Synthesis of stabilized silver nanoparticles exposed to hydrochloric acid

A.M. Atta, H. A. Allohedan*, A.O. Ezat and Z. A. Issa
Surfactant Research Chair, Chemistry Department, College of Science, King Saud University, P.O.Box - 2455, Riyadh - 11451, Saudi Arabia(*hlohedan@ksu.edu.sa)

ABSTRACT:

The bioavailability of ingested silver nanoparticles (AgNPs) depends in large part on initial particle size, shape and surface coating, properties which will influence aggregation, solubility and chemical composition during transit of the gastrointestinal tract. In this respect, different types of citrate-stabilized AgNPs coated with poly(vinyl-pyrrolidone) (PVP). Modified thiol derivatives of polyethylene glycol, polyacrylamides were exposed to synthetic human stomach fluid (SSF) (pH 1.5) and changes in size, shape, zeta potential, hydrodynamic diameter and chemical composition were determined during a 1 hr exposure period using Surface Plasmon Resonance (SPR), High Resolution Transmission Electron Microscopy/ Energy Dispersive X-ray Spectroscopy (TEM/EDS), Dynamic Light Scattering (DLS) and X-ray Powder Diffraction (XRD) combined with Rietveld analysis. Exposure of AgNPs to SSF produced stabilized SPR peak at 414 nm which changed according to the exposure time and the conditions of preparation of AgNPs. Changes in zeta potential, aggregation and morphology of the particles were also observed as well as production of silver chloride which appeared physically associated with particle aggregates.

Keywords: silver nanoparticles, acidic stability, core-shell, aqueous media.

1. INTRODUCTION

The antimicrobial action of silver nano particle (AgNP) has led to apply it in medical which required stability to stomach fluid (pH 1.5) [**1-3**]. Silver is a noble metal with an inert chemical reactivity in its bulk form and is listed below hydrogen in the activity series of metals. If the reaction between Ag nanoparticles and HCl can occur, the product will be silver chloride (AgCl), which is an insoluble precipitate [**4**].

There were three broadly defined categories used to reduce silver salts. The first one based on the use of relatively strong reducing agents, such as sodium borohydride,[**5**] hydrazine,[**6**] and tetrabutylammonium borohydride [**7**], to prepare silver nanoparticles. The second one is based on using the irradiation technique of the solution containing silver ions with γ-ray [**8**], ultraviolet or visible light [**9**], and microwave [**10**] and ultrasound irradiation [11]. The third route involves heating the solution of silver salt without commonly used reductants [**12**] or prolonged reflux silver solution in the presence of a weak reducing agent, such as glucose,[**13**] sodium citrate [**14**], dimethylformamide [**15**], potassium bitartrate [**16**], ascorbic acid [**17**], and alcohols or polyols [**18**]. Variety of stabilizers or coating agents have been used in the silver preparation mentioned above to achieve the best control of size, size distribution, shape, stability, and solubility of silver nanoparticles. Thiol derivatives [**19**] are the most common coating agents employed to stabilize silver colloids, even though aniline,[**20**] long-chain amines [**21**], surfactants [**22**], starch [**23**] and carboxylic compounds [24] have also been used. Polymers such as poly(vinyl pyrrolidone) [**25**], polyacrylonitrile [**26**], and polyacrylamide **[27**], are also important protective agents, which can effectively control shape, size, and stability of silver nanoparticles. For example, with the refluxing method, poly(vinyl pyrrolidone) can direct the growth of silver into nanowires [**28**]. To our knowledge, there have been no reports on the production of chemical stable of Ag nanoparticles toward HCl, whose reaction has been proved impossible for the bulk Ag. Because bioavailability of ingested AgNPs will likely depend on the aggregation state and chemical properties of particles after modification in the acidic environment of the stomach, the primary objective of this preliminary study was to investigate physical and chemical changes that occur during exposure of AgNPs to synthetic stomach fluid (SSF) system and HCl.

