Low Temperature, Water Based Synthesis of Silver Nanoparticles with Antimicrobial Activity

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Abstract

A classical silver nanoparticle preparation method is the polyol process [1, 2] that is carried out in polyol solvents at high temperature. Other methods are also known that rely on the use of organic solvents or water as the reaction medium [3]. However there are relatively few synthesis methods with low environmental impact. Aminosilanes were previously suggested only for solvent based synthesis and in large molar excess [4-9], but they can be used in water based reaction medium too.

A new green synthesis process is described here that uses only water, silver nitrate, aminosilane [N-(2-aminoethyl)-3-aminopropyltrimethoxysilane] and reducing agent to synthesize silver nanoparticles. Silver nanoparticles were successfully prepared in high concentration (1000 ppm Ag) with diameter below 30 nm based on the analysis of UV-Vis spectra of the nanoparticle dispersions. The particle size was easily controlled by first preparing small seeds and then introducing additional complexed silver ions to deposit more silver on the initial seed particles. This led to the progressive formation of larger particles. It was confirmed that aminosilane plays a crucial role in the nanoparticle formation since its replacement by a polyamine (Jeffamine T-403) bulk silver precipitation was observed instead of nanoparticle formation. The use of aminosilane also provides amino and silanol functional groups on the nanoparticles that can promote reversible aggregation of the particles and enhance particle adhesion on surfaces. This is useful in antimicrobial treatments. Preliminary experiments indicated excellent antimicrobial activity. Thin layers of spray deposited silver nanoparticles on ceramic tiles were able to prevent bacterial growth completely.

Key words: Silver nanoparticle, green synthesis, antimicrobial activity

1. INTRODUCTION

Stable metal nanoparticle dispersions were first described by Faraday in 1857 [10]. Since this initial publication, there has been a large variety of processes described that can produce metal nanoparticles, including silver sols. However, the most successful synthesis methods to convert silver ions into silver nanoparticles, such as the polyol process [1, 2], have relied on the use of solvent medium and high temperature that is considered energy intensive and not environmentally friendly. Although attempts have been made to reduce the environmental impact of the synthesis, many of these methods still rely on significant amount of organic solvent or they are unable to produce nanoparticles in high concentration [3]. In general, the synthesis methods require a silver salt solution, a stabilising agent and a reducing agent to create the silver nanoparticles.

Since silver nanoparticles are finding increasingly wide applications, for example as conductive inks [11-12] or antimicrobial agents [13], there is a need for selecting the reaction medium, reactants, and stabilising additives such that the synthesis process can be carried out on an industrial scale while minimising environmental impacts. Based on a few literature reports, particularly useful stabilising agents appeared to be aminosilanes. Their application had been described in various solvent based synthesis processes as well as the creation of silver doped solids [4-9]. However, there seems to be no report on using these compounds in water-based systems to produce nanoparticle dispersions. Thus, in this work, experiments were carried out to evaluate the suitability of an aminosilane in the water-based synthesis of silver nanoparticles.

2. METHODOLOGY

2.1 Materials and Synthesis Process

The following materials were used: Analytical grade silver nitrate as the silver ion source; N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (Silquest A-1120, from Momentive) as the nanoparticle stabiliser; formaldehyde 37% in water, diluted as needed; ammonia 25% in water, diluted as needed; trimethylolpropane tris[poly(propylene glycol), amine terminated]ether (M_n=440), also known as Jeffamine T-403 from Huntsman Corporation, ion exchanged (deionized) water as the reaction medium. Generally, the nanoparticle synthesis was carried out by firstly making an aqueous solution of the aminosilane and a solution of silver nitrate and formaldehyde mixture. The

aminosilane was let to stand a few hours to allow hydrolysis before use while the silver nitrate-formaldehyde mixture was used immediately after mixing the precursor stock solutions since it was not stable. The silver nitrate-formaldehyde solution was added to the warm aminosilane solution and heated to 60 °C for several minutes while stirring.

Initially formed nanoparticles were further grown in size by adding an aqueous solution of silver ions complexed with either ammonia or Jeffamine T-403.

2.2 Particle sol characterisation

Particle sols were characterised by UV-Vis spectroscopy using UV3101PC UV-VIS-NIR Scanning Spectrometer.

