

CHAPTER 4

RESULTS AND DISCUSSION:

PROPERTIES OF SILVER AND COPPER

NANOPARTICLES

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In this phase of the present work, model nanostructured surfaces were prepared in order to examine the correlation between the wetting behaviour and their parameters, i.e. particles size, density, topography etc. As mentioned in Chapter 2, two conditions are necessary to produce a superhydrophobic surface: (1) a specially-designed roughness or texture on the surface; (2) an intrinsically hydrophobic material for the outermost layer. The steps of the approach to have a superhydrophobic surface are depicted in figure 4.1.

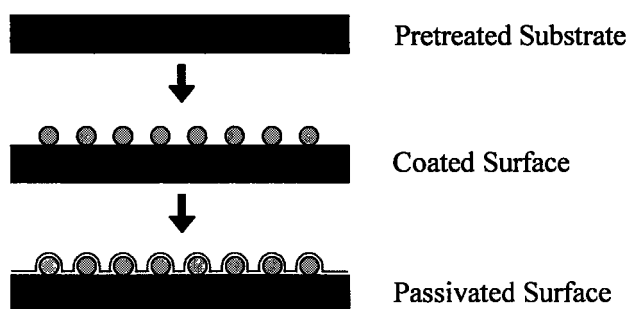


Figure 4.1: Schematic illustration of two-step process to prepare superhydrophobic surfaces.

It involves a substrate, which is usually pre-treated, and some kind of micro/nano-sized coating. The textured surface is then covered with another substance, which makes the entire surface hydrophobic. The nanoparticles must be close together enough such that water can not penetrate between them (i.e. almost touching). These surfaces are commonly referred to as composite surfaces, because of high chance of having a composite mixture of water-solid interface area and water-air interface area underneath a macroscopic water droplet on the surface. By varying the size and the separation between the particles it is possible to prepare surfaces where the water droplet is pinned or rolls off easily. Among different fabrication methods available, spin coating was selected herein as the main

coating method for bringing the nanoparticles on the substrate surfaces. Spin coating is a commonly used technique for preparing uniform thin films on flat substrates.

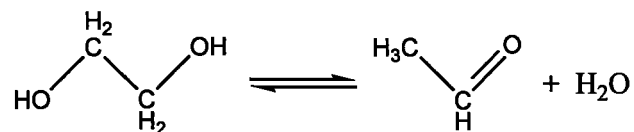
4.1 Silver Nanoparticles

Three different approaches were attempted to prepare silver nanoparticles needed to make rough model surfaces. The experimental details and achieved results are as follows:

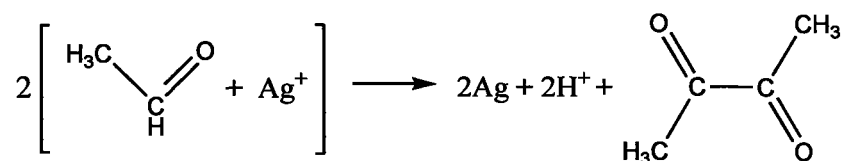
4.1.1 Silver Nanoparticles Type 1

The alcohol-base process is one of the most efficient ways for the preparation of fine powders of easily reducible metals [159,172]. Alcohol-medium preparation of nanoparticles can be carried out using two approaches: (a) the “precursor heating” method, where a solution of metal salt in alcohol is prepared at room temperature then heated to the reaction temperature, and (b) the “precursor injection” method, in which a metal salt solution is injected into a hot solvent [173]. In the former approach, the rising rate for temperature is the main parameter governing the particle size. On the other hand, the injection rate and the reaction temperature are determining factors of the latter method. A precise control of temperature is essential to have more uniform particle size distribution (monodispersity) [173]. The second approach was followed here.

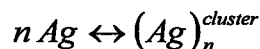
Under the effect of heating or additives, dehydration reaction of EG takes place where one molecule decomposes to two molecules of water and acetaldehyde. This reaction is reversible and can be affected by catalysts and by the pH of the solution [174].



In the presence of Ag ions, a second reaction occurs in which simultaneous double oxidation of acetaldehyde leads to diacetyl and reduction of Ag^+ generates neutral Ag atoms [175]. The generated organic molecules are volatile and leave the solution as bubbles. Therefore, the reaction is almost irreversible.



The generated Ag atoms in the solution associate to form small clusters, which are dynamic entities having continuous aggregation–dissociation evolutions.



When the solution reaches a saturation level of Ag atoms, the clusters absorb the excess atoms and grow to a critical size and thus form nuclei, which are the first stable entities of the metal [176].



The number and size of the nuclei depend on the reduction-oxidation potential of the reaction (redox), temperature, concentration of reactants and additives, and the properties of the solvent [157]. These nuclei grow rapidly and the Ag atom concentration is lowered to a point below the nucleation concentration, but high enough to allow particle growth to continue at a rate that can consume all the generating metal atoms [172]. As more metal

atoms are generated, the primary particles can continue to grow by diffusion to form larger single-crystal particles, or they may aggregate to form poly-crystal particles. The free growth of the particles leads to the particle sizes up to several micrometers and finally they precipitate, with a wide range of shapes and sizes (poly-dispersed).