2. EXPERIMENTAL:

2.1. Synthesis of poly (oxyethylene)thiol monomethyl ether : *P*-toluenesulfonyl chloride (0.05 mol, 9.82g) in 80 ml of methylene chloride was added dropwise to a mixture of 0.05 mol (27.5g) of poly(ethylene glycol)monomethyl ether having molecular weight 550 g/mol(MPEG-550) and 0.05 mol (5.06g, 3.67ml) of triethylamine over 1 hour at 0°C. The mixture was then stirred overnight at room temperature. A white triethylamine hydrochloride precipitate was filtered off and washed with 50 ml of methylene chloride. The methylene chloride was removed under reduced pressure to leave pale yellow oil, which was purified by flash chromatography on silica using dichloromethane and acetonitrile (3:1, v/v) Solvents were evaporated to give poly(oxyethylene) tosylate monomethyl ether: (65% yield), colorless oil in both cases

Poly(oxyethylene)tosylate monomethyl ether (0.036 mol) and thiourea(3.1 g) mixed with 100 mL of ethanol and refluxed for 24hrs. The mixture cooled and mixed with

solution of (4.1 g) NaOH, water (5mL) and ethanol (50 mL). The mixture was refluxed for 3hrs under nitrogen atmosphere. The reaction mixture cooled and neutralized with 0.1 M of HCl. Solvents evaporated and the residue dissolved in ether and dried over Na_2SO_4. The ether evaporated to give pale yellow oil of poly(oxyethylene) thiol monomethyl ether (PEGSH; 86% yield).

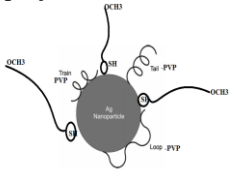
2.2. Synthesis of silver nanoparticles: Citrate-stabilized silver nanoparticles were prepared by dissolving 9mg of silver nitrate in 50mL of water and bringing it to boiling. A solution of 1% sodium citrate (1 mL) was added under vigorous stirring. The solution was kept at a boil for 1 h, and then allowed to cool to room temperature. The silver nanoparticles were purified by ultracentrifugation (30 min at 30 000 rpm), followed by redispersion in water. The typical yield of citrate-stabilized silver nanoparticles was around 65% (with respect to silver).

PVP-coated silver nanoparticles were synthesized by adding 1 g of poly(vinyl pyrrolidone), PVP molecular weight 40 000 g mol^{-1}) and 0.01 g of PEGSH with silver nitrate solution. The reaction completed as reported for citrate stabilized silver nanoparticles.

2.3. Characterization of AgNP: X-ray powder diffraction (XRD) patterns were recorded using a D/max 2550 V X-ray diffractometer. Transmission electron microscopy (TEM) micrographs were taken with a JEOL JEM-2100F. Ultraviolet visible (UV–vis) absorption spectra were obtained with a Techcomp UV2300 spectrophotometer. Different concentrations of aqueous solutions of HCl (0.1 M- 1M) were used to evaluate the stability of the synthesized AgNP to acidic media. It is well established that the synthetic stomach fluid was prepared using deionized distilled (DDI) water and contained HCl (0.42 M) and glycine (0.40 M) pH 1.5 [**29].**

3. RESULTS AND DISCUSSION

The fundamental application problem of silver NPs is connected with the sufficient stability of their dispersions allowing the prevention of the aggregation process because the generation of spacious aggregates leads to a loss of the silver activity [**30].** Therefore various surfactants and polymers are commonly applied to stabilize these metal colloids [**31**]. The enhancement of stability of aqueous dispersions of the silver NPs can be obtained via two kinds of protecting mechanisms. The first one is based on the steric repulsion, which displays a stabilizing effect with the assistance of polymers and non-ionic surfactants that are immediately adsorbed at the phase interphase [**32**]. The balance between the attractive and the repulsive forces is strongly dependent on the thickness of the adsorbed layer [**33**], which is, in the case of polymers, dependent not only on the chain length but also on its adsorption mode [**34**, **35**]. The second mechanism of the dispersion system stabilization is based on an electrostatic repulsion. The surface charge of the disperse phase can be enhanced by the ionic surfactant addition providing the electrostatic protection of the NPs to adhere to one another. In the present article, the work extended to synthesize more stable AgNP based on more stabilized citrate AgNPs. In this respect, Poly(ethylene glycol) monomethyl ether were modified to thiol which can self-assembled on AgNPs in the presence of PVP as stabilizer. In this so-called tail mode, the polymer molecule interacts with the solid particle surface only via the end of the polymer chain (scheme **1**), which represents a typical interaction mode for the polymer of a high molecular weight having a long linear polymer chain that is not branched.



