www.arpnjournals.com

MORPHOLOGY AND OPTICAL PROPERTIES OF AGNPS: EFFECT OF REDUCING AGENT TO SURFACTANT RATIO

Suriati Ghazali and Nureen Noordin
Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang, Lebuhraya Tun Razak, Gambang, Kuantan
Pahang, Malaysia
E-Mail: suriati@ump.edu.my

ABSTRACT

The synthesis of nanomaterials have attracted a great deal of attention these recent years due to their wide application in many scientific and technological field. Silver nanoparticles, among all other metals, have been investigated because of their unique optical, electronic and chemical properties that depends on their shape and sizes. The main objective of this work is to study the effect of reducing agent to surfactant ratio on the morphology and optical properties of silver nanoparticles. It is believed that the ratio of reducing agent to surfactant plays a significant roles in controlling the size and shapes of the synthesized nanoparticles. In this work, the silver nanoparticle was firstly synthesized via chemical reduction method of AgNO3 with the help of Sodium Borohydride as a reducing agent and Cetyltrimethylammonium Bromide (CTAB) as a surfactant. Different concentration of CTAB and NaBH4 were used in this study ranging from 0.5mM to 1.0mM and 2mM to 4mM, respectively. From this study, it can be observed that high concentration of NaBH4 to low concentration of CTAB produces a larger particles as the presence of CTAB at low concentration in the solution is not enough to inhibit the rapid growth of AgNPs. Meanwhile, the opposite effect were observed at low concentration of NaBH4 to high concentration of CTAB where the AgNPs formed are much more distributed as the growth of silver atoms were inhibited after the reduction process occurs. The low concentration of NaBH4 causes the reduction of silver ions to be at a slower phase, giving time to the CTAB to form a barrier and inhibit growth of AgNPs and thus, avoiding agglomeration. The different reducing agent and surfactant concentration used give rise to the effect of reducing agent to surfactant ratio towards the morphology and optical properties of as-synthesized AgNPs. The resulting AgNPs were then characterized by X-ray diffraction analysis, Field Emission Microscopy (FESEM) and UV-vis analysis. Results from UV-Vis showed the highest absorbance peak at ~410 nm which indicates the silver nanoparticles formation. From the result obtained, it can be suggested that the best ratio of reducing agent to surfactant is at 2.00 with NaBH4 and CTAB concentration at 3 mM and 1.5 mM respectively. At this ratio, the distribution of AgNPs are more improved with less agglomeration.

Keywords: silver nanoparticles, reducing agent, surfactant, ratio field emission scanning electron microscopy, UV-Vis absorption, X-ray diffraction.

INTRODUCTION

Silver nanoparticles (AgNPs) have been considered as one of the most important materials from the view point of their possible practical usage. Recently, silver nanoparticles have been studied because of their extraordinary antibacterial and fungicidal activity which made them extremely popular in a diverse range of consumer products including plastics, soaps and textiles which increase their market value (Quang *et al.* 2013). However, it's application depends highly on the properties of silver nanoparticles, which is size of the particles, size distribution and surface charge (Soukupová *et al.* 2008). As an example, a research conducted by Shekar *et al.* (2013) showed that AgNPs at 10 nm exhibits more antimicrobial activity compared to AgNPs at 100 nm size particles. In synthesis of nanoparticles, the selection of reducing agent and surfactant is very crucial as its could influence the formation of the nanoparticles and hence affect the size, shapes and distribution of nanoparticles. Smaller size and narrow size distribution of nanoparticles is very important to make it suitable to be commercialized in any applications (Shekar *et al.* 2013).

In general, AgNPs can be synthesized by using chemical or physical methods. In physical approach, the

AgNPs can be synthesized by evaporation-condensation using a tube furnace, thermal decomposition methods to produce silver particles in powder form, using a small ceramic heater (Jiang *et al.* 2011) and also by arc discharge method (El-Nour *et al.* 2010). As compared to chemical method, the physical method often utilizes physical energies such as thermal and arc discharge in order to produce very narrow size distribution of silver nanoparticles. It can also permit producing large quantities of silver nanoparticles samples in a single process and may be the most useful method to produce. However, according to Quang *et al.* (2013), certain drawbacks of physical method are considered such as the primary costs for investment, large space of tube furnace, large consumption of energy and time consuming has been reported.

