A WET CHEMISTRY SYNTHESIS OF SILVER NANOPARTICLES FROM BULK
MATERIAL

by

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Abstract

An easier, cheaper and scalable method to obtain silver nanoparticles, AgNPs, directly from the bulk material has been obtained. Two different solvents were tried, water and ethylene glycol, the coating agent was polyvinylpyrrolidone, PVP, and two different silver sizes were used, micron size powder and silver shots, millimeter size. It was seen that changing the size of bulk silver, the temperature of reaction, the amount of oxygen, the concentration of PVP and its molecular weight all had an important influence in the synthesis of nanoparticles. Different morphologies could be obtained when these parameters were adjusted ranging from spheres to triangles and hexagons. A complex mechanism is proposed: during the first step, bulk silver is oxidized by oxygen in solution, forming a thin layer of oxidized silver on the surface. Then, PVP acts as a reducing agent at the oxidized surface, where silver becomes Ag^0 again. At the same time that PVP reduces the oxidized silver back to metallic silver; it coordinates with the silver atoms acting as a protecting agent. That coordination between PVP and silver pulls out the atoms and produces a detachment of silver atoms from the bulk surface. These silver-PVP complexes in solution later combine to form silver nanospheres and evolve to rods first and then triangles and hexagon with longer reaction time.

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Chapter 1 - Introduction

Nanomaterials are an outstanding, growing field that has attracted special attention in physics, chemistry, biology, engineering and materials science. Metal nanoparticles, specially silver and gold, have unique chemical and physical properties including optical, electronic, magnetic, and catalytic properties.[1] At this length scale, the properties of a given material deviate significantly from its bulk counterpart and allow size and shape to provide useful control over those properties. These optical absorption properties are associated with collective oscillations of free electrons at the metal surface and they are called surface plasmon resonances. These surface plasmon resonances can be observed in a UV-Vis spectrometer where an absorption plasmon peak would appear at different wavelengths depending of the composition, size and shape of the nanoparticles. Spherical particles exhibit a single absorption peak, where other shapes such as rods, triangular prisms, and cubes can exhibit multiple absorption peaks at different wavelengths due to multiple electron oscillations in the surface of the nanoparticle. Therefore, intrinsic properties of a metal nanoparticle are mainly determined by its size, shape and composition. In principle, one could control any one of these parameters to fine-tune the optical properties of the nanoparticle.

Among these metal nanostructure, silver nanoparticles (AgNPs) have attracted a great deal of interest in various fields such as the environment, biomedicine and bio-labeling, catalysis, chemical analysis, solar energy, optics and electronics.[2,3] Among all these application, AgNPs exhibit an special importance for its bactericidal and fungicidal activity that has made them extremely popular in a diverse range of consumer products, including plastics, soaps, pastes, food and textiles, increasing their market value.[4]

According to BBC Research (www.bbcresearch.com) the global market for nanotechnology products was valued at $22.9 billion in 2013 and increased to about $26 billion in 2014. This market is expected to reach about $64 billion by 2019, a compound annual growth rate (CAGR) of 20% from 2014 to 2019. Also, according to the Project on Emerging Nanotechnologies (PEN, http://www.nanotechproject.org) over 1300 manufacturer-identified, nanotechnology-enabled products have entered the commercial market place around the world. Among them, 24% of the products are utilizing nanosilver, this has made silver nanoparticles the largest and fastest growing class of NPs in consumer products applications. For all these reasons, finding a cheap, easy and scalable process for nanoparticles synthesis, especially silver, has become a crucial issue in the world.[5]

Silver nanoparticles synthesis has been studied in many different systems through the last two decades to gain control of their shape and size. In most cases, a metal salt precursor, usually $AgNO_3$, is reduced in solution in the presence of a stabilizing agent, which prevents aggregation and improves the chemical stability of the formed AgNPs. These colloidal methods are advantageous for two main reasons: the equipment needed and procedure are fairly simple, and the synthesis mechanism is well known providing a fine control in size and shape of nanoparticles. These reactions are mainly governed by two linked effects, thermodynamics, with temperature, and kinetics, with reactant concentration, solubility and reaction time.[2,3] However, some different strategies with different mechanism have been proved to synthesized silver nanoparticles.

Various approaches to the synthesis of metal nanoparticles have been reported such as chemical reduction, electrochemical, γ-radiation, laser ablation solvothermal, hydrothermal, photochemical, sonochemical, and sputtering methods, aqueous solution phase synthesis

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microemulsion techniques, a polyol process and an organic-water two phase process.[1-9] AgNPs can be produced with various sizes and shapes depending on these fabrication methods. The different shapes of AgNPs include spheres, rods, wires, and plates, which can be produced by varying the manufacturing method.[10]

Most of these methods are based on wet chemistry where a salt precursor ($AgNO_3$ for silver) is reduced by some reducing agent from Ag^+ to Ag^0 nanoparticles, and a capping agent prevents those formed nanoparticles from coalescing and precipitating. However, there are two main disadvantages, the cost of the salt precursor and lack of scalability. To obtain these silver nanoparticles the bulk metal needs to be treated to obtained silver nitrate for further use. Many different metal salt reduction methods have been studied but they usually show a lack in scalability into industrial scale.

Laser ablation and sputtering are the most known physical methods where no chemistry is involved in the synthesis of the nanoparticles. Bulk silver is used instead of a salt precursor and the yield of nanoparticles obtained is high. However, the instruments used are expensive and these processes do not provide a fine control of the shape and size of the synthesized nanoparticles.

In this research a novel method is presented where AgNPs are obtained with most of the advantages of both metal salt reduction and physical synthesis methods. The advantages of this method allows production of silver nanoparticles in an easier, cheaper and scalable way as never seen before. As the metal salt methods, this novel synthesis of AgNPs is simple and the instrumentation needed is much cheaper compared to those used in physical synthesis. On the other hand, this novel synthesis has one advantage from the physical methods, the precursor used is bulk silver not silver salt. Besides its lower cost, bulk silver does not need any treatment for its

use, opposite from the treatment needed for nanoparticles production from a silver nitrate compound.

The mechanism proposed for this novel synthesis method is the following: the surface of bulk silver gets oxidized due to the oxygen in solution forming a thin surface layer with Ag^+ atoms. At the right temperatures, PVP reduces those Ag^+ atoms on the surface while attaching to them and pulling them out of the metal surface into solution. These silver-PVP complexes combine to form silver nanoparticles protected by PVP from agglomeration. After the formation of these AgNPs, mostly spheres, they will evolve into rods, and then into triangles and hexagons.

Chapter 2 - Experimental Section

Materials

Silver powder of 3-5 µm size or silver pellets of 2.5 millimeter size in average, PVP with different molecular weights (PVP10=10,000; PVP40= 40,000; PVP360=360,000), and ethylene glycol were all obtained from Sigma Aldrich, and DI water was also used in specific cases.

Instrumentation and characterization

All the experiments were done in a glass round bottom flask with a condenser and a heat mantle in open air as seen in Figure 1.[6] For EDX analysis, a Hitachi S-3500N scanning electron microscope (SEM) was used. The temperature of the solutions were measured with a glass thermometer with, approximately, ±5C variation. For sample analysis, aliquots of 0.25mL were taken from solution and, immediately, analyzed with a Micropack DH-2000 spectrophotometer. Further characterization was achieved with TEM images acquired with a CM-100 transmission electron microscope. In order to remove excess PVP in all the samples, which always affects the clarity of TEM pictures, acetone was added to the solution and then centrifuged for 15 min at 11000 rpm. Then, the supernatant was removed and the precipitate was redispersed in DI water and centrifuged again at same speed and time. Then, this last step was repeated once more and the supernatant became clear, showing the absence of AgNPs. The precipitate was redispersed in a small amount of DI water, then dropped on a TEM copper grid and oven-dried at 60C for 30 minutes. For the Fourier-transform infrared (FTIR) analysis all samples were used in a Nicolet Nexus 670 spectrometer and mixed with potassium bromide pellets.
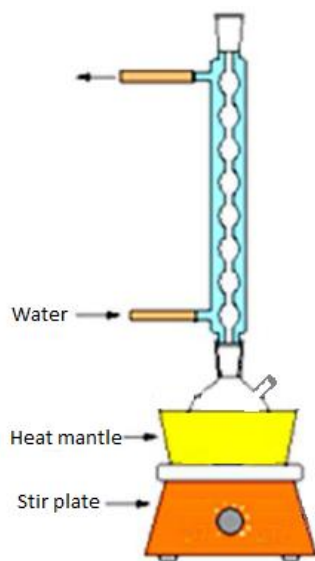
Figure 1.Experiment set-up where reactions were carried out.

Synthesis of Silver nanoparticles

A standard experiment was carried out by the following steps: to a 20ml ethylene glycol solution of PVP (6mM), 20mg of silver powder or 2g of silver pellets were added. This mixture was heated by the heat mantle at different temperatures, ranging from 60C to 195C and a stir plate acted with a stir bar to agitate the solution, continuously. When oxygen or argon was bubbled, a needle was inserted into the solution and the gas was bubbled in a gentle manner.