To have nanoparticles with desirable properties, the growing and the aggregation processes must be controlled. A number of materials have been reported to act as protective agents for controlling the colloidal particle growth. Among them, PVP is one of the most commonly used (figure 4.2) [159,172]. Adding a precise amount of PVP inhibits the possibility of bonding the newly reduced Ag atoms and controls the particle size distribution.

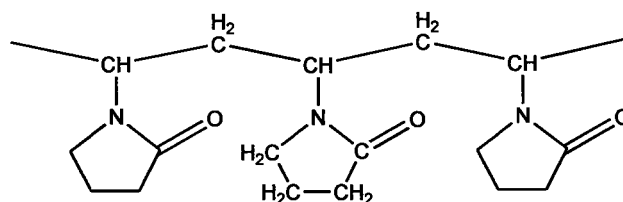


Figure 4.2: A group of three monomers in a PVP polymer chain.

It is worth noting that having a reaction termination step is essential after achieving a desirable colloid. This can be done by adding a proper amount of acetone [177].

UV-visible spectrometry is the standard measurement to trace the shape and size evolution of Ag nanoparticle during the growth process because Ag nanostructures with different shapes and sizes exhibit different surface plasmon resonance bands at different frequencies [178]. Appendix C includes more details about UV-visible spectrometry. Figure 4.3a shows the variation of the UV-visible absorption spectra of a Ag colloid, taken

at various reaction times from 1 to 60 min (after the addition of AgNO_3 and PVP). The strong resonance peak at 420nm clearly shows the presence of Ag particles [179]. At the initial stages, the solution exhibits a transparent pale brown color. After 5min, the solution turns slightly opaque and its color changes to dark yellow. The change in color implies that the most of Ag^+ ions are coordinated with PVP molecules [180].

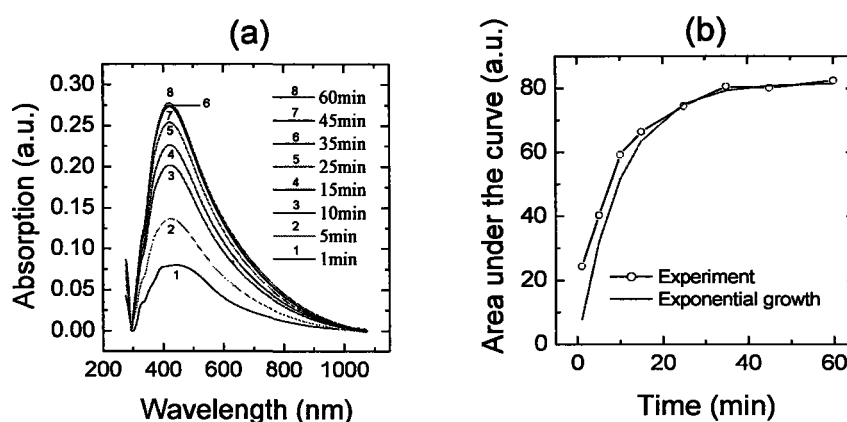


Figure 4.3 : Time evolution of nanoparticles in UV-visible spectra (a) the absorption spectra in different instants, and (b) the area under the curves in (a).

The appearance of plasmon resonance peak around 420 nm indicates the formation of nearly spherical Ag nanoparticles. Over time, the peak intensity increases and it became narrower, stating an increase in the number of Ag nanoparticles in the reaction solution. As the reaction proceeds over about 35 min, no obvious changes in the absorption spectrum are observed in figure 4.3a. The number density of the particles is proportional to the area of the absorption curve. The increment in this quantity in figure 4.3b is mostly related to the

larger number of particles with the same size distribution range, as no shift in peak position is seen.

The above mentioned experiment can provide stable Ag colloids which can keep their properties for more than two months (verified with UV-vis spectra). The reaction is not fast and can be terminated at any time to inhibit the particles from further growth by adding large amounts of acetone in the mixture [177]. Precise selection of ingredient quantities and reaction parameters may lead to desirable range of particle sizes and shapes. The particles did not precipitate on the flask walls and remained in the solution even after cooling down. Also, the molar ratio of AgNO_3 and PVP monomers was not high (~ 1.5), therefore removing of PVP from the particles was by washing with 1-2 fold acetone.