Due to aforementioned disadvantages of physical method, many researchers reported the chemical method includes chemical reduction, polyol, thermal decomposition, laser ablation, electron beam irradiation, and the in-situ chemical route (Dang *et al.* 2012). Chemical reduction method involved simple and convinient way to synthesize AgNPs. Khan *et al.* (2013) also states the advantages of using chemical reduction

www.arpnjournals.com

method as it is cost effective, easily scaled up for large scale synthesis and there is no need to use high pressure, energy and temperature. However, using the chemical reduction method, the formation of AgNPs can be greatly influenced by the concentration of reducing agent and surfactant used which give rise to the effect of reducing agent to surfactant ratio on the production of AgNPs.

Moreover, different sizes of the as-synthesized nanoparticles were mainly depends on the following situations: 1) If the number of nuclei increased faster than that of total ions, smaller particles would be obtained. 2) If the increase of nucleus number was proportional to that of total ion number, the particle size might remain unchanged. 3) When the number of nuclei remained constant or increased slower than that of total ions, the particle size would become larger with the increase of ion concentration. As this work using chemical reduction method in order to synthesize AgNPs, therefore the present paper reported the choice and the ratio concentration of reducing agent and surfactant in controlling the morphology of the silver nanoparticles.

MATERIALS AND METHODS

The materials used were as follows: Silver nitrate, $AgNO_3$ (MERCK, 99% purity) were used as a precursor. The reducing agent and surfactant used are Sodium Borohydrade, $NaBH_4$ (MERCK, MW=40,000) and Cetyltrimethyl Ammonium Bromide, CTAB (MERCK, 99%) respectively.

The preparation procedure of AgNPs was described as follows: The precursor of silver nitrate was prepared at 1.0×10^{-3} M. Meanwhile, for CTAB and $NaBH_4$, the concentration were varied from 0.5 mM to 1.5 mM in order to investigate the effect of reducing agent to surfactant ratio on the morphology of the AgNPs. In this work, 10 ml of $AgNO_3$ were added into a 30ml of CTAB in a conical flask and were stirred using a magnetic stirrer at a rate of 800 rpm. 30 ml of freshly prepared $NaBH_4$ were then added into the solution while stirring is continued for 40 minutes until the solution reached room temperature. The colour changes of the silver were observed. The as-synthesized Ag colloid are then stored in an amber bottle and kept in low temperature. In order to remove the unreacted resultants, silver nanoparticles suspensions were centrifuged (12000 rpm, 15 minutes) and washed thrice, followed by re-dispersion of de-ionized water before undergo characterization using UV-Vis, XRD, and SEM.

RESULT AND DISCUSSION

Varying the ratio of reducing agent to surfactant leads to formation of silver colloids with different color, schematically presented in Figure-1. In this synthesis process, the addition of silver nitrate into the solution containing $NaBH_4$ and CTAB results in the changes of solution colour, indicating the formation of silver nanoparticles during the reaction process. The changes in solution colour marks the reduction of Ag^+ to Ag^0. Figure 1, shows that at any constant $NaBH_4$ concentration, the

solution colour of silver nanoparticles becomes lighter from 0.5 mM to 1.0 mM of CTAB. The changes in colour observed are due to the characteristic of the surface plasmon resonance (SPR) of nanoparticles in the solutions. According to Sharma *et al.* (2009), SPR happens as the electron cloud of the particles oscillate and absorb electromagnetic radiation at a particular energy which were determined by the size and geometry of the nanoparticles. This size and geometry of the AgNPs subsequently were depended on the concentration as well as ratio between reducing agent to surfactant. The changes in colour at 0.5 mM to 1.0 mM of CTAB as observed in this work also correlates with previous work by Rivero *et al.* (2013) which stated that smaller particles (caused by higher concentration of surfactant to reducing agent) posses a lighter colour trend.
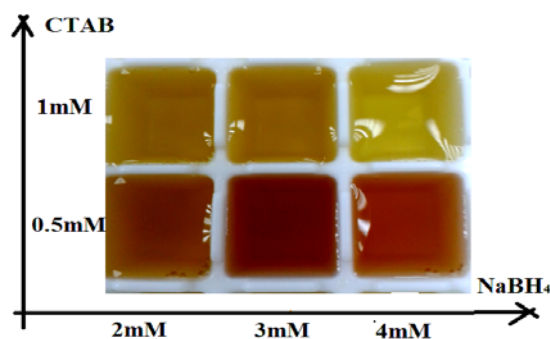

Figure-1. Colour mapping of as-synthesized AgNPs.