Chapter 3 - Results and Discussion

Synthesis of silver nanoparticles

The standard experiment consisted on a 20ml solution of ethylene glycol with 6.6mM PVP40 using 20mg of Ag powder (3-5μm) as metal precursor and heated at 120C. The spectra from the UV-Vis shown in Figure 2, shows an absorbance plasmon peak at 410nm after 30min of heating. The plasmon peak at that wavelength indicates the formation of silver nanoparticles as seen in many other researches.[1-5] Also, in Figure 2, a prominent peak indentified with silver appears in the EDX spectra confirming the existence of silver nanoparticles in this standard experiment. Different parameters are studied in order to understand the synthesis and formation of silver nanoparticles from bulk material. These different factors analyzed are: temperature, role of ethylene glycol, role of PVP, water, oxygen, PVP molecular weight and concentration and the type of bulk silver.
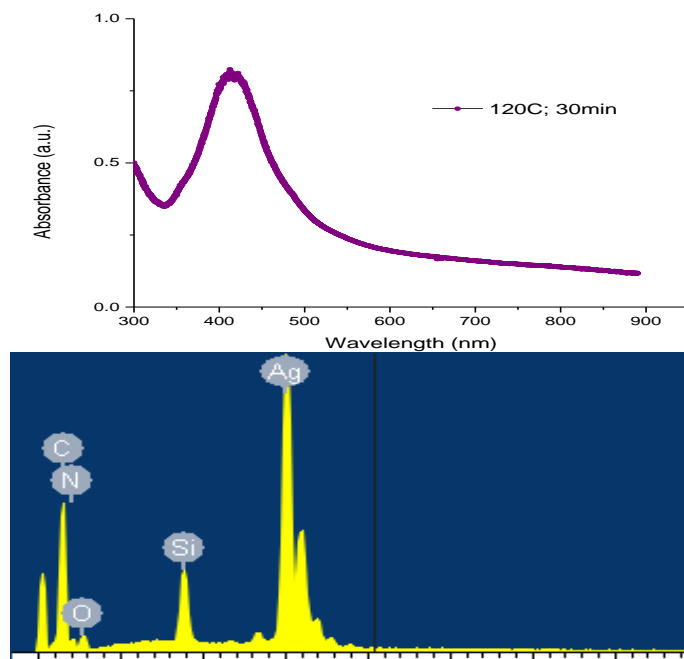
Figure 2. For the standard experiment a) UV-Vis at maximum absorption and b) EDX analysis

Temperature

To study the effect of the temperature, it was the only variable changed and the rest of the parameters were kept constant from the standard experiment. For each of the temperatures, the UV-Vis absorption peak at 410nm grew until a maximum was observed. This maximum was determined as the point where either the peak shifts (redshift) to other wavelengths or a secondary peak appeared at higher wavelengths. The absorbance peak at 410nm shows the existence of spherical AgNPs in solution and its absorbance maximum determines the amount of spherical nanoparticles. Even though, spherical nanoparticles were produced at all temperatures analyzed, experiments done in the range of 75 to 120C show the most prominent peaks, whereas, at higher temperatures from 120 to 195C results show a much smaller peak as seen in Figure 3. The heating time needed to obtain the maximum absorption peaks increased with greater temperatures. Therefore, temperature plays a critical role in the yield on AgNPs where the best

yields of nanoparticles were obtained at low temperatures. To be able to understand the process of synthesizing AgNPs , a further study of the role of the solvent, ethylene glycol, and capping agent, PVP, at different temperatures must be carried out.
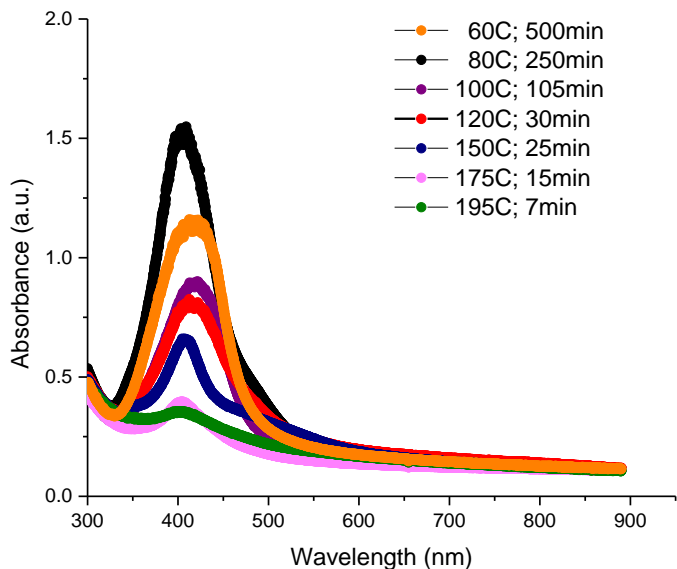
Figure 3.UV-VIS spectra for different temperatures

Role of ethylene glycol

Ethylene glycol is the most important glycol commercially available and is used as an antifreeze and coolant. It has been used in the polyol process as a solvent and also as a reducing agent to obtain different shapes of AgNPs with PVP as a coating agent.[7-14] This behavior can be understood from its structure which has both hydroxyl groups at the end, providing it with both hydrophilic and reducing power, see in Figure 4. At temperatures over 120C, ethylene glycol can also react with oxygen in the system, creating a water molecule and aldehyde compound as seen in Figure 5.[15] This glycolaldehyde byproduct, GA, is a much stronger reducing agent than ethylene glycol, but, in our experiments, when GA is formed above 120C the yield of

nanoparticles greatly diminished. Despite being a stronger reducing agent, GA does not produce more AgNPs.
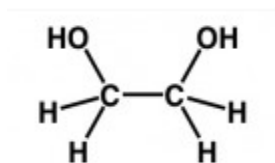
Figure 4. Molecular formula for ethylene glycol

$$2HOCH_2CH_2OH + O_2 \rightarrow 2HOCH_2CHO + 2H_2O$$
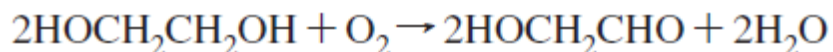
Figure 5. Reaction of ethylene glycol with oxygen above 120C

In order to analyze the effect of GA in the synthesis of AgNPs, one simple experiment was done where a silverless solution with PVP and EG, was heated for 1h at 170C to make sure that enough ethylene glycol transformed into glycolaldehyde. After preheating for an hour, the solution was cooled down to 100C and 20mg of silver powder were added to the solution and no AgNPs were produced at all. On the other hand, when the reaction was performed at the same temperature of 100C without any preheating an important amount of nanoparticles were obtained as seen in Figure 6. As stated before, at temperatures of 100C and below, PVP is the main reducing agent in the system, even better than ethylene glycol.
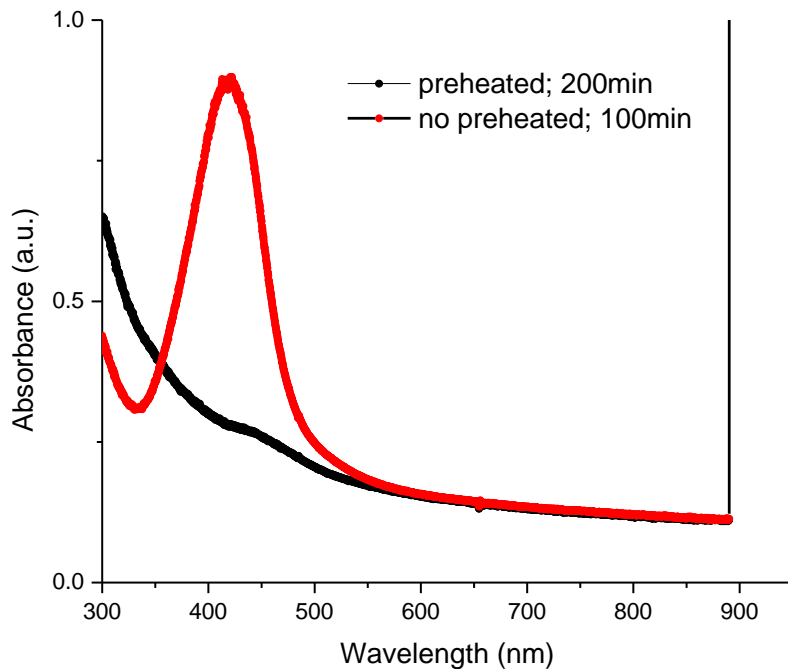
Figure 6. Reaction at 100C with and without preheating at 170C.

Hence, even though the reducing power in the preheated experiment was much stronger with the production of GA, no particles were produced. So, it is not a matter of the overall reducing power in the solution but a matter of which compound is reducing. Therefore, PVP needs to be the reducing agent in the system in order to obtain a large amount of nanoparticles.

Role of PVP

Poly(vinylpyrrolidone), PVP, has received special attention because of its high chemical stability, nontoxicity, and excellent solubility in many polar solvents.[1,2] It has an unique structure, possessing carbonyl group attached to a pyrrolidone ring as seen in figure 7.[7]
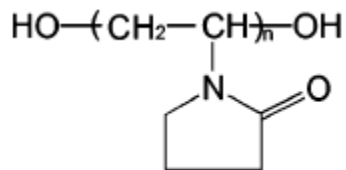
Figure 7. Molecular structure of Poly(vinylpyrrolidone).