On the other hand, preparation of rough surfaces based on metallic nanoparticles, as one goal of this study, required relatively large amounts of such particles, which is not a straightforward task. Doubling the concentration of reactants leads to higher agglomeration rate and a much wider UV-vis spectrum, indicating a larger distribution of particle sizes. The reaction is also time-consuming and it takes four five hours including the preheating and cooling periods. Although having many adjustable parameters gives the flexibility to the reaction, but it makes the reaction hard to control and small inadvertent changes in parameters may result in unwanted outcomes. The UV-vis test showed that results were different when reaction was performed in an ordinary flat-bottom beaker or in a round-bottom flask. Apparently, in the case of beaker the circulation is not uniform throughout the solution so much wider UV-vis curves were achieved. Very precise control of the reaction temperature was also important. To have a better heat exchange rate between a planer hot-

plate and round flask, a bronze part was designed, which acted as both a heat conductor and heat capacitor (figure 3.1). Using this heat conductor led to much more reproducible experiments. The injected solutions of AgNO_3 and PVP are at room temperature so the injection rate can strongly influence the solution temperature and finally the achieved result. Although the experimental parameters used in this work were close to those applied by others [159], the particles obtained here spherical rather than cubic. The difference could be explained by the use of an automatic injection system and more precise control of solution temperature in the work of Sun and Xia [159].

Figure 4.4 shows SEM images of Ag nanoparticles prepared in alcoholic medium. These particles were washed with acetone three times to get rid of PVP traces then deposited on Si substrates. The Ag particles are almost spherical with distinguishable facets. It is worth mentioning that the particles in the SEM images were separated from colloid by using a centrifuge system which separates the bigger particles from liquid easier compared with smaller particles. It is possible that very small particles remained in the liquid and therefore one can not find them in figure 4.4.

At least 10 different AFM images of a nanoparticle-coated silicon substrate were analyzed in order to understand the size distribution of nanoparticles. According to the manufacturer, the applied tapping-mode tip of AFM had a radius of curvature on the order of 30-50 nm which can lead to an increased apparent diameter of ~ 15 nm for each particle. However, this error has been neglected here. The selected size categories and the calculated percentage for each are depicted in figure 4.5. The range of particle sizes in these images is from 100 nm to 600 nm with an approximate average of 361 nm.

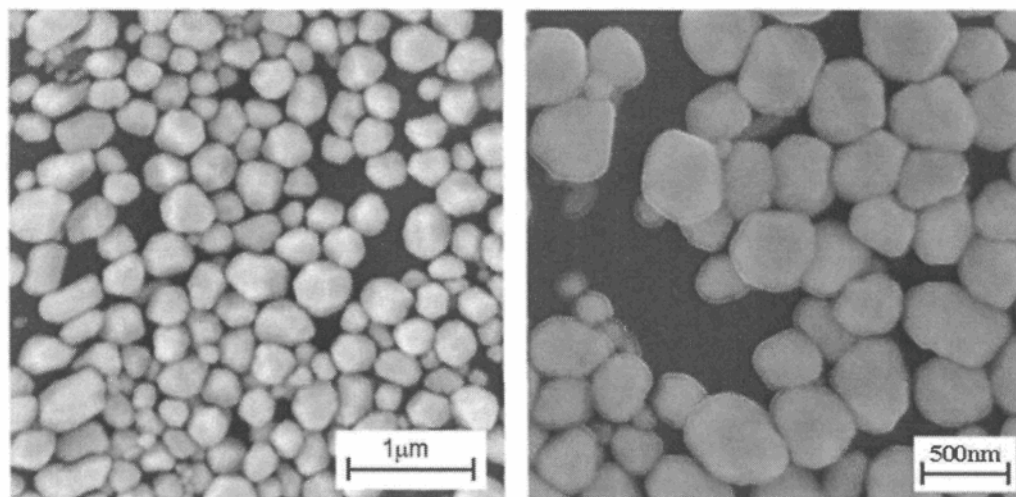


Figure 4.4: SEM images of silver nanoparticles prepared through precursor injection into alcohol medium at 160°C.

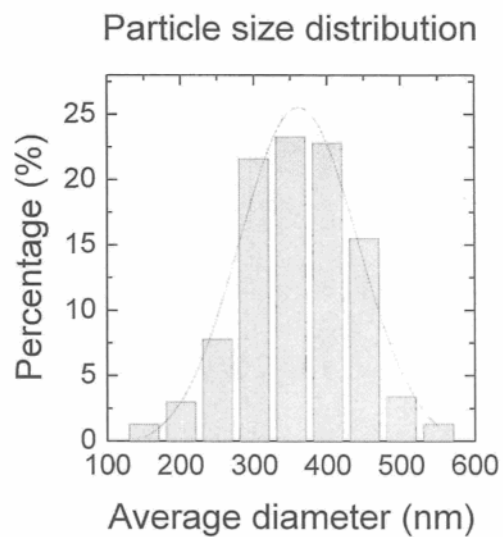


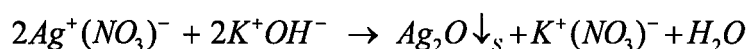
Figure 4.5: Size distribution of silver nanoparticles of type 1.