scheme 1. Drafts of possible modes of how polymers can be bonded on the silver NP surface.

For the purpose of this study, there were tested two groups of polymers, based on polyethylenglycol (PEG) and polyvinylpyrrolidon (PVP) that are commonly used as stabilizers of the aqueous NP dispersions. Considering the structural and chemical differences between both groups, a distinctively different bonding strength of the polymer molecules on the surface of the silver NPs was expected. In aqueous solution of PVP or PEGSH silver nitrate was reduced with sodium citrate. Silver nanoparticles were obtained. The reaction equation are as follows:

$$3AgNO_3+Na_3C_6H_5O_7 \text{ (sodium citrate)}=$$
$$3Ag+C_5H_6O_5 \text{ (3-ketoglutaric acid)}+3NaNO_3+CO_2 \quad (1)$$

It was a preferable way here using polymer to obtain stable nanoparticles, such as PVP and PEGSH. These polymers have certain polymerization degree and chain length, which can protect the nanoparticles from aggregation [**36**]during the reduction of silver nitrate. The polymers of the PVP group are bonded stronger on the silver NP surface through the nitrogen atom in their molecule, while PEGs are weakly bonded via the oxygen atom. The studied polymers from the PEG group accomplish a marginal influence on the aggregation stability of the aqueous silver NP dispersion, possibly excluding PEG 550. The slightly higher stabilizing effect of the PEG 550, having the lowest molecular weight among the tested PEG polymers, could be probably connected with the fact that the used concentration (1% w/w) of this modification, and therefore can generate a more compact surface layer on the silver NP surface. The three kinds of silver nanoparticles (Ag NPs) used in this study were citrate AgNP, PEGSH coated AgNP and PVP-PEGSH coated AgNPs used to study the reactivity of AgNPs toward HCl solutions. They were freshly prepared and purified with an ultracentrifuge as described in the experimental section. On the other hand, three different molar concentrations of aqueous HCl 0.1, 0.5 and 1M were prepared to investigate the reactivity of AgNps for 1 h time interval.

A set of TEM images, and UV-vis absorption spectra of the dispersed nanoparticles in water is presented in **Figure 1**. As

can be seen from this figure, these nanoparticles are relatively monodispersed in size. The preservation of the nanodimensional character of the system modified by PEGSH, with limited interparticle interactions, is also evident from the UV/vis absorption spectra (Figure1) exhibiting relatively intense surface plasmon peak at 405 nm. The average particle size of the AgNPs changed from 6 nm to 25 nm and 65 nm by coating AgNPs with PEGSH and PVP/PEGSH, respectively.

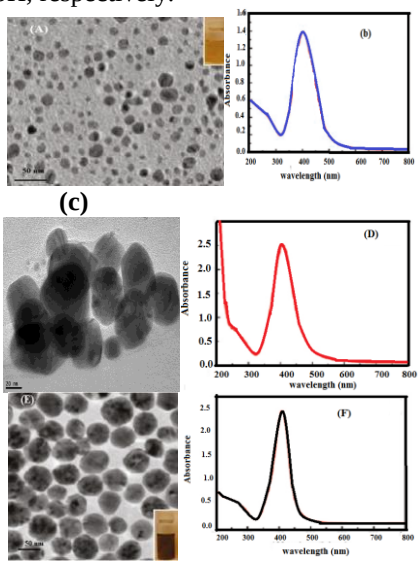


Figure 1. Set of images for silver nanoparticles: TEM image of the citrate AgNP (A) Its UV-vis absorption spectrum (B); TEM image of PVP/PEGSH Ag NPs(C), its UV-vis absorption spectrum(D); TEM image of PEGSH Ag NPs(E) and its UV-vis absorption spectrum(F).