2.3 Antimicrobial characterisation

Antimicrobial tests were carried out by first spraying a uniform layer of dilute silver nanoparticle dispersion onto glazed ceramic tiles. After one day of drying, an aliquot of 0.1ml Staphylococcus Aureus (ATCC 6538) dispersion containing 10^3 CFU (Colony Forming Unit) was inoculated onto the coated tile and also on an uncoated tile for reference. After 15 minutes, the ceramic tiles were swabbed with 3M™ pipette swab and 1ml of the diluted solution was transferred onto 3M™ Petrifilm™. The Petrifilm™ was incubated for 24 hours at 37 °C and examined for colony formation.

3. RESULTS & DISCUSSION

3.1. Nanoparticle properties as a function of synthesis conditions

A basic synthesis reaction was carried out by heating an aqueous aminosilane solution (Silquest A-1120, 74.70g and 0.367% by weight) to 45 °C and adding a solution of freshly prepared silver nitrate and formaldehyde (12.90 g solution containing 1.09% $AgNO_3$ and 0.048% formaldehyde). The solution was heated to 60 °C and became dark amber within minutes. Heating at 60 °C was maintained for 10 minutes. After the reaction was completed, the sol was stored for 12 days and an additional 1.69 g of 0.37% formaldehyde solution was added to react with any residual silver ions (same amount as used in the initial reaction). The resulting sol, referred to as NP-SOL-1 contained 1002 ppm silver metal. The concentrated sol was dark amber. The UV-Vis spectrum of the sol diluted to 10 ppm Ag content with water is shown in Figure 1 with peak centred near 400 nm. This peak indicates the appearance of surface plasmon resonance and it is characteristic of nanoparticles below 30 nm size [14, 15]. The lack of change in the spectrum after storage of the sol also indicates that there is no noticeable change in particle size over a six-week storage period.

It was observed that reaction to form nanoparticles takes place even when there is no reducing agent (formaldehyde) included. This can be attributed to the reducing nature of the amine in the aminosilane. However, the reaction is slow and incomplete when reducing agent is not added.

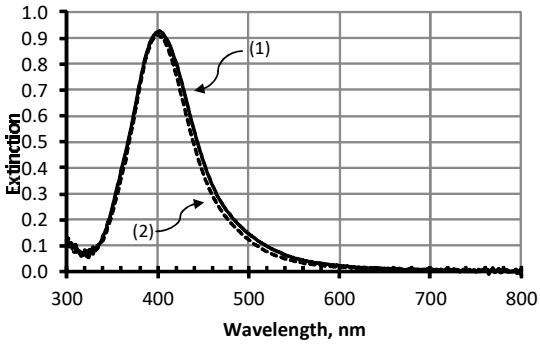

Figure 1.: Extinction spectra of nanoparticle dispersion of NP-SOL-1: (1) measurement after storage at 1002 ppm silver concentration for 6 days, diluted to 10 ppm silver concentration just before measurement (solid line), (2) measurement after storage at 1002 ppm silver concentration for 45 days diluted to 10 ppm silver concentration just before measurement (dashed line).

The effect of reaction conditions on the nanoparticle formation were further investigated by varying the composition during synthesis. In these experiments, primary populations of nanoparticles were prepared and then grown to larger size by supplying additional silver ions complexed with either ammonia or with Jeffamine T-403. The introduction of additional silver ions deposited additional metal onto the seed particles and larger particle sizes could be made depending on the amount of silver ion additions. The investigated reactions are summarised in Table 1 and Table 2 for ammonia and T-403 complex forming ligands, respectively. The change in size is readily revealed by the colour of the sols as the surface plasmon resonance and corresponding light absorption band position shifts to lower energies (longer wavelength). UV-Vis spectra of particles made in the two-step preparation are shown in Figure 2. Absorption peak at near 500 nm and over 600 nm can be observed. This indicates significantly larger particles near 100 nm diameter (~500 nm absorption) and more than 136 nm size (>600 nm absorption) from comparison to published spectra [14, 15]. In addition to change in the absorption properties, the larger particles also displayed diminished sol stability as the particles underwent sedimentation.

In order to check the role of aminosilane in the nanoparticle preparation, an experiment was carried out where no aminosilane was used; instead 20.51 g of an organic amine (Jeffamine T-403) solution was prepared at 0.083% concentration and heated to 45 °C. Addition of some silver nitrate formaldehyde solution resulted (14.26 g containing 0.26% silver nitrate and 0.179% formaldehyde) resulted in the rapid precipitation of silver without nanoparticle formation confirming the crucial role of aminosilane in the nanoparticle formation.