The rate of reduction from silver ions to atoms depends highly on the concentration of $NaBH_4$ used. During the reaction process, the atoms were reduces and then nucleate in small clusters that further grows into particles. The size and shape of the nanoparticles can be controlled depending on the availability of atoms, which in turn depends on the silver salt to reducing agent concentration ratio. Equation 1 below shows the reduction of silver nitrate by the presence of $NaBH_4$.

$$AgNO_3 + NaBH_4 \rightarrow Ag + H_2 + B_2H_6 + NaNO_3 \quad (1)$$
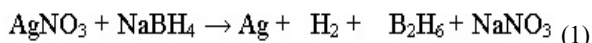
The characteristic of the surface plasmon resonance for this silver nanoparticle was further determined by UV-Vis analysis shown in Figure-2. From Figure-2, it can be seen that the highest peak was represented by sample that prepared at ratio of 2.0 (2.0 mM $NaBH_4$: 1.0 mM CTAB). As the CTAB concentration increases with decreasing ratio of reducing agent to surfactant, the graph shows a higher peak of absorbance value and shorter wavelength.

Meanwhile, the lowest peak was represented by sample at ratio 4.0 (2.0 mM $NaBH_4$: 0.5 mM CTAB) as observed in Figure-2. At this ratio, a secondary peak is formed because the as-synthesized nanoparticles are not stable due to the low presence of CTAB. The scattering spectrum of UV-vis is typically very sensitive to the

www.arpnjournals.com

aggregation state of the sample. The optical properties of silver nanoparticles changes when particles aggregate and the conduction electrons near each particle surface become delocalized and shared amongst neighbouring particles. When this occurs, the surface plasmon resonance shifts to lower energies, causing the absorption and scattering peaks to red-shift, having a broader wavelengths. As the particles destabilize, the original extinction peak will decrease in intensity. This were usually caused by the reduced stability of nanoparticles, which in turn broaden the peak or a formation of a secondary peak at longer wavelengths due to the aggregations of silver nanoparticles (Bohren *et al.* 2000).
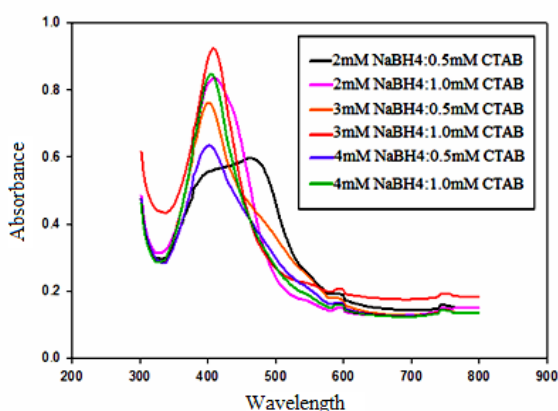

Figure-2. Absorbance spectra of as-synthesized AgNP.

Moreover, as shown in Figure-2, it can be seen that at constant concentration of CTAB, the lower ratio of reducing agent to surfactant results in a higher absorbance value. The absorbance value mainly designates the quantity of the silver nanoparticles that were reduced in the solution, therefore it suggested that the presence of low concentration of NaBH$_4$ which leads to lower ratio of reducing agent to surfactant are more favourable and has effectively increase the reduction process of Ag$^+$ to Ag^0. This is in accordance with previous work by Sileikate *et al.* (2008) that the increase in the absorption value shown in the UV-vis indicates the increase amount of as-synthesized silver nanoparticles produced. Apart from that, the shape of the curve implies the uniformity of the size of particles where a much narrower curve, shows a more uniformed distribution of AgNPs. Hence, from the UV-Vis in Figure-2, for example at 3.0 NaBH$_4$: 0.5 CTAB and 3.0 NaBH$_4$: 1.0 CTAB, the lower ratio of reducing agent to surfactant results in more narrower shape which implies better uniformed distribution of AgNPs. Increasing of CTAB concentration indicates the effectiveness of CTAB to act as a surfactant by producing a barrier by the enhancement of electrostatic forces between the nanoparticles to avoid agglomeration (Beyer, 2012).

FESEM image

The growth of AgNPs after reduction can be inhibited by the use of surfactant. When nanoparticles are in solution with the presence of surfactant, it will associate with the nanoparticle surface to establish a double layer of charge that stabilizes the particles and prevents aggregation, producing a much distributed AgNPs. Figure-3 (a) and 3 (b) shows the micrograph of the as-synthesized silver nanoparticles that were prepared at different ratio of NaBH$_4$ to CTAB. It can be seen that when the concentration of CTAB increases, the dispersion of silver nanoparticles was considerably improved, where the silver nanoparticles produce are less agglomerated.