Figure 2 is a set of digital images of the suspensions and UV-vis absorption spectra of Ag NPs under these different HCl conditions. A comparison of these digital images shown in this figure indicates that the HCl affected the stability of citrate AgNPs and gradually changed the color from yellow to green to turbid white precipitated to the bottom of the vial. The stability data of citrate AgNP is also supported by the UV-vis absorption spectra which acquired with time (Figure 2B). Under 0.1M aqueous HCl conditions, the absorption peak of Ag NPs disappeared completely. The decrease might be caused by the gradual increase in average particle diameter due to the Ostwald ripening process.

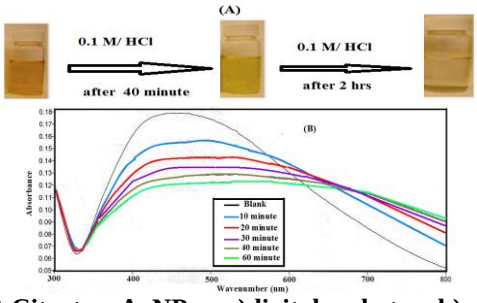


Figure2:Citrate AgNPs a)digital photo b) UV-vis absorption spectra at interval times in 0.1 M HCl.

The data was supported by TEM photos of citrate AgNPs (**Figure 3**) which indicated the formation of aggregates when they exposure to 0.1 M aqueous HCl solution.

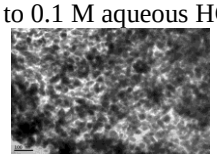


Figure 3:TEM of citrate AgNP after exposure to 0.1M HCl.

The similarity of the effect of HCl on PVP/PEGSH coated nanoparticles is also evident from the UV-vis absorption spectrum (**Figure 4** A) even though the overall stability of the PVP/PEGSH coated Ag NPs are better than the citrate NPs. Under 0.5M aqueous HCl, a new absorption peak appeared at higher wavelength. The appearance of this new peak is an indication of the formation of aggregates [**37].** Likewise, this slight decrease might be caused by the gradual increase in average particle diameter due to the Ostwald ripening process. However, the coating on the NPs clearly has a strong effect on their stability as demonstrated by the differences in **Figures 3 and 4**. We supposed that the appearance of a broad band consisting of three peaks implied that a thin layer of silver oxide (Ag_2O) formed on the surface of silver nanoparticles, and the colloids were the mixture of silver nanoparticles with and without silver oxide layers. The shoulder peak around 420 nm was indicative of the presence of AgNPs without Ag_2O layers, and the absorption band at ca. 450 nm suggested the existence of Ag/Ag_2O core-shell structures. The intensity of the peak implied the amount of the corresponding structure in the sample, and the thickness of Ag_2O layers on the Ag surface could be inferred from the position of the absorption band at ca. 450-470 nm.

The formation of aggregates was also confirmed by TEM images taken after 10 hrs (**4 B**). From this TEM image, it is evident that the nanoparticles aggregated and linked together, forming "chain"- like nanostructures. This means that the aggregates were stable in suspension **[38]**. The TEM image (**4 C**), taken after 24 hrs, shows that the nanoparticles were aggregated and formed much bigger particles. These results indicate that HCl is capable of initiating and accelerating the aggregation of silver nanoparticles, but the stability of the aggregates depends on the coating. Both of the PVP-coated and citrate coated nanoparticles aggregated, but the aggregates formed from the former were stable in suspension.