Table 1. Reactant compositions for the preparation of silver sols using silver-ammonia complex for particle growth. Reaction mixtures turned amber within a minute after adding silver nitrate-formaldehyde solution into 45 °C silane solution.

Sample name	Mass ratios of components					$AgNO_3$ concentration in primary particle preparation	Heating at 60 °C for*	Final Ag metal content	Colour of diluted sol
	In primary particle preparation			In particle growth					
	$AgNO_3$	Silane	CH_2O	$AgNO_3$	NH_3				
NP-SOL-2	0.26	0.32	0.070	0.74	0.16	0.091%	5 + 9 +1 min	0.10%	Blue
NP-SOL-3	0.50	0.66	0.090	0.50	0.11	0.122%	5 + 6 + 5 min	0.10%	Red
NP-SOL-4	1.00	1.32	0.090	-	-	0.145%	11 min	0.09%	Amber

* The numbers designate the following: 1st number indicates time to form the initial particle population, 2nd number indicates the time to add the silver complex and 3rd number is reaction time after adding the silver complex.

Table 2. Reactant compositions for the preparation of silver sols using silver-T-403 amine complex for particle growth. Reaction mixtures turned amber within a minute after adding silver nitrate-formaldehyde solution into 45 °C silane solution.

Sample name	Mass ratios of components					$AgNO_3$ concentration in primary particle preparation	Heating at 60 °C for*	Final Ag metal content	Colour of diluted sol
	In primary particle preparation step			In particle growth step					
	$AgNO_3$	Silane	CH_2O	$AgNO_3$	T-403 amine				
NP-SOL-5	0.13	0.16	0.089	0.87	1.52	0.026%	5+5+10 min	0.10%	Blue
NP-SOL-6 ‡	0.25	0.33	0.088	0.75	1.30	0.049%	5+4+11 min	0.10%	Red
NP-SOL-7	0.50	0.65	0.089	0.50	0.86	0.091%	5+3+12 min	0.10%	Deep yellow
NP-SOL-4	1.00	1.32	0.090	-	-	0.145%	11 min	0.09%	Amber
NP-SOL-8 ‡	1.00	1.31	0.088	-	-	0.158%	10 min	0.10%	Amber

* The numbers designate the following: 1st number indicates time to form the initial particle population, 2nd number indicates the time to add the silver complex and 3rd number is reaction time after adding the silver complex.
‡ This composition was used for antimicrobial tests.

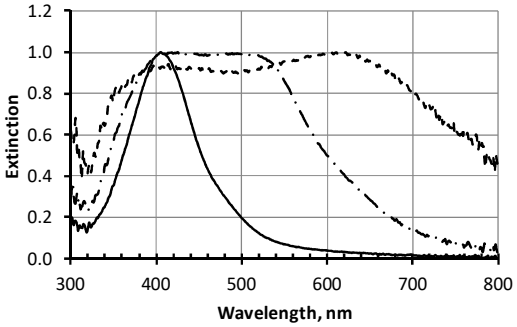

Figure 2. Extinction spectra of silver sols by UV-Vis spectroscopy after storage at approximately 1000 ppm silver concentration for 1 day and dilution to 10 ppm silver concentration just before measurement. Solid line: NP-SOL-2; das-dot line: NP-SOL-3; dashed line: NP-SOL-4.

3.2. Antimicrobial tests

The nanoparticle sol NP-SOL-6 containing 0.33 parts aminosilane for 1 part silver nitrate in the synthesis was diluted to 500 ppm silver concentration and used to spray a thin layer of nanoparticles onto ceramic tiles. The antimicrobial test indicated complete inhibition of bacterial growth.

A sol with higher proportion of aminosilane NP-SOL-8 with 1.31 parts aminosilane for 1 part silver nitrate in the synthesis was also evaluated for bacterial growth inhibition. The sol was diluted to 500 ppm and sprayed onto ceramic tile. Bacterial growth was inhibited to 93% compared to the reference.

The two sol samples evaluated differed in aminosilane content as well as in size. Both of these variables could contribute to the difference in bacterial inhibition efficacy. A potential mechanism of bacterium deactivation is the penetration of the nanoparticle into the cell. This is generally more effective with smaller particle size. Thus, based on this, larger particles may enter the cells less easily and should be less active. Since larger particles were found more active in destroying bacteria the influence of aminosilane is expected to be the key factor in the different activities of the sols since aminosilane can persist on the surface of the nanoparticles and reduce silver ion production that contributes to bacterium deactivation.