Table 4.1: Size distribution groups of silver nanoparticles of type 1, shown in figure 4.5.

Average diameter (nm)	Mid-size (nm)	Percentage
<174	150	1.3
175-224	200	3
225-274	250	7.8
275-324	300	21.6
325-374	350	23.3
375-424	400	22.8
425-474	450	15.5
475-524	500	3.4
>525	550	1.3

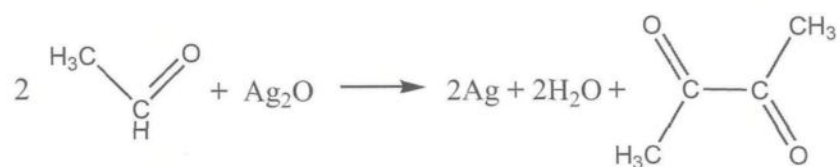
4.1.2 Silver Nanoparticles Type 2

Although the previous synthetic method is well-known and controllable, for our purpose it is quite time-consuming and complex. More rapid synthesis of nanoparticles, able to speed up the total process, was considered as more attractive. In aqueous state, silver nitrate solution has acidic pH (5 for 2% w/v). By adding strong bases, Ag^+ ions precipitate without being reduced as a solid mass of silver oxide. For example, in case of KOH we have:



In presence of Ag_2O , the solution color changed to dark brown-black. The precipitation rate completely depends on the amount of PVP in the medium and higher PVP concentration reduces the particle sizes and increases the precipitation period.

Further conversion of Ag_2O to Ag particles was performed through the reaction below:



In this reaction, after adding KOH the color changes to green-brown indicating the presence of silver nanoparticles, as shown in figure 4.6.

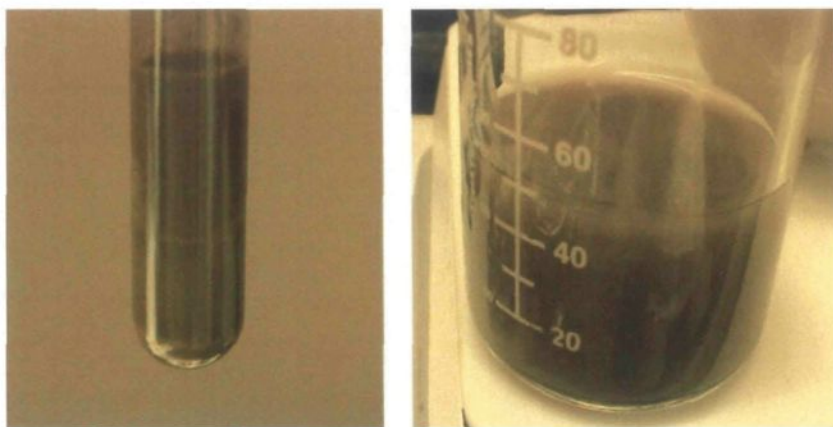


Figure 4.6: Colloid of silver nanoparticles prepared in aqueous basic medium.

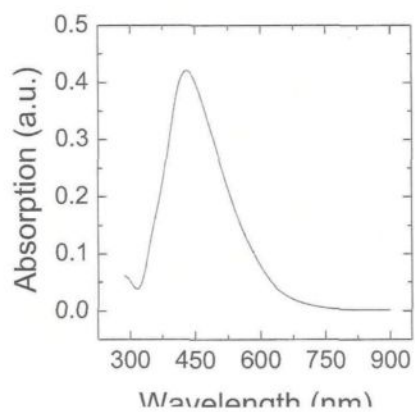


Figure 4.7 : UV-visible absorption of silver nanoparticles in basic medium.

Figure 4.7 presents the UV-visible spectrum of the as-prepared colloidal Ag particles in basic medium. Similar to the previous experiment, the prominent absorption peak at around 430 nm confirms the presence of Ag nanoparticles in the solution, compatible with reported in the literature [179].

Because of the strong base (KOH), the reaction is fast and the time evolution of particles is not possible. Immediately after injection of KOH into the mixture, a green-brown color appears indicating the presence of nanoparticles and it does not change with passing the time. This observation agrees well with UV-visible study which indicates no change in the absorption curve over time, except a decrease in amplitude caused by precipitation of particles after more than one day.

This method is fast, simple and practical. No heat source or hot-plate is required and only stirring is sufficient. It is also scalable and can be performed in higher quantities without a major change in results. No difference in UV-vis spectra was found between experiments with either flat-bottom or round-bottom flasks. Injection rate was not important too. On the other hand, the reaction is fast and not traceable with UV-vis. The particles are not very uniform in shape and removal of PVP from them is more difficult because of the higher ratio of PVP/Ag as compared to the previous experiment.