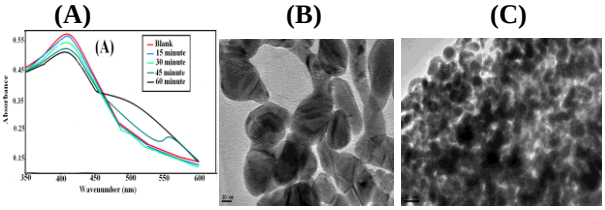


Figure4: PVP/PEGSH AgNPs a) UV-vis absorption spectra at interval times in 0.5 M HCl, b) TEM after exposure to 10 hrs in 1M HCl and C) TEM exposure to 24 hrs in 1M HCl.

The XRD pattern in Figure 5a shows that the product prepared consisted of metallic Ag with a cubic structure. The broadening of peaks indicates very small sizes of Ag crystallites. XRD (Figure 5b) indicates that the white product is a single phase of AgCl with a cubic structure. This means that Ag nanoparticles can react with HCl to form AgCl, showing unusually high chemical reactivity toward HCl [**4**].

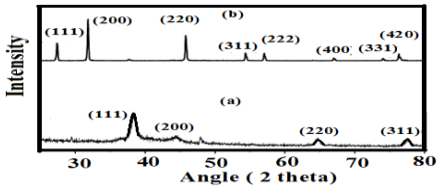


Figure 5: XRD patterns of samples. (a) citrate Ag nanoparticles and (b) the product of AgCl obtained from the reaction of citrate AgNP with hydrochloric acid.

X-ray diffraction patterns for PVP/PEGSH coated AgNP, before and after exposure to 0.5 M and 1 M HCl, were represented in figure 6.

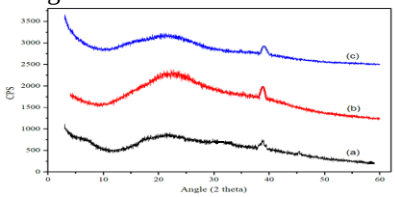


Figure 6: XRD patterns of a)PVP/PEGSH coated Ag, b)after exposure to 0.5M HCl and c) 1M HCl for 10 hrs.

They showed that the bulk structure of the compositions contained a polymeric amorphous phase, that was displayed in WAXS profiles by two diffusive overlapped maxima at (2- theta)15.8 and 21.8, and crystalline Ag nanoparticles, that was confirmed by characteristic crystalline peaks of silver (111) at (2- theta)38.8 [**39**]. The appearance of these peaks indicated the formation of crystalline Ag nanoparticles with tetragonal facetcentered cubic lattice [**39**].

REFERENCES:

[1] S. Y. Liau, D. C. Read, W. J. Pugh, J. R. Furr and A. D. Russell, Lett. Appl. Microbiol. 25, 279, 1997.

[2] S. Kittler, C. Greulich, J. Diendorf, M. Koller and M. Epple, Chem. Mater. 22, 4548, 2010.

[3] Y.S. Kim, J.S. Kim, H.S. Cho, S.D. Rha, J.M. Kim and J.D. Park, Inhalation Toxicol 20, 575, 2008.

[4] L.Li and Y-J. Zhu, J. Coll. Inter. Sci. 303, 415, 2006.

[5] Y. S.Shon and E.Cutler, Langmuir 20, 6626, 2004.

[6] A.Taleb, C.Petit, M.P.Pileni, Chem. Mater. 9, 950, 1997.

[7] N.R.Jana, X.G.Peng, J.Am.Chem.Soc. 125, 14280, 2003.

[8] A.Henglein, M.Giersig, J.Phys.Chem.B 103, 9533, 1999.

[9]A.Callegari, D.Tonti, Nano.Lett.3, 1565, 2003.

[10] F.Gao, Q. Y.Lu, Chem. Mater. 17, 856, 2005.

[11] G. Carotenuto, G. P.Pepe, Eur. Phys. J. B 16, 11, 2000.