It is a commonly used capping agent that not only selectively induces the formation of Ag nanocrystals, but also stabilizes the resultant colloidal suspension via steric repulsion.[9] Also, it has been suggest that electron could cloud strongly partial to the oxygen in the polar carbonyl group (C=O), leaving a negative charge localized at the oxygen atom and a positive charge localized at the nitrogen atom as shown in Figure 8.[6] Thus, chemical reduction may occur between PVP and metal ions by a process in which metal ions could receive electrons from C=O and form atomic metal as seen in Figure 9.
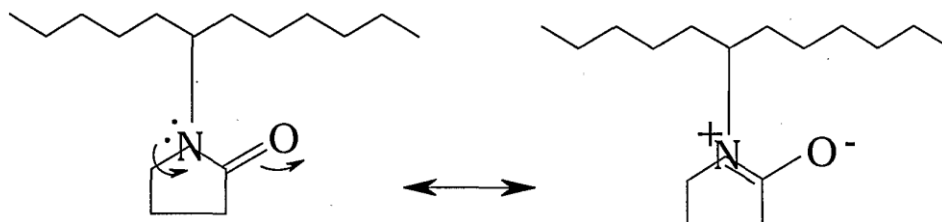
Figure 8. Partial electron donation of nitrogen to oxygen
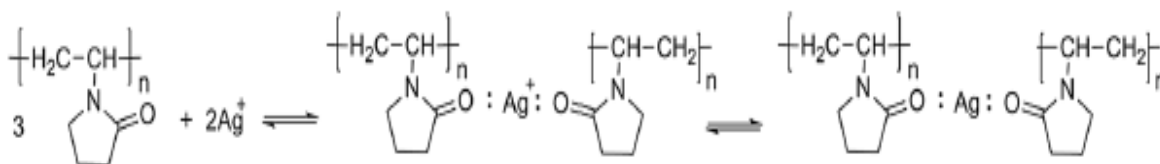
Figure 9. Reduction and bond between Ag^+ ions and PVP molecules.

After this reduction occurs, the bonding between the oxygen in the carbonyl group and the silver remains stable. Both factors would provide an ability to generate active reducing and binding sites and the polymer will promote the formation of crystals. [8-10] In order to understand the bonding between C=O and silver, FT-IR spectra was measured for pure PVP and PVP coated AgNPs. FT-IR generates a transmission spectra showing the unique chemical bonds and the molecular structure of the sample material. As seen in Figure 10, the double bond C=O is represented in the peak at 1665cm-1 for the pure PVP sample. When the PVP coated AgNPs were analyzed that peak shifted to 1605cm-1. This shifts shows a change in the bonding strength of C=O, given by the coordination of the oxygen with the silver.

These results are in concordance with our hypothesis where PVP, through the oxygen in the carbonyl group, needs to act as the coordinating and reducing agent with silver in order to obtain nanoparticles. Therefore, if the oxygen in the carbonyl group of PVP were blocked, it will not able to coordinate with silver and no nanoparticles should be formed.
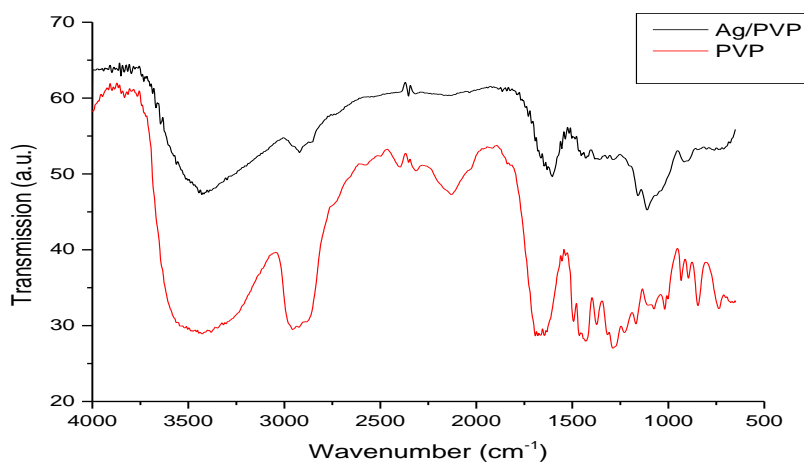
Figure 10. FT-IR spectra for pure PVP and AgNPs from the standard experiment

Water effect

In contrast to ethylene glycol solutions, when water is involved in the solution the PVP unit is capable of forming two hydrogen bonds with a water molecule through the two unshared electron pairs at the oxygen atom in the carbonyl group. The unshared electron pair at the nitrogen atom has been shown to be never involved into hydrogen bonding.[12] Consequently, the reduction and coordinating power of PVP is strongly limited since the electron pair at the oxygen atom are blocked by two water molecules as seen in Figure 11.
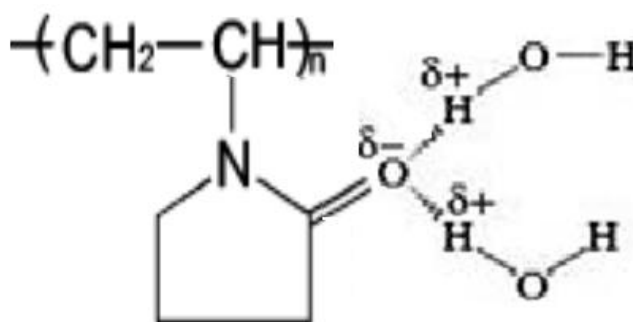
Figure 11. Hydrogen bonding between water and PVP

In order to study the effect of water in this process, different experiments were done at the same PVP and Ag concentrations but different percentages of ethylene glycol to water: 100-0, 80-20, 60-40 and 0-100. From Figure 12, an increase in the total amount of water in solution gives much lower amount of AgNPs synthesized. These results are in great concordance with our hypothesis of PVP reducing and removing Ag atoms from the metal surface through the bonding with the oxygen in the carbonyl group of PVP. Since water interacts with oxygen through hydrogen bonds, PVP cannot reduce and remove silver atoms out of the bulk material and, therefore, AgNPs are not formed.
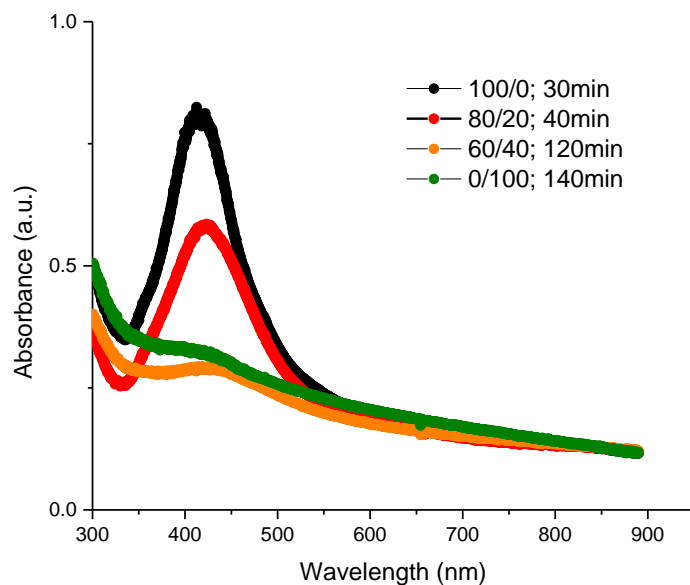
Figure 12. UV-Vis spectra of reactions at different ratios of ethylene glycol and water (EG/W).

Oxygen influence

All the experiments above were carried out under air atmosphere. Mainly, this would cause addition of oxygen to the solution picked up from its interface with air. To study the influence of O_2 in our synthesis, it is necessary to proposed two different experiments, one where O_2 is completely removed and another one with addition of extra O_2. In order to remove all the oxygen from our system, the standard solution with ethylene glycol, silver powder and PVP was bubbled with Ar for 15 min before heating at 120C to remove any possible oxygen molecule in solution. After this step, a needle was inserted into the solution through which argon bubbled in a gentle manner while the reaction was occurring. In the case of bubbling extra oxygen, the same

procedure was performed with the only difference that no oxygen was bubbled before the heat treatment.

From Figure 13, it is observed that no AgNPs were formed when oxygen was removed from the solution or extra oxygen was added. This suggests that, for the first case, the surface of the bulk silver cannot get oxidized in the absence of O_2 and, thus, PVP cannot reduce and extract any silver atoms from the surface. In the case when extra O_2 is in solution, there is a fast and continuous oxidation of silver surface done by the extra oxygen molecules that overwhelms the mild reducing power of PVP. From these results, it is shown that only under air atmosphere, there is an optimum amount of oxygen to be able to form AgNPs.
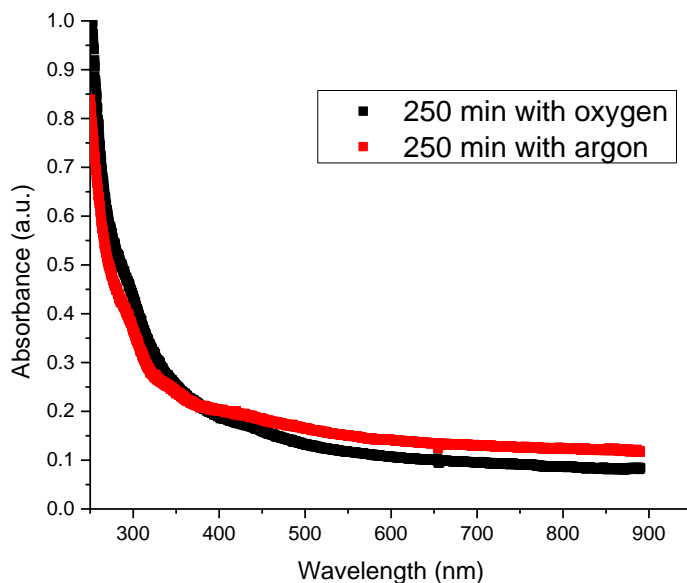
Figure 13. UV-Vis spectra of reactions under argon and oxygen atmosphere