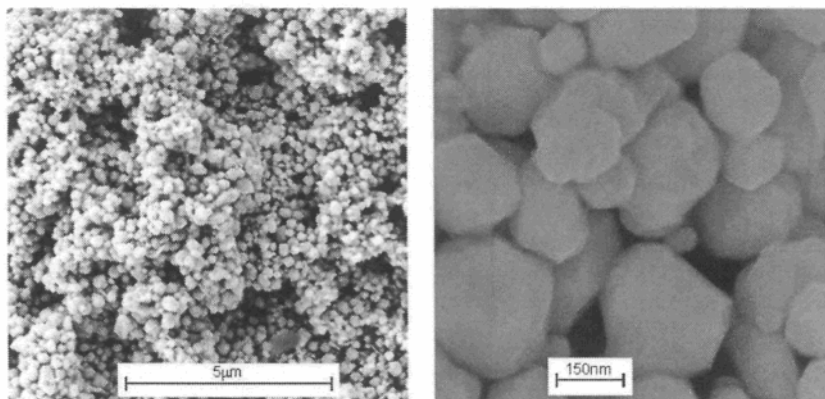


Figure 4.8: SEM images of silver nanoparticles of type 2, prepared in basic medium.

Figure 4.8 illustrates SEM images of Ag nanoparticles prepared in aqueous basic medium. The range of particle sizes in these images is from 80 nm to 400 nm with an average of ~263 nm, presented in figure 4.9.

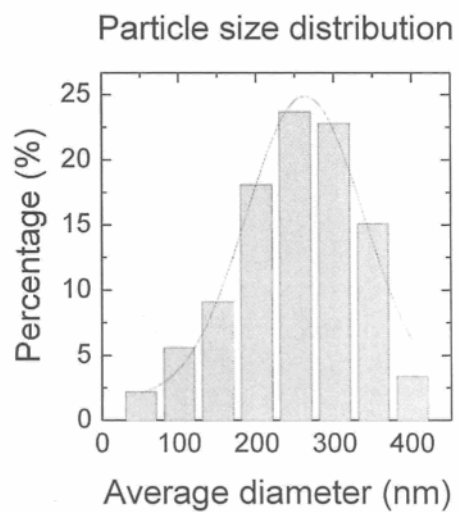


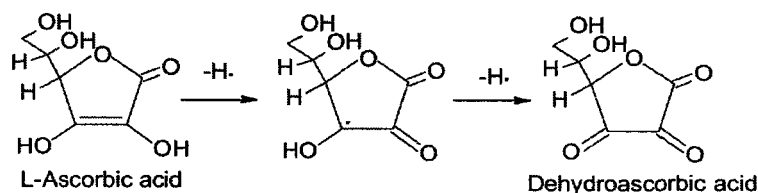
Figure 4.9: Size distribution of silver nanoparticles of type 2.

Table 4.2: Size distribution groups of silver nanoparticles of type 2, shown in figure 4.9.

Average diameter (nm)	Mid-size (nm)	Percentage
<74	50	2.2
75-124	100	5.6
125-174	150	9.1
175-224	200	18.1
225-274	250	23.7
275-324	300	22.8
325-374	350	15.1
>375	400	3.4

4.1.3 Silver Nanoparticles Type 3

Ascorbic acid ($C_6H_8O_6$) can react as a reducing agent via oxidation to semidehydroascorbate radical and dehydroascorbic acid [181], as shown in figure 4.10. The released hydrogen radicals react rapidly with free hydroxyl radicals and oxygen and prevent the nanoparticles from oxidation.

**Figure 4.10: Antioxidation mechanism of ascorbic acid [181].**

Thus, Ag^+ ions can be reduced to metal silver by ascorbic acid according to the following reaction [182]:

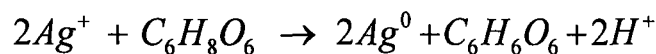


Figure 4.11 illustrates SEM images of Ag nanoparticles prepared in acidic medium. The particles are almost spherical. In absence of EG, the reaction was fast and the resulting solution was dark-gray color, indicating agglomeration process and large particles formations. The rapid precipitation of the colloid confirmed this fact. Addition of 25% (by volume) of EG reduced the rate of diffusion growth and the final colloid had a pale gray color with much longer stability.

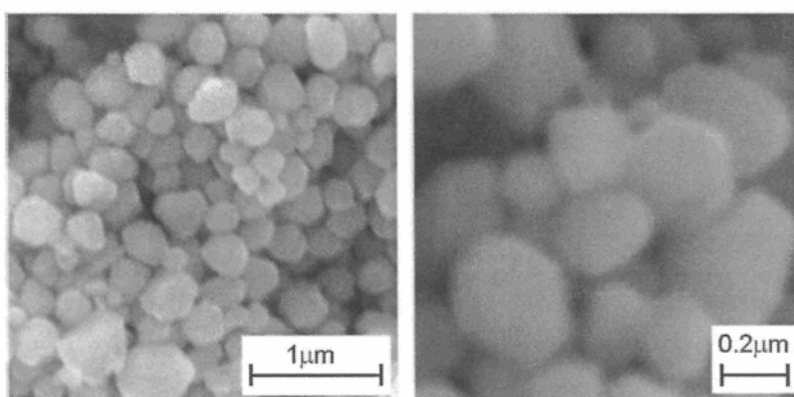


Figure 4.11: SEM images of silver nanoparticles prepared in acidic medium.

