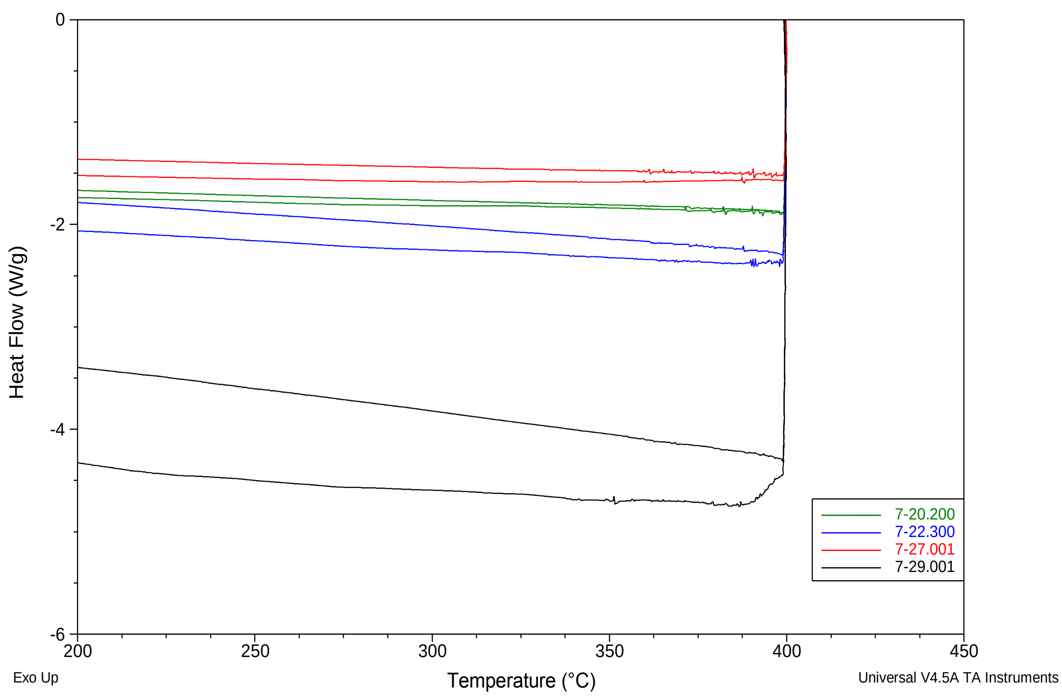
Figure 7. SEM image of silver nanorods.

The most interesting results were from the large scale 140 ^{o}C synthesis. It was anticipated that cubes would be the majority particle-shape formed. Product from this synthesis was the purest single shape sample produced contained almost 100% rods. The temperature when the reaction was stopped was still in the 140 degree temperature range, so it was deemed that the temperature was not the reason for this unexpected result. A possible explanation for this result is with the reaction being scaled up the kinetics could have been affected causing rods to form during the synthesis instead of cubes.

The DSC analysis results, shown in Table 1, did not show any major energy changes. The small peaks seen on the lines are assumed to be from PVP and ethylene glycol being removed from the particles. There are no peaks large enough that would represent sintering. The samples need to be examined under a scanning electron microscope to see if any sintering occurred. It is also recommended that the DSC analysis be ramped up to a higher temperature.

DSC analysis did not show any major differences in sintering temperatures that could be linked directly to particle shapes. Sample 7-20.2 had the most amount of undesirable particles mixed with rods, but its line still lies between the purest rod sample, 7-27, and sample 7-22.3 which had a small amount of undesirable particles mixed with rods. So, this shows no recognizable differences between the three samples. Sample 7-29 was composed of mainly cubes. It does show a slight difference between the energy absorption of rods and cubes. To determine if cubes and rods have a different sintering temperature, the DSC analysis would need to be conducted at a higher temperature or a different style of analysis would need to be conducted.

Table 1. Nanorod DSC Analysis



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