Influence of PVP Molecular Weight

Molecular weight, MW, has been studied by several research groups for different polymers through the last years and has been found to have an influence in their abilities to coat and grow nanoparticles. Shorter chains of PVP cause a smaller steric effect which results in incomplete coating of silver nanocrystals and they may aggregate together.[16-19] Also, with the increase of MW in PVP, a stronger interaction between Ag^+ ions and PVP was estimated.[20] Consequently, a study for three different molecular weights of 360,000; 40,000; and 10,000 with same concentration and temperature, is provided with the only inconvenience that for the highest MW (360,000) the concentration could only be 1/9 of the other two samples. This problem arises from the poor solubility of PVP360 in ethylene glycol at 120C. As seen in Figure 14, for a low molecular weight of 10,000 the yield of AgNPs is very low compared to the yield obtained with a MW of 40,000. For our MW of 360,000 some nanoparticles were obtained, and we could expect that if the right amount PVP concentration could be reached, the yield of AgNPs should be much higher, perhaps more than for PVP40. Taking in account these advantages and disadvantages, no further analysis of MW was carried out and only PVP40 was used since it provided the most successful results.
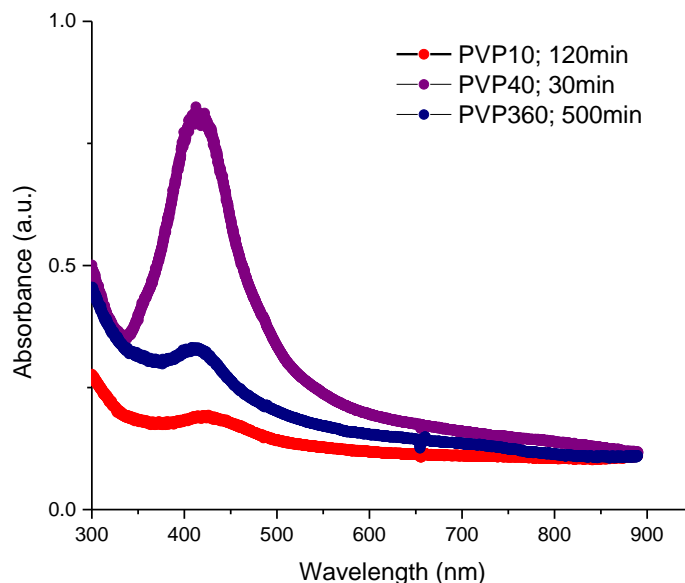
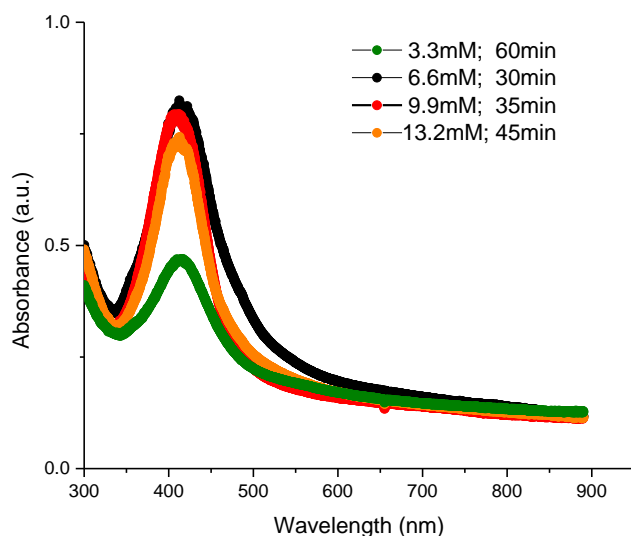**Figure 14**. UV-Vis spectra of reactions at different PVP molecular weight

Effect of PVP concentration

In previous experiments the size of AgNPs produced was varied using different concentration of PVP during the synthesis process. It was shown that at high concentration of PVP, smaller spheres were obtained since the high amount of PVP compounds offer a strong stable ability to prevent aggregation of Ag atoms or nanoparticles. A better uniformity in sizes and shapes of AgNPs was obtained for higher concentrations, as well.[20] The reason may be that at those higher values of concentrations, PVP forms a thicker coating layer with the surface of the metal avoiding aggregation and, also, weaker selective adsorption to different faces. This results in the growth of smaller size and isotropic AgNPs. [9,20]

A study of different concentration of PVP40 was carried out in order to determine if PVP concentration has any important influence in the synthesis of AgNPs. Different concentrations were studied where in our standard experiment the concentration was [PVP]=6.6mM at 120C. As seen in Figure 15 the maximum absorption peak were represented for each concentration. When a [PVP]=3.3mM was used, fewer nanoparticles were produced since the plasmon peak shows a

smaller value than for the rest of the higher concentrations. The other concentrations [PVP]=6.6mM, 9.9mM, 13.2mM do not show any important difference in their maximum value, all of them give, approximately, the same amount of nanoparticles. Also, the times where those maximum values are reached are really close to each other for concentrations above [PVP]=6.6mM. This suggests that above a PVP concentration of 6.6mM, the reduction and coordinating power do not increase in a significant manner when synthesizing AgNPs, then, a saturation must have been reached at a PVP concentration of 6.6mM.

Figure 15. UV-Vis spectra of reactions at different PVP40 concentrations.

Pellets as bulk silver

Precursors have played an important role in all the synthesis method developed to produce AgNPs. In previous reactions, silver powder was used as silver precursor, now Ag pellets (2.5mm average diameter) were also analyzed to be able to compare the importance of the size of the bulk metal. When pellets were used, the only temperature range where AgNPs were obtained was between 100C and 150C where this range was greater, 60C to 195C, with Ag powder. When

the temperature was set at 80C, 175C or 195C, no AgNPs were obtained when pellets were used. From pellets, as seen when Ag powder was used, for the lower temperatures the reaction was slower, but for both temperatures, 100C and 120C, the yield of AgNPs was considerably increased, as seen in the maximum absorption peaks in Figure 16.
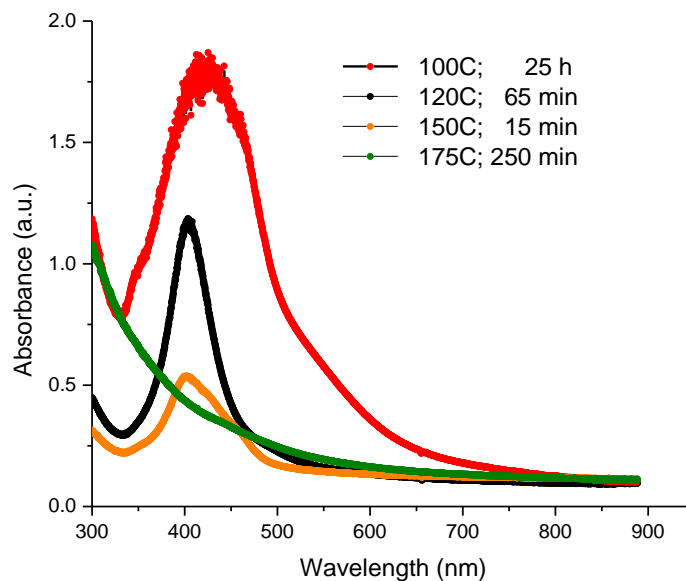
Figure 16. UV-Vis spectra of reactions at different temperatures with Ag pellets as precursor.

From all these data results, some insights of the method of synthesizing nanoparticles out of bulk material can be extracted. First, oxygen must be available in solution to form a thin layer of oxidized silver on the surface of the bulk. Then, PVP must reduce and coordinate with the silver ions in the surface transforming them back into Ag^0. When this reduction process occur, PVP coordinates with the silver atoms acting as a protecting agent and this bond pulls out the silver producing their detachment from the bulk surface. The steps of this mechanism are shown in Diagram 1.
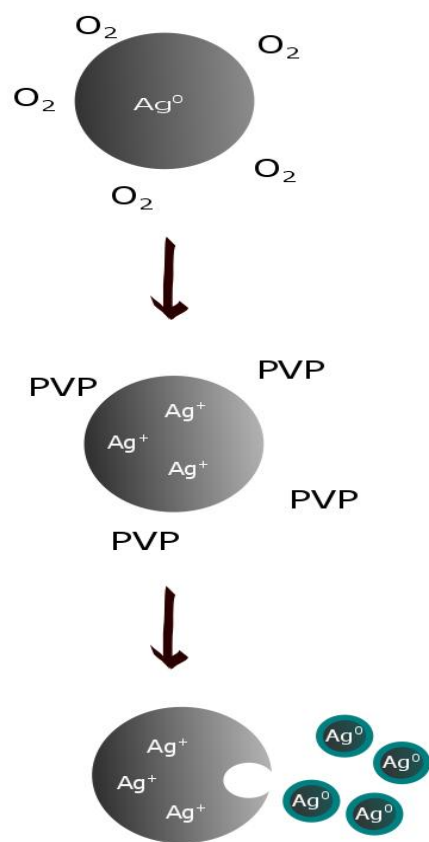
Diagram 1. Proposed mechanism for the formation of AgNPs coated with PVP (blue layer).