Table 4.3: Size distribution groups of silver nanoparticles of type 3, shown in Figure 4.12.

Average diameter (nm)	Mid-size (nm)	Percentage
<70	50	1.5
70-109	90	3.6
110-149	130	12.4
150-189	170	27.8
190-229	210	27.8
230-269	250	14.9
270-309	290	9.3
>310	330	2.6

As shown in figure 4.12, in this case the particles had a size range from 50 nm to 300 nm with an average of ~ 194 nm. Figure 4.13 depicts the UV-visible spectrum of the as-prepared colloidal Ag particles in acidic medium. Here, the peak position is at ~ 490 nm.

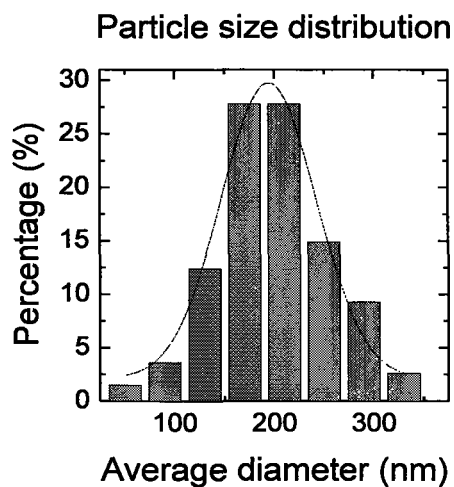


Figure 4.12: Size distribution of silver nanoparticles of type 3.

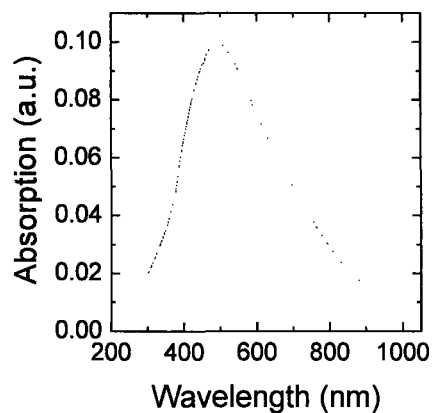


Figure 4.13: UV-visible absorption of silver nanoparticles in acidic medium.

This method is also fast and practical. No heat source or hot-plate is needed and only stirring suffices. The reaction vessel is not affecting and no difference in UV-vis spectra was detected by from experiments with flat-bottom or round-bottom flasks. The reaction is also scalable and can be performed in higher quantities with similar results. Injection rate was not important too. The particles were protected from oxidation and had relatively uniform size and shape (as seen in figure 4.11).

Due to rapid reaction, tracing the particle evolution with UV-vis was not possible. Separation of PVP from the particles was even more difficult because of high PVP/Ag ratio. The reaction should be terminated by adding large amounts of water, otherwise agglomeration leads to big formations which precipitate rapidly on the vessel walls.

4.2 Copper Nanoparticles

4.2.1 Copper Nanoparticles Type 1

In this experiment, EG was used as the solvent and not as a reducing agent. Although EG could serve as a reducer in many other cases, it could not be used as a reducing agent in a solution of Cu (II) [183]. It has been also reported that ascorbic acid alone can not reduce copper salt [184] or leads to very tiny particles [181]. In the present experiment, high temperature EG medium helps facilitate the reduction of Cu^{2+} ions at a temperature higher than the boiling point of water. Figure 4.14 shows a SEM image of Cu nanoparticles prepared in this experiment. Many different shapes and sizes of the particles are observed.

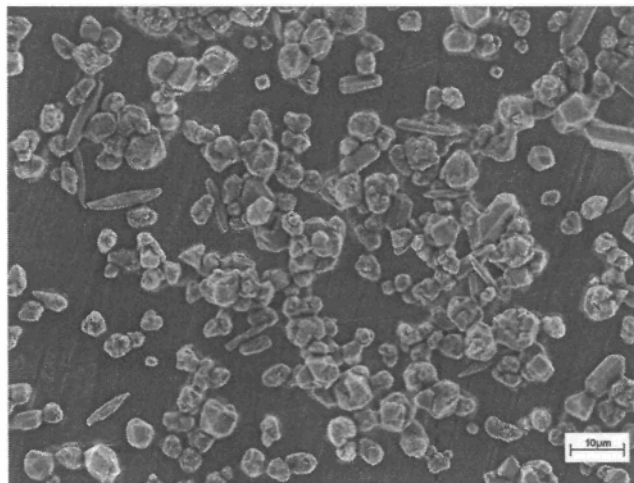


Figure 4.14: SEM image of copper nanoparticles of type 1, prepared in alcohol medium.