The ratio between reducing agent and surfactant on the effect of AgNPs properties was furthur proved by a research conducted by Seoudi *et al.* (2011). Their experiment uses NaBH$_4$ as a reducing agent and DDT (dodecanethiol) as a surfactant. Their findings stated that the particle size increases due to the agglomeration which lead the formation of polydisperse silver nanoparticles with decreasing DDT.
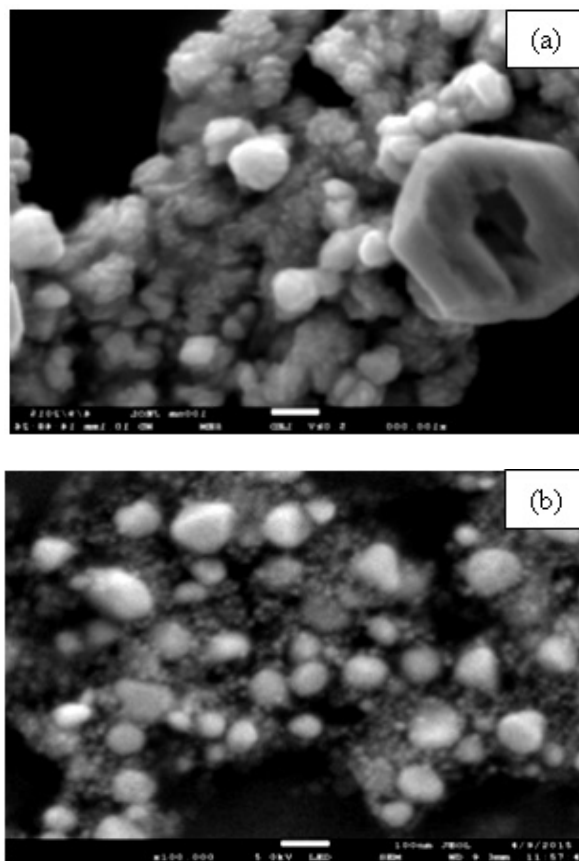

Figure-3. SEM micrograph of silver nanoparticles prepared at (a) 3mM NaBH$_4$:1.0mM CTAB, (b) 3mM NaBH$_4$:1.5mM CTAB.

From the result, it is clearly seen that the presence of both the reducing agent and surfactant plays an important role to the properties of AgNPs. When the

www.arpnjournals.com

reducing agent concentration used is increased, the reduction of silver ions to AgNPs occurs more rapidly depending on the availability of the silver atoms. These atoms will then grow and aggregate to become larger particles. To inhibit and control the growth of silver atoms, a surfactant is needed. High concentration of NaBH$_4$ to low concentration of CTAB produces a larger particles as the CTAB presence inside the solution is not enough to inhibit the rapid growth of AgNPs due to the availability of silver atoms. Low concentration of NaBH$_4$ and high concentration of CTAB will produce the opposite effect. The AgNPs formed are much more distributed because the growth of silver atoms are inhibited. The low concentration of NaBH$_4$ causes the reduction of silver ions to be at a slower phase, giving time to the CTAB to form a barrier and inhibit growth of AgNPs and thus, avoiding agglomeration.

Figure-4 shows the representative of the EDX result of the as-synthesized silver nanoparticles. The result shows that 56.51% of Ag at 3.0 keV are correspond to the binding energy of AgL, 15.81% of Al, 10.9% of C and 11.29% of Cu. The presence of element silver peak confirms the reduction of silver although the presence of small percentage of impurities. The presence of the small carbon and aluminium peaks are due to the adhesion of carbon tape and the aluminium stud.
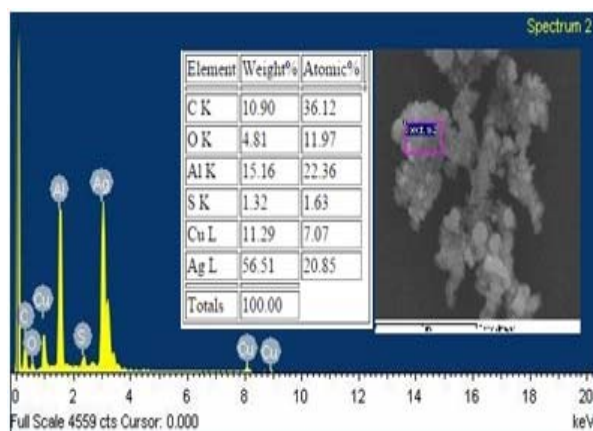

Figure-4. Representative EDX result for as-synthesized AgNPs.