Shape evolution of silver nanoparticles

A silver nanoparticles synthesis mechanism is presented as a novel procedure to obtain nanoparticles directly from bulk materials without using any metal salt or highly expensive equipment, such as lasers or microwaves. In addition to this discovery, control of the size and shape must be achieved because of several applications depend on particles shape and size. Different shapes of silver nanoparticles have size and shape sensitive surface plasmon resonance, SPR, bands and, hence, diverse applications in optics, electronics, sensors, surface enhanced Raman spectroscopy (SERS), catalysts, biological detection and drug delivery.[13]

Among the various shapes of silver nanostructures, triangular silver prisms or disks have recently attracted great attention because their SPR bands can be widely tuned by controlling the particle aspect ratio. Mainly, two methods have been used for Ag prism synthesis: chemical reduction of metal salts and photochemical growth.[20-25] In general, the former chemical reduction method is better than the photochemical method for mass production of silver prisms, which is necessary for industrial applications.

Another successful method was performed by Zhang et al.[15] where they used not only silver salt but also metallic Ag nanoparticles such as wires and spheres as sources of prisms. However, in their experiments, metallic Ag particles were completely dissolved to Ag^+ ions by H_2O_2 and reduce back to Ag^0 by $NaBH_4$. Tsuji et al.[23] took this last experiment one step further and demonstrated that Ag prisms can be prepared from various Ag nanostructures such as spherical nanoparticles, nanorods, cubes, and bipyramids without complete dissolution of metallic Ag particles to Ag^+. Simultaneous addition of H_2O_2 and $NaBH_4$, where oxidation of metallic Ag nanostructures and re-reduction of Ag^+ to Ag^0 occur at the same time.

All these methods rely on the theory that triangular nanoplates and nanorods evolve by an Ostwald ripening process starting from spherical Ag nanoparticle precursors. This is shown in the progressive growth in particle size concomitantly with the shape evolution. Oswald ripening is the process of forming large particles by the aggregation of smaller particles into greater particles.[15,16]

Temperatures

From our observations in the UV-Vis spectra and TEM pictures for different reaction temperatures, a similar process must be occurring since Ag nanospheres are being transformed into triangles and hexagons of greater size. The different peaks in the UV-Vis spectra show the evolution in the shape of AgNPs with reaction time. Figure 17 represents the spectra evolution for the standard experiment where 20mg of Ag powder was added to a PVP40, 6.6mM, 20 ml solution in ethylene glycol, and heated at 120C. As seen before, after 30 minutes of reaction there is a prominent peak at 410nm that represents the silver nanoparticles with a sphere-like shape. At 55 minutes two new features appear one broad shoulder above 500nm and a small peak at 350nm. The broad shoulder appearing above 500nm represents the in-plane dipole surface plasmon band of anisotropic shapes as prisms. The weak, sharp peak at 350nm corresponds to an out-of-plane dipole plasmon transition of triangular prisms, and it is known to be related to the thickness of the prisms.[17] For this reason, this peak only appears when triangles start to form. However, most of the particles have not fully transform from spheres to these shapes, as seen in the TEM pictures in Figure 18. After 24 hours these two peaks related to anisotropic shapes completely disappear and the peak at 410nm increases again and become much broader, indicating a polydisperse system of Ag nanospheres in solution. For his reason, some etching

must be happening after the prisms are obtained that convert them back to spheres with a wide range of sizes. The limitations of our UV-Vis spectrometer affect the measurements below 300nm, then, slightly affecting the peak at 410nm.
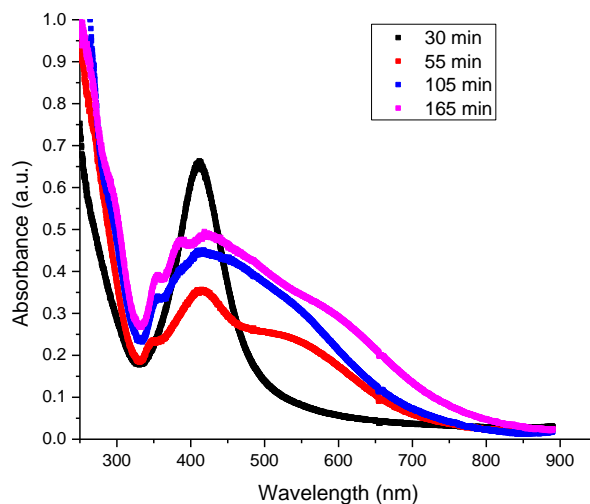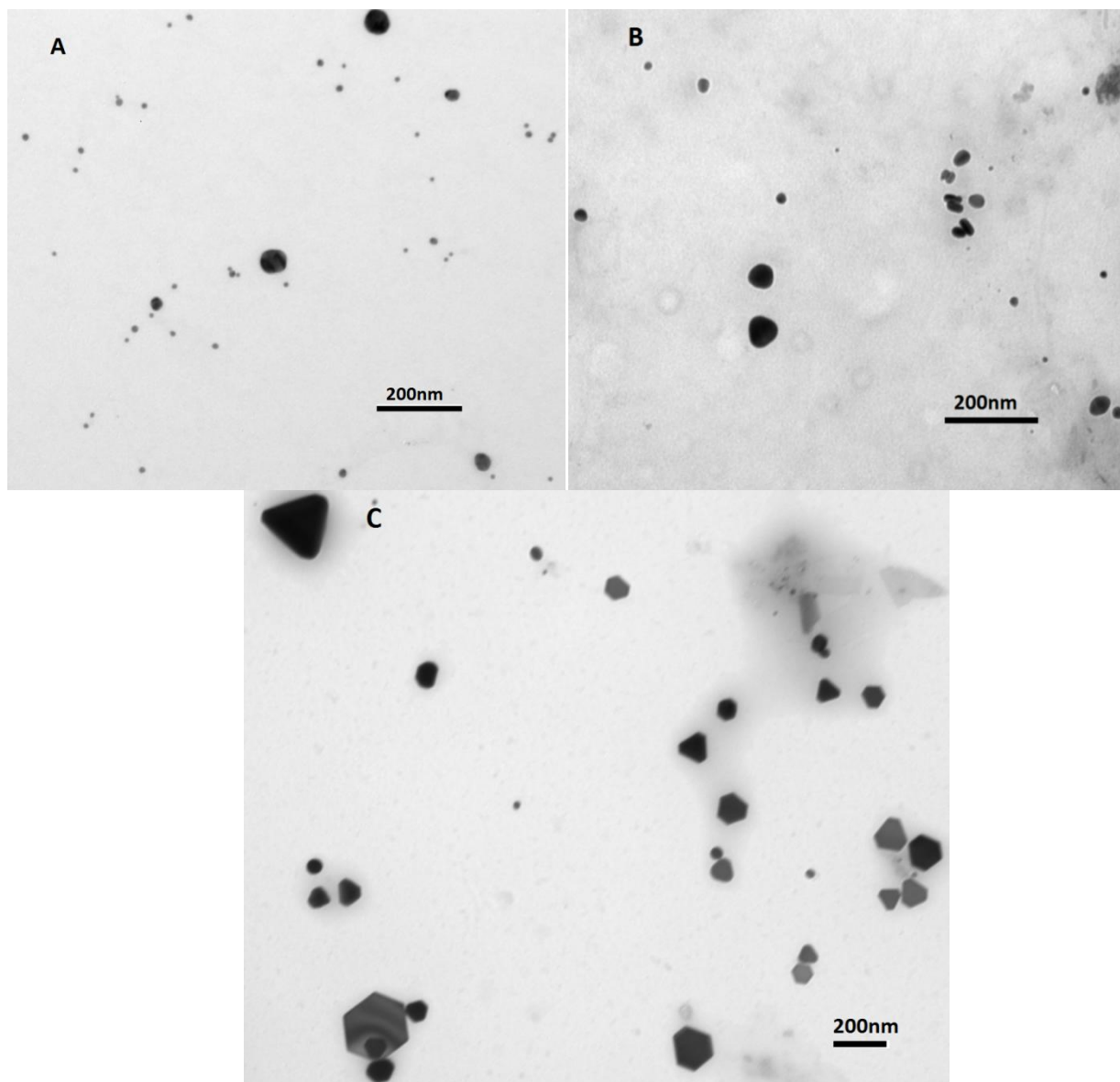

Figure 17. UV-Vis spectra evolution with time at 120C.