Conclusion

Using N-(2-aminoethyl)-3-aminopropyltrimethoxysilane as stabilising agent in silver reduction with a reducing agent, it was shown that small diameter silver nanoparticles can be readily generated in aqueous medium fast and at moderate temperature not exceeding 60 °C. In addition, no solvent is needed in the reaction. Relatively high silver concentration can be used (up to 0.1% metal content was demonstrated). Particle size can be readily controlled by first creating a primary particle population and then growing the size of the primary particles by further addition and reduction of silver ions. The synthesis method can provide scalable reaction method to produce silver sols in industrial quantities for antibacterial use. It was demonstrated that some of the produced nanoparticles can fully suppress bacterial growth.

It was found that different nanoparticle sols had different antibacterial efficacy. Preliminary results suggest that this could be due to the amount of aminosilane used in relation to silver. However further experiments are needed to elucidate the correlation between particle composition and its antibacterial activity. In addition, more detailed characterization of silver nanoparticles, including direct size measurement, is desirable to correlate synthesis conditions with nanoparticle properties.

REFERENCES

1. P. Y. Silvert et al., "Preparation of Colloidal Silver Dispersions by the Polyol Process. Part 1- Synthesis and Characterization", *J. Mater. Chem.*, 1996, vol. 6(4), pp. 573-577.

2. P. Y. Silvert et al., "Preparation of Colloidal Silver Dispersions by the Polyol Process. Part 2- Mechanism of Particle Formation", *J. Mater. Chem.*, 1997, vol. 7(2), pp. 293-299.

3. A.Y. Olenin and G.V. Lisichkin, "Metal Nanoparticles in Condensed Media: Preparation and the Bulk and Surface Structural Dynamics", *Russian Chemical Reviews*, 2011, vol. 80(7), pp. 605-630.

4. Y.J. Choi, and T.-J. Luo, "Self-Assembly of Silver – Aminosilica Nanocomposites through Silver Nanoparticle Fusion on Hydrophobic Surfaces", *Applied Materials and Interfaces*, 2009, vol. 1(12), pp. 2778-2784.

5. Y.-J. Choi et al., "Spontaneous Formation of Silver Nanoparticles in Aminosilica", *J. Sol-Gel Sci. Technol.,* 2009, vol. 51, pp. 124-132.

6. I. Pastoriza-Santos, and L.M. Liz-Marzan, "Formation and Stabilisation of Silver Nanoparticles through Reduction by N,N-Dimethylformamide", *Langmuir*, 1999, vol. 15, pp. 948-951.

7. S. Bharathi et al., "Direct Synthesis and Characterisation of Gold and Other Noble Metal

Nanodispersions in Sol-Gel Derived Organically Modified Silicates", *Langmuir*, 1999, vol. 15, pp. 1929-1937.

8. S. Devarajan et al., "Bimetallic Nanoparticles: A Single Step Synthesis, Stabilization, and Characterization of Au-Ag, Au-Pd, and Au-Pt in Sol-Gel Derived Silicates", *J. Coll. Interface Sci.*, 2005, vol. 290, pp. 117-129.

9. S. Harish et al., "Role of pH in the Synthesis of 3-Aminopropyl Trimethoxysilane Stabilized Colloidal Gold/Silver and their Alloy Sols and their Application to Catalysis", *Mat. Chem. Phys.*, 2011, vol. 127, pp. 203-207.

10. M. Faraday, "The Bakerian Lecture: Experimental Relations of Gold (and Other Metals) to Light", *Philosophical Transactions of the Royal Society of London*, 1857, vol. 147, pp. 145-181.

11. United States Patent 7,931,941 to M.A. Mastropietro and G.A. Jablonski.

12. United States Patent 7,655,161 to H.-Y. Cho et al.

13. United States Patent 6,939,568 to R.E. Burrell et al.

14. D.D. Evanoff, G. Chumanov, "Size-Controlled Synthesis of Nanoparticles. 2. Measurement of Extinction, Scattering, and Absorption Cross Sections", *J. Phys. Chem. B*, 2004, vol. 108, pp. 13957-13962.

15. D.D. Evanoff, G. Chumanov, "Synthesis and Optical Properties of Silver Nanoparticles and Arrays", *Chem. Phys. Chem*., 2005, vol. 6, pp. 1221-1231.