The qualitative analysis of as-synthesized silver nanoparticles was further confirmed by using XRD. As shown in Figure-5, the intensive diffraction peak was detected at a 2θ value of 38.18°with (111) lattice plane of face centered cubic (fcc). However, the presence of other spurious diffractions in Figure-5 is might be due to crystallographic impurities in samples. Moreover, according to Oliveira *et al.* (2005), XRD patterns of the nanoparticles also can exhibit several size-dependent features, leading to anomalous peak positions, heights, and widths as nano-sized particles are expected to present a lattice contraction due to high surface pressure, and a distinctive non-crystalline atomic arrangement.
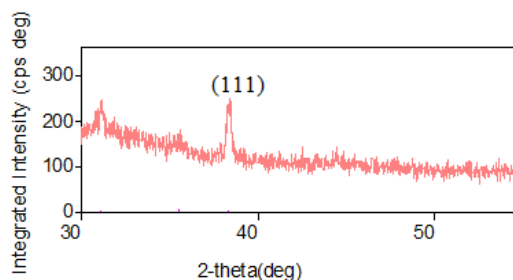

Figure-5. Representative XRD result for as-synthesized AgNPs.

CONCLUSIONS

As a conclusion, it was proved that the ratio of reducing agent to surfactant does affect the morphology and distribution of the as-synthesized AgNPs. The presence of surfactant may inhibit the growth of AgNPs, preventing it to agglomerate and forming larger particles. However, too high presence of CTAB which causes the decrease of ratio will lowers the functionility of reducing agent to reduce the silver ion to AgNPs. Hence, a reduction of silver ion will be slower and gives a lower number of absorbency value. In this study, it is concluded that the best AgNPs was produced at ratio of 2.00 where the NaBH$_4$ concentration is at 3.0 mM and CTAB at 1.5mM.

REFERENCES

[1] Beyer, K. (2012). Influence of Capping Agents on Silver Nanoparticle (Ag-NPS) Toxicity to Nitrifying Bacteria. San Diego: San Diego University.

[2] Bohren, C. F., & Hoffman, D. R. (2000). Absorption and Scattering of Light.   Springer ed , 536-665.

[3] Chen DH and Wu SH. (2000). Controlled Synthesis of Nanoparticles in   Microheterogeneous Systems. Chemistry of Materials 12 , 599-606.

[4] Dang TMD, T. L. (2012). Influence of surfactant on the preparation of silver nanoparticles by polyol method. Adv. Nat. Sci.: Nanosci. Nanotechnol.3 , 1-2.

[5] El-Nour A, K. M.-W. (2010). Synthesis and applications of silver nanoparticles.   Arabian Journal of Chemistry vol 3(1) , 136-139.

[6] Jiang XC, C. W. (2011). Role of temperature in the growth of Silver Nanoparticles   Through Synergetic Reduction Approach. Nanoscale Res. Lett 6:32 , 2-9.

[7] Khan Z, H. J.-T. (2013). Preparation and characterization of silver nanoparticles using aniline. Arabian Journal of Chemistry , 1-5.

[8] Rivero P.J, G. G. (2013). Effect of both protective and reducing agents in the synthesis of multicolor silver nanoparticles. Rivero *et al.* Nanoscale Research Letters, 8: 101, 2-9.

[9] Seoudi R, S. A. (2011). Effect of stabilizing agent on the morphology and optical properties of silver nanoparticles. Physica E 44, 440-446.

[10] Sharma VK, Y. R. (2009). Silver Nanoparticles: Green Synthesis and their Antimicrobial Activity. Colloid Interf.Sci , 83-96.

[11] Shekar A, S. M. (2013). Size-controlled silver nanoparticles synthesized over the range 5-100nm using the same protocol and thier antibacterial efficacy. Royal Society of Chemistry , 3974-3981.

[12] Sileikate A, P. J. (2008). Investigation of Silver Nanoparticles Formation Kinetics During Reduction of Silver Nitrate with Sodium Citrate. Material Science, 21-27.

[13] Soukupova, J. K. (2008). Comprehensive study on surfactant role on silver nanoparticles (NPs) prepared via modified Tollens process. Materials Chemistry and Physics, Vol. 111, Iss. 1 , 77-81.

[14] Oliveira MM, Ugarte D, Zanchet D, Zarbin AJ, (2005). Influence of synthetic parameters on the size, structure, and stability of dodecanethiol-stabilized silver nanoparticles. Journal of Colloid and Interface Science 292:429-35.

[15] Quang HT, V. Q.-T. (2013). Silver nanoparticles: synthesis, properties, toxicology, applications and perspectives. . Adv. Nat. Sci: Nanosci. Nanotechnol. 4 033001 , 1-5