When the temperature was reduced to 100C, a more clear evolution was observed than the experiment at 120C. At first, spheres were obtained with sizes ranging from 5 to 50nm, then, after 185min some rod-like particles and small triangles appeared, and after 250min, all the particles were either triangles or hexagons with a significant polydispersity as seen in TEM pictures in Figure 19 . This shape evolution with can be also observed in the appearance of a broad peak at 575nm and the disappearance of the peak at 410nm after 250min in the UV-Vis spectra from Figure 20.
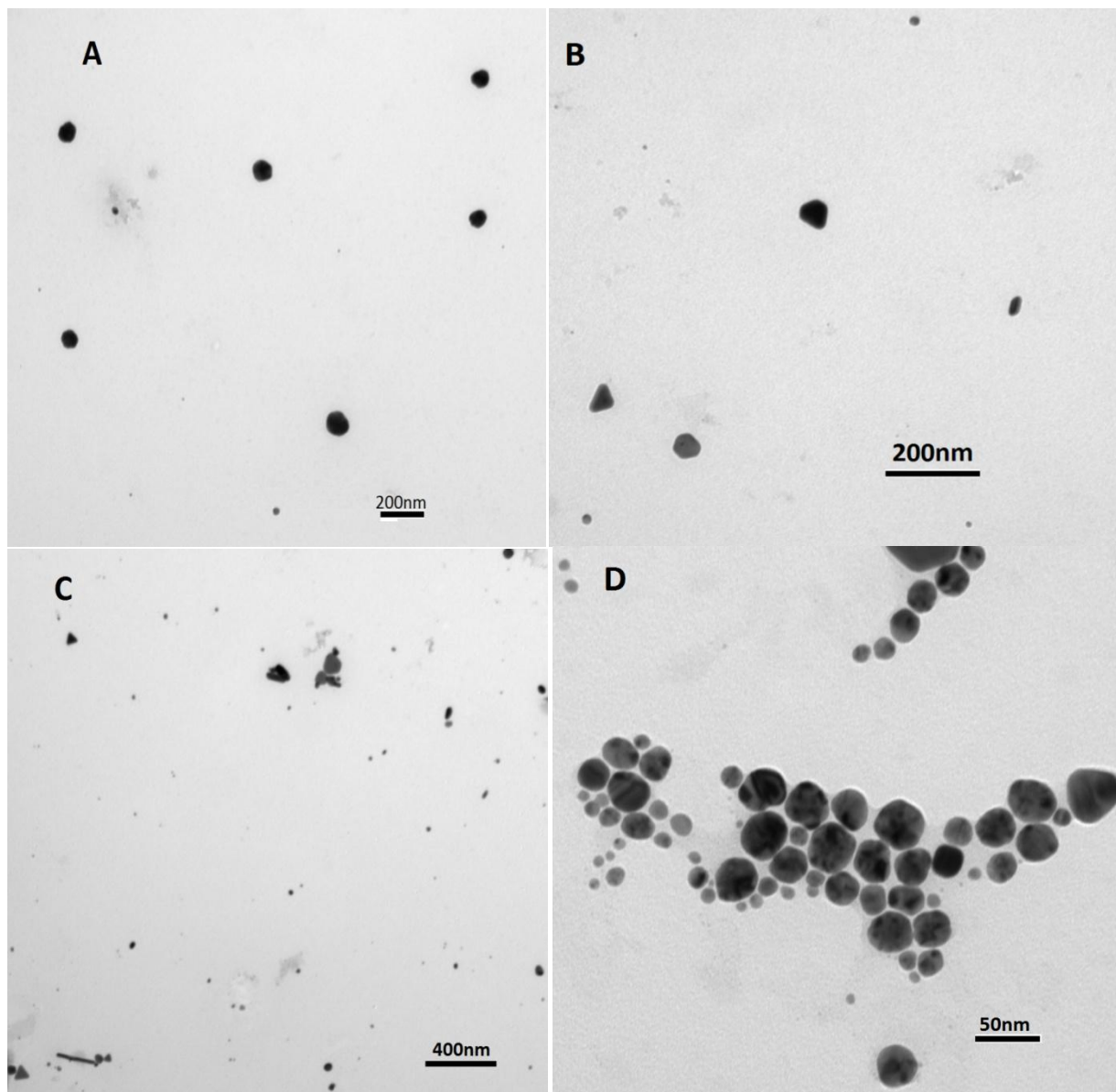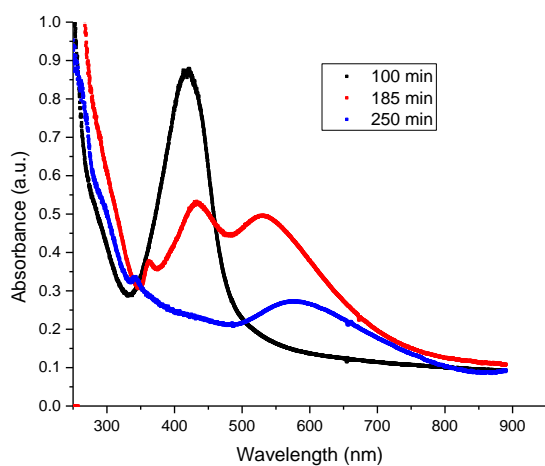
Figure 18. TEM images for 6.6mM of PVP40 with Ag powder at T=120C and times A) 30min,

B) 55min, C) 165min and D) 24h.

Figure 19. TEM images for 6.6mM of PVP40 with Ag powder at T=100C

and times A) 100min, B) 185min and C) 250min

Figure 20. UV-Vis spectra evolution with time at 100C

If the temperature was dropped to 80C, a similar behavior was found with the only difference of a time delay in the evolution from spheres to prisms as it is seen in the UV-Vis spectra in Figure 21.
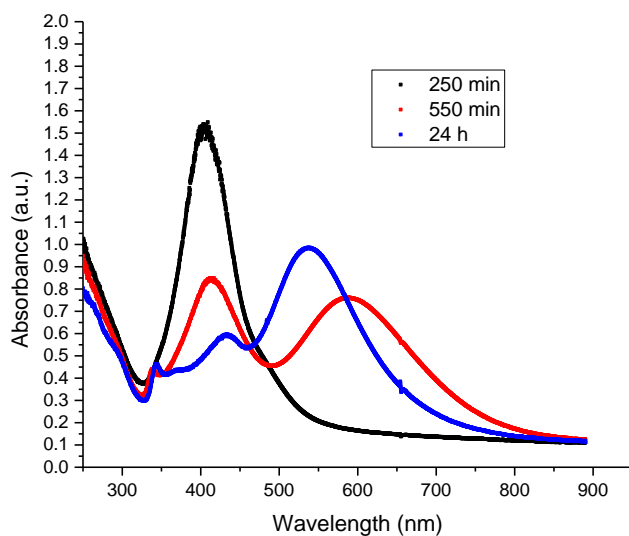
Figure 21. UV-Vis spectra evolution with time at 80C

It was seen before that a small amount of AgNPs are produced when reaction temperatures are increased above 120C. When the temperature was set at 175C, an evolution of the plasmon peaks is observed in the UV-VIS spectra shown in Figure 22. Its evolution to prisms is quicker but not

as effective as reactions at lower temperatures. During this evolution, a plasmon peak a smaller peak above 500nm, indicating the formation of some triangles and rods.
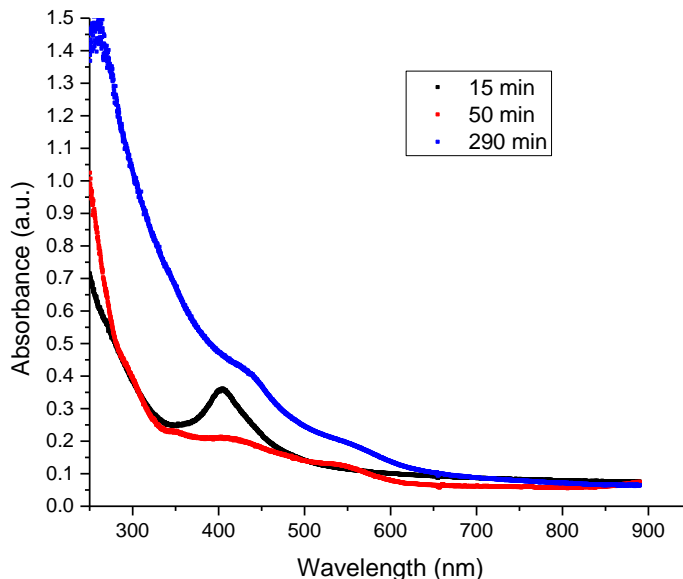
Figure 22. UV-Vis spectra evolution with time at 175C.

As a result, temperature plays an important role for the formation of Ag prisms, where reactions performed at 80 and 100C gave the highest yield of triangles, even though, the rate of reaction was slower than at higher temperatures. If the reaction was held above 120C, there was only a partial transformation of spheres into triangles or hexagons.

PVP concentration

Concentration of PVP was found not to have much influence in the yield of AgNPs as long as it was held above 6.6mM. Then an analysis of different concentrations at a temperature of 120C was carried out to understand the role of PVP in the size and shape of the nanoparticles. As shown before in the standard experiment, when the concentration of PVP was 6.6mM and temperature was set at 120C, some spheres converted into rods and, later, into triangles. For a