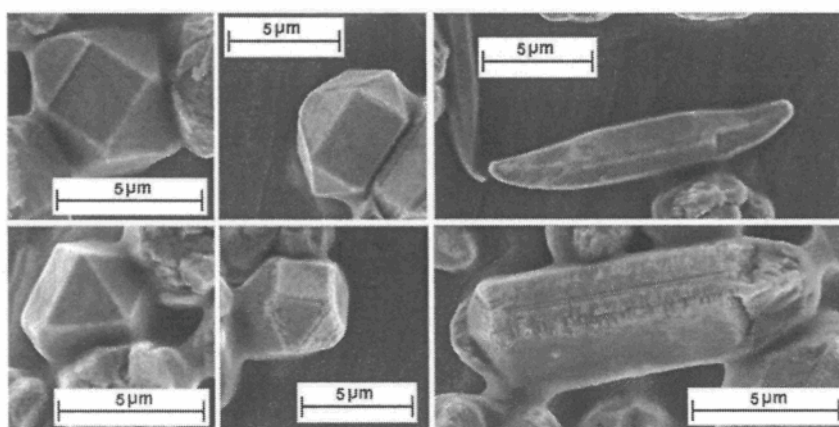


Figure 4.15: SEM images of different morphologies of copper particles of type 1.

Figure 4.15 depicts six different morphologies of copper particles found in the outcome of this experiment. The particles are in micrometer range with clear facets. Some reasons can be considered for the growth of large particles, such as difference in case of Cu compared with Ag, lower capping power of PVP for copper compared with silver and dissimilarity in reducing agent. Apparently, the last one is the most important one.

Figure 4.16 shows the UV-visible spectrum of the Cu particles. The prominent absorption peak at around 650 nm is close to those reported in the literature [183].

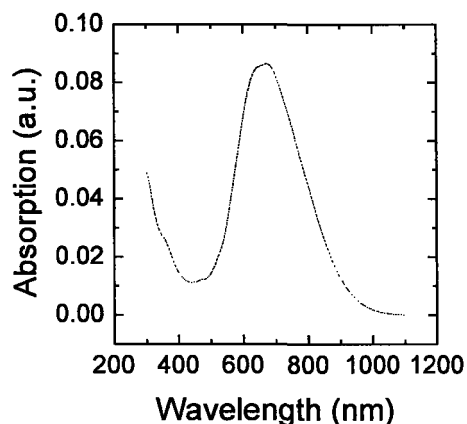


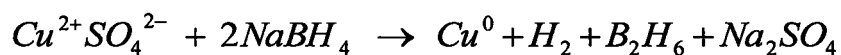
Figure 4.16: UV-visible absorption of copper particles prepared in alcohol medium.

It was detected that Cu particles precipitated on the flask walls even during initial steps of the reaction. Also, the colloid after centrifugation was not stable and the particles precipitated very fast. All these observations confirm the large sizes for particles in agreement with the SEM images in figure 4.15. At temperatures below 100°C, reaction rate was observed to be much lower and the reaction did not start under 70°C. Presence of very large particles caused some difficulties in separation procedure using centrifuge and the large fraction of copper mass was consumed by large particles. The reaction is very sensitive to injection rate of reactants which can strongly influence the temperature and finally particle size. To be evaporated, the water content of the injected ascorbic acid absorbed high amount of energy and decreased the solution temperature. To compensate for

this, it was necessary to use a temperature sensor inside the solution rather than the hot-plate sensor. Also, the thermal contact between the round-bottom flask and bronze heat conductor should be good enough to transfer the absorbed heat of boiling. Immediately after finishing the water in the mixture, a sharp increase in temperature is likely to happen so the temperature set point should be reduced in advance. This makes the procedure somewhat complex and far from being reproducible or scalable.

4.2.2 Copper Nanoparticles Type 2

In an initial step, copper particles were produced by reduction of Cu^{2+} ions with sodium borohydride, via this reaction.



This is approved by the appearance of a yellow color. NaBH_4 is a strong reducing agent which can produce instantaneously a large density of nucleation centers. The generation rate of reduced atoms is so high that these atoms reach together and form lots of clusters and finally many small particles.

Figure 4.17 depicts the UV-vis spectrum with an absorption peak at 260 nm. For this test a quartz cuvette was necessary to record a meaningful spectrum starting from 220 nm. The obtained particles were very sensitive to oxygen, which caused their instability. Even with N_2 purging, the yellow color of their solution turned to pale-blue of the initial solution after 30 min. In absence of purging, the particles got oxidized and finally black precipitate of copper oxide appeared within 30 min. In addition, due to its high amount, removing of

PVP from such small particles could not be done. This fact led to failure of SEM imaging and only some images of burned material were obtained. AFM was not helpful too.