[12] Zhang, Z. P. J. Mater. Chem. 2003, 13, 641-643.

[13] P.Raveendran, J.Fu, J.Am.Chem. Soc. 125, 13940, 2003

[14] S. Weihong, Z. Xiaoxiao, Y. Hongzong, S. Panpan, L. Xiaoyan, Chinese J. Chem. 27, 717, 2009.

[15] I.Pastoriza-Santos, L. M. Liz-Marzan, Langmuir 15, 948, 1999.

[16] Y. W.Tan, X. H.Dai, Y. F.Li, D. B. Zhu, J. Mater. Chem. 13, 1069, 2003.

[17] G. J.Lee, S. I.Shin, Mater. Chem. Phys. 84, 197, 2004.

[18] Y. G.Sun and Y. N. Xia, Science 298, 2176, 2002.

[19] Y. S. Shon and E.Cutler, Langmuir 20, 6626, 2004.

[20] Y. W.Tan, Y. F. Li, D. B. Zhu, J. Colloid. Interface Sci. 258, 244, 2003.

[21] M.Green, N.Allsop, G.Wakefield, P. J.Dobson, J. L.Hutchison, J. Mater. Chem. 12, 2671, 2002.

[22] L. M. LizMarzan, I. LadoTourino, Langmuir 12, 3585, 1996.

[23] P.Raveendran, J. Fu, S. L.Wallen, J. Am. Chem. Soc. 125, 13940, 2003.

[24] X. Z.Lin, X. W.Teng, Langmuir 19, 10081, 2003.

[25] C.Luo, Y.Zhang, X.Zeng, Y.Zeng, Y.Wang, J. Colloid Interface Sci. 288, 444, 2005.

[26] Z. P.Zhang, M. Y. Han, J. Mater. Chem. 13, 641, 2003.

[27] Q. Yang, F.Wang, K. B.Tang, C. R.Wang, Z. W.Chen, Y. T. Qian, Mater. Chem. Phys. 78, 495, 2002.

[28] Y. G. Sun, Y. D. Yin, B. T. Mayers, T. Herricks, Y. N.Xia, Chem. Mater. 14, 4736, 2002.

[29] D.F. Evans, G. Pye, R. Bramley, A.G. Clark, T.J. Dyson, J.D. Hardcastle. Gut 29, 1035, 1988.

[30]. S.Shrivastava, T.Bera, A.Roy, G.Singh, P.Ramachandrarao, D. Dash, Nanotechnology 18, 9, 2007.

[31] L.Kvıtek, A.Panacek, J. Soukupova, M. Kolar, R. Vecerova, R.Prucek, M. Holecova and R. Zboril, J. Phys. Chem. C 112, 5825, 2008.

[32] R. J. Hunter, Double Layer Interaction and Particle Coagulation. In Foundations of Colloid Science, 2nd ed.; Oxford University Press: New York, pp 635, 2001.

[33] K. S.Chou, Y. S. Lai, Mater. Chem. Phys. 83, 82, 2004.

[34] D. F.Evans, H. Wennerstrom, Polymers in Colloidal Systems. In The Colloidal Domain: Where Physics, Chemistry, Biology, and Technology Meet; Wiley-VCH: New York, pp 316, 1994.

[35] L. M. Liz-Marzan, I. Lado-Tourino, Langmuir 12, 3585, 1996.

[36]. T.Selvan,; J. P. Spatz,; H. A. Klock, Adv. Mater. 10, 132, 1998.

[37] T. Kim,; C. H. Lee, S. W. Joo, K. Lee, J. Colloid Interface Sci. 318, 238, 2008.

[38] Y. Cheng, L.Yin, S.Lin, M.Wiesner, E. Bernhardt, and J. Liu, J. Phys. Chem. C 115, 4425, 2011.

[39] E. A. Becturov, S. E. Kudaybergenov, A. K. Garmagambetova, R. M. Iskakov, J. E. Ibraeva, S. N. Shmakov, Almaty 274, 2010.