concentration of 9.9mM for PVP, from the UV-Vis spectra shown in Figure 23, spheres were obtained after 35 minutes, at 45 minutes triangles started to form and all the spheres were completely transformed into triangles and hexagons. These results are consistent with the TEM pictures shown in Figure 24, where most of the AgNPs were triangles and hexagons after 180 minutes of thermal heating. At the highest concentration of PVP, 13.2mM, spheres did not transform into other shapes as seen in the UV-Vis spectra in Figure 25. Only an increase in size occurred shown with the small red shift of the plasmon peak at 410nm and the appearance of small peak at 350nm, showing the existence of few prisms. After 23h, these prisms became spheres with a broad size range, as seen when the concentration of PVP was 6.6mM.
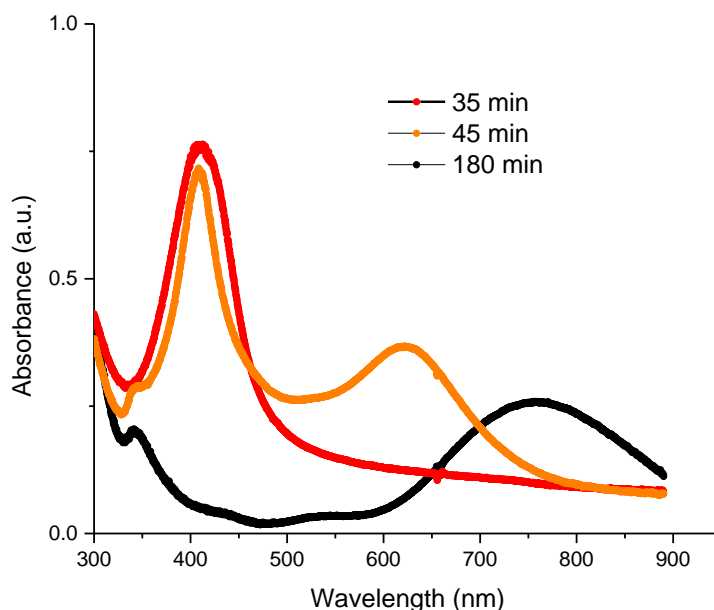
Figure 23. UV-Vis spectra evolution with time and a PVP concentration of 9.9mM
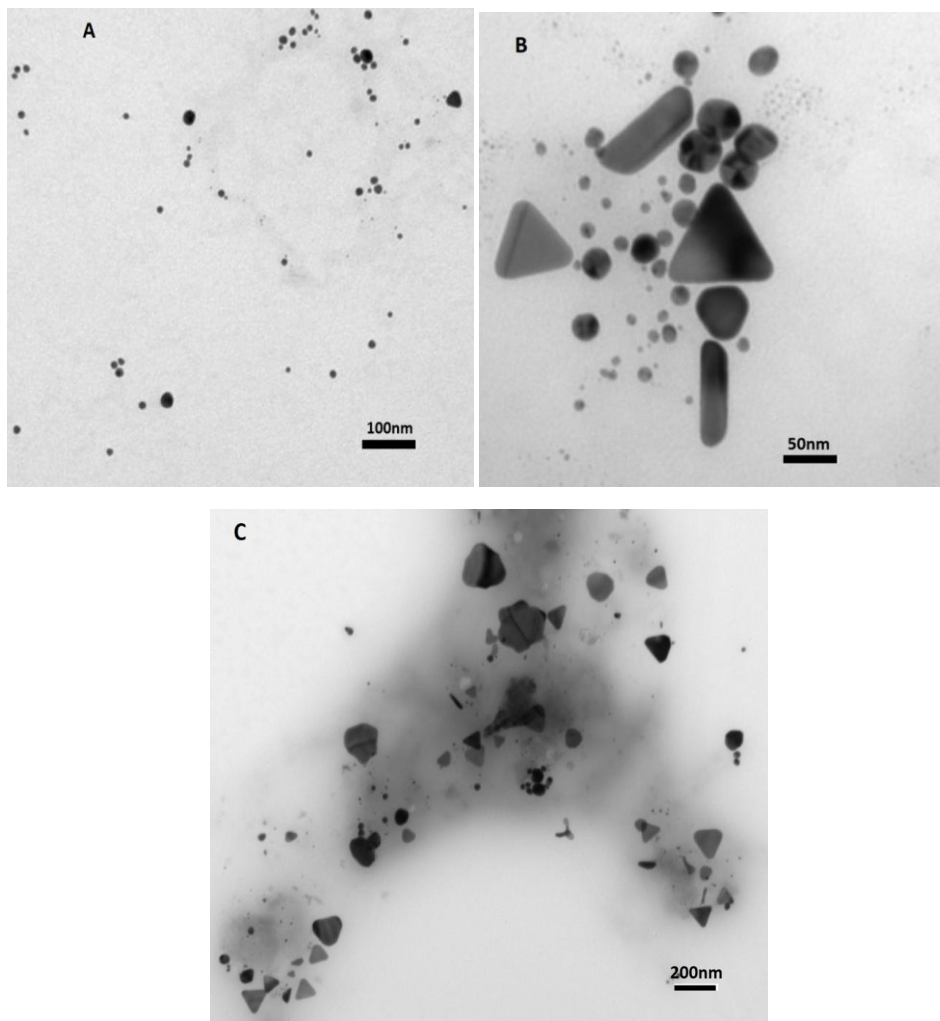
Figure 24. TEM images for 9.9 mM of PVP40 with Ag powder at T=120C, A) 35min, B) 45min and C) 180min.

Therefore, for all these different concentrations, it is found that the best yield of triangles is achieved with a PVP concentration of 9.9mM, when the concentration was lower at 6.6.mM, only a fraction of the spheres transform to rods and triangles and when this concentration was higher at 13.2mM triangles were barely formed, obtaining polydispersed spheres after a long time of reaction. Then, too much or too little PVP will not promote the formation of triangles at a high yield as seen with the proper concentration of 9.9mM.
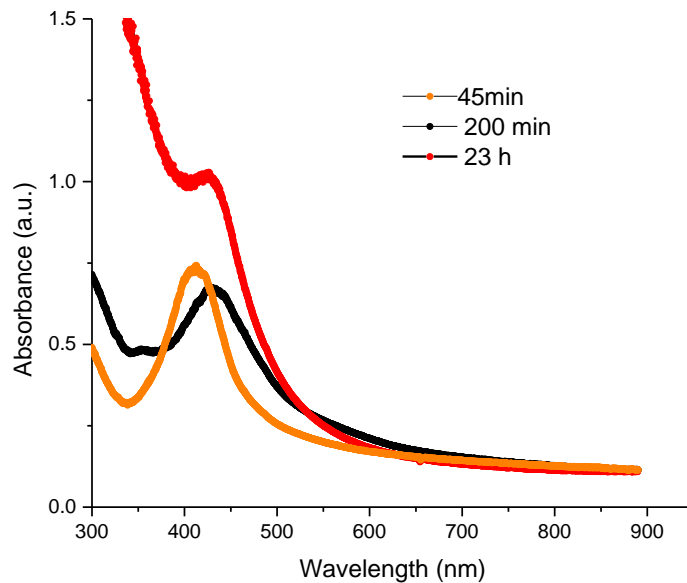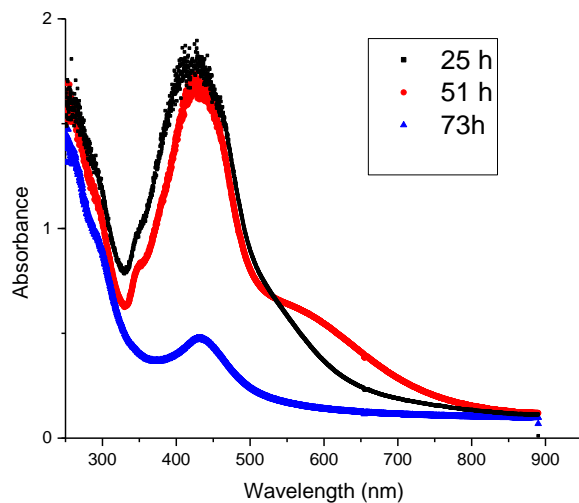
Figure 25. UV-Vis spectra evolution with time and a PVP concentration of 13.2mM.

Pellets as bulk silver

Another factor that was observed was the differences between using different sizes of bulk material with silver pellets and silver powder. When pellets were used as the bulk material in the synthesis, AgNPs were only obtained if the temperature was set between 100C and 150C. Also, for the lowest temperatures the production of AgNPs was higher and the reactions were slower. When the reaction was carried out at 100C an important amount of silver nanospheres were obtained and some of these spheres evolved into triangles and hexagons after 51h. From Figure 25 , this small peak shows that a small portion of the spheres become rods and, maybe, triangles, but after 73h, this peak disappeared and the plasmon band around 410nm decreased considerably. This long term evolution where particles are etched and reduced in size has been observed before in the standard experiment at 120C. Another temperature analyzed with pellets was 120C and similar results were obtained like the silver powder at the same temperature. As

seen in Figure 26, the UV-Vis spectra shows how most of the spheres are transformed into triangles and rods and, convert back to spheres after 22h for the reaction at 120C.