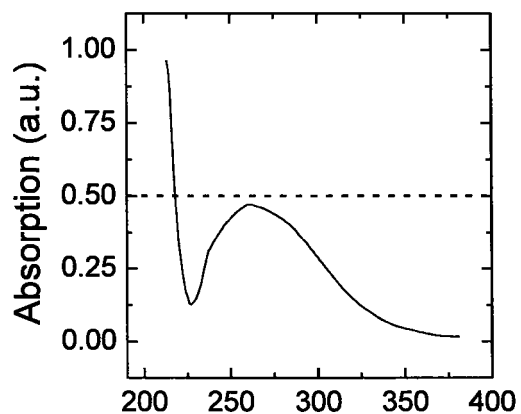


Figure 4.17: UV-visible spectrum of copper nanoparticles of type 2, prepared using NaBH_4 .

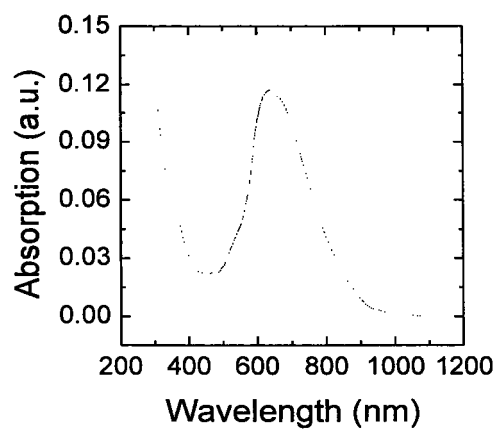


Figure 4.18: UV-visible spectrum of copper particles prepared using NaBH_4 followed by ascorbic acid.

Although ascorbic acid can not effectively reduce copper ions, it can be used to continue the reduction process which is initiated by other reducing agents. Herein, after generation of small Cu particles by reduction of Cu^{2+} by NaBH_4 , the remaining ions were reduced and joined the particles to produce larger ones. This fact was verified by UV-vis spectrum of figure 4.18. An absorption peak appeared at 635 nm which indicates the presence of larger particles.

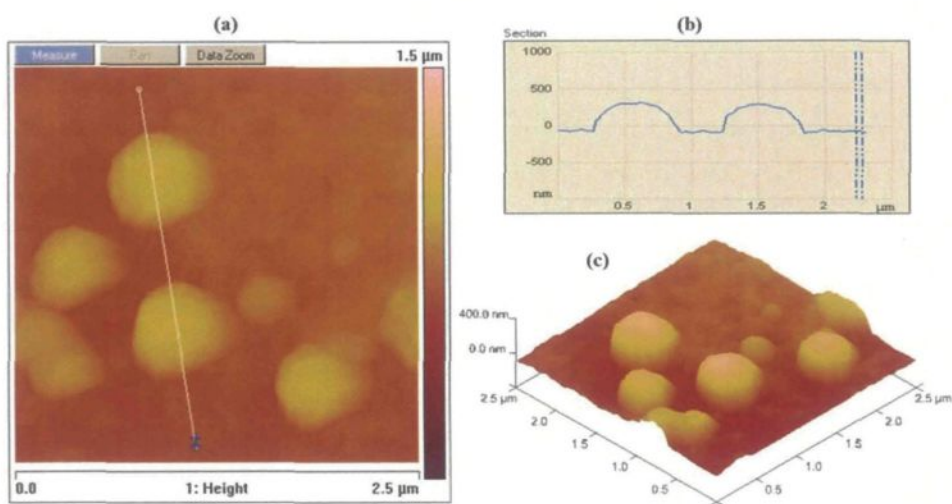


Figure 4.19: AFM results of copper nanoparticles prepared using NaBH_4 followed by ascorbic acid: (a) 2D image, (b) cross section along the white line in (a), and (c) 3D image of (a).

The particles were washed and coated on silicon and dried well for AFM imaging (see figure 4.19). Such particles were found to be almost spherical with average diameter of ~ 400 nm. No other shape was observed for the particles.

4.3 Summary

Experiments have been carried out to study three preparation methods for silver nanoparticles and two approaches for copper nanoparticles. Also, the outcomes of each experimental method have been discussed. From the obtained results, the following conclusions can be drawn:

- Different approaches are required to synthesize nanoparticles of different sizes or shapes. Depending to the type of material, a unique approach must be selected.
- In the case of silver, the largest particles were obtained by injecting precursor to alcoholic solution and the smallest ones by using ascorbic acid in aqueous/alcoholic medium.
- In the case of copper, reduction of copper sulphate with ascorbic acid in alcoholic medium resulted in larger particles compared with the particles prepared in two-step process: sodium borohydrate and ascorbic acid in aqueous/alcoholic medium.
- Silver nanoparticles were adequately stable and their colloid kept their properties for more than one month. Copper particles have generally limited stability and higher affinity to get oxidized or precipitate.