Figure 26. UV-Vis spectra evolution with time at T=100C using pellets as Ag precursor.
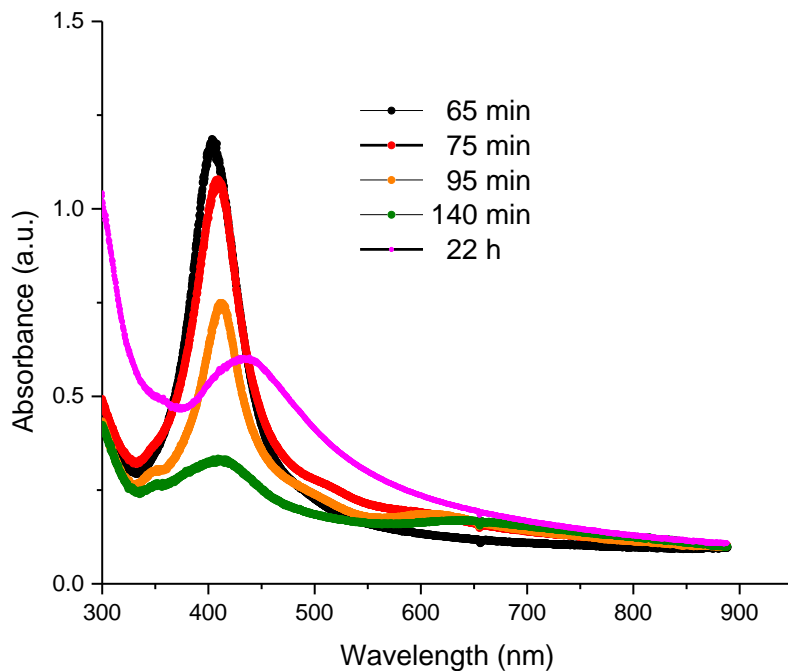
Figure 27. UV-Vis spectra evolution with time at T=120C using pellets as Ag precursor.
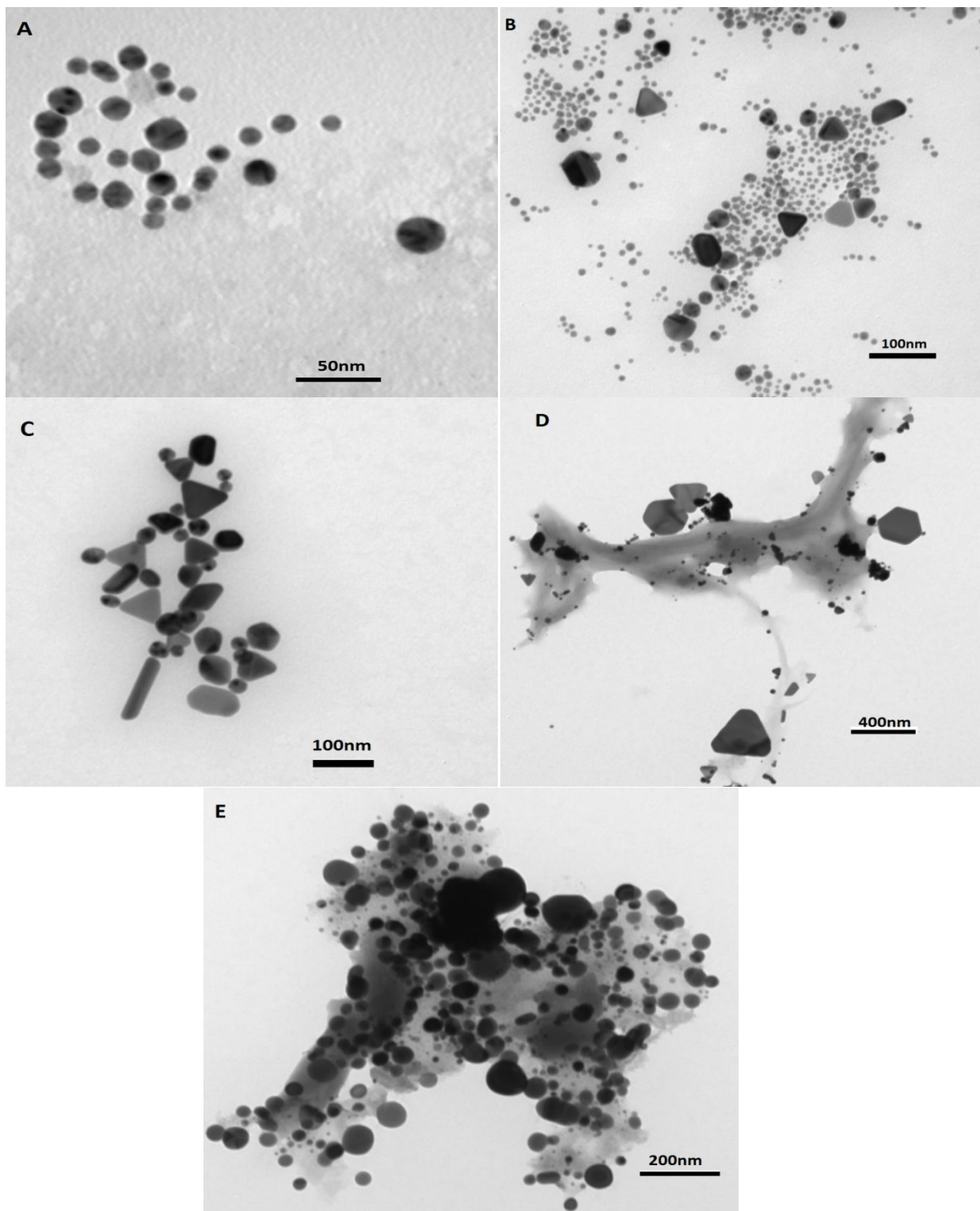
Figure 28. TEM images for 6.6mM of PVP40 at T=120C using pellets A) 65min,

B) 75min, C) 95min, D) 140min and E) 22h.

Figure 29. UV-Vis spectra evolution with time at T=150C using pellets as Ag precursor.

This analysis from the UV-Vis spectra is consistent with the TEM pictures seen in Figure 27 where after 22h the etching of AgNPs occurs, converting them in spheres and reducing their size. For even higher temperatures at 150C, shown in Figure 28, only 15 minutes into the reaction a peak showed around 400nm, after 25 minutes a shoulder ap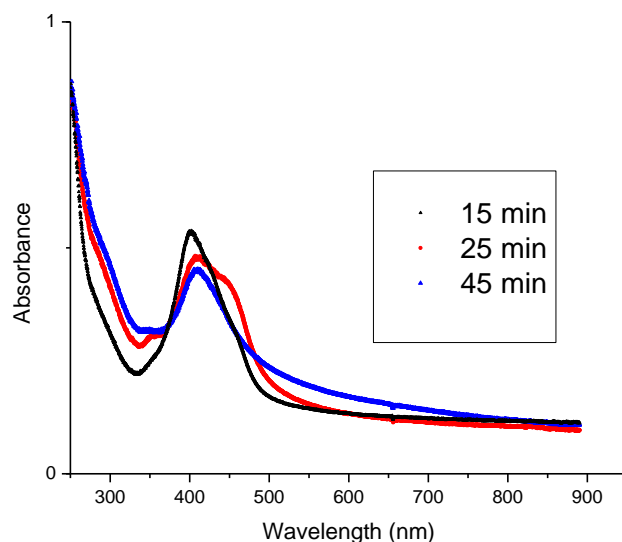peared at higher wavelengths and the characteristic peak of prisms thickness at 350nm. These peaks shows the transformation of some spheres into prisms and rods, and, finally, after 45 min only a peak at 410nm remained showing the existence of only spheres in solution due to the mentioned etching effect.

To sum up, different shapes and yields of AgNPs can be obtained changing the temperature, polymer concentration or the bulk silver. Higher temperatures would increase the rate of reactions but slower reactions give much better yield of anisotropic shapes. Regarding PVP concentration influence, the best one found to obtain more prisms was 9.9mM since higher values will protect the spheres from growing and smaller amounts will not help promote the reshaping. After long times, an etching effect occurs in the AgNPs where all the different shaped nanoparticles are converted back into spheres with a reduced size where this etching process was

observed in other experiments with silver and other metals.[26-30] When silver pellets were used, the amount of AgNPs obtained is much higher, but the reshaping of these nanoparticles into prisms did not occur as effectively as when Ag powder was used as the precursor. Therefore the mechanism proposed for the reshaping of AgNPs is shown in Diagram 2. Spheres are always obtain at first, they can later coalesce with each other forming rods. Then, from these rods and other spheres, triangles and hexagons of much greater size can be formed.
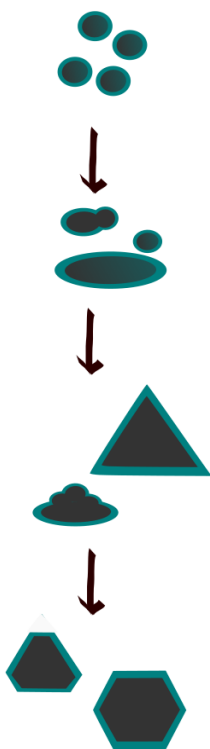
Diagram 2. Proposed mechanism for the change in shape of AgNPs. Evolution time changes with temperatures and PVP concentration

Chapter 4 - Conclusion

A novel method to obtain silver nanoparticles has been achieved in an easy, cheap and scalable manner. A complex mechanism occurs with bulk silver getting oxidized by oxygen in solution, forming a thin layer of oxidized silver on the surface of the bulk material. Then, PVP in solution acts as a reducing agent at the oxidized surface, where silver becomes Ag^0 again. When PVP reduces the oxidized silver back to metallic silver; it, also, coordinates with the silver atoms acting as a protecting agent. That PVP coating bond pulls out the atoms and produces a detachment of silver atoms from the bulk surface. After coalescing with each other, silver nanospheres can morph into prisms, triangles and hexagons. This evolution depends on the amount of PVP on solution, the temperature of the reaction and the type of bulk silver used as precursor. After long times, all the AgNPs transform back into spheres due to a etching process that breaks down the anisotropic particles into spheres of smaller size.

One of the advantages of this method is that all the materials used during the synthesis of these nanoparticles are commonly used in industry, ethylene glycol as antifreezer in cars or PVP as a binder in the pharmaceutical industry. Also, the instrumentation used consisted only on a heating mantle, a condenser and a round bottom flask; all these materials can be obtained for a reasonable price. Lastly, the metal precursor used, bulk silver, provides an important reduction of the price from those synthesis of AgNPs where silver nitrate was the precursor.

Even so, more research needs to be carried out in order to obtain a better understanding of this process and, therefore, be able to apply it at an industrial scale. For future experiments more aspects of this method must be understood as quantifying the yield of AgNPs for each experiment, the reusability of silver powder not converted into AgNPs, obtaining other anisotropic particles , acquiring a synthesis with a higher degree of monodispersity, using other

agents rather than PVP that could reduce and protect the silver particles and analyze the influence of the bulk silver surface area when using pellets or powder.

To conclude, an innovative method has been discovered that could reduce dramatically the price of synthesizing nanoparticles at an industrial scale. Silver was the metal used during this research but if the right materials are used this process may work with other elements as copper, gold, aluminum, iron, palladium, zinc or nickel.

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