

PREPARATION AND USE OF SILVER NANOPARTICLES

FIELD OF THE INVENTION

The invention relates to the preparation of silver nanoparticles using efficient and low cost method in aqueous medium, and the use of the synthesised nanoparticles.

BACKGROUND OF THE INVENTION

The preparation of aqueous metal nanoparticle sols has been known since such sols were first prepared by M. Faraday (1857) "The Bakerian Lecture: Experimental Relations of Gold (and Other Metals) to Light" *Philosophical Transactions of the Royal Society of London*, vol. 147 pp. 145-181. Metal nanoparticles have been proposed for several applications since then due to their specific properties. For instance, silver particles have been used for antimicrobial applications as described, for example, in United States Patent 6,939,568 to R.E. Burrell et al.; for conductive inks as described, for example, in United States Patents 7,931,941 to M.A. Mastropietro & G.A. Jablonski, and 7,655,161 to H.-Y. Cho et al.; for sensors as exemplified by United States Patent 6,537,498 to N.S. Lewis et al.; and many other applications.

There are several approaches in the art to make small particles of metals, including silver. When the particles are made from solution to prepare a suspension of particles, the process generally starts by choosing a solvent or water for the dissolution of reactants, selection of a stabiliser for the nanoparticle, selection of a precursor to supply metal ions, and choosing a reducing agent to convert metal ions into their metallic form. Further, the conditions of mixing of the reactants need to be closely controlled. Several examples of this general procedure are known in the art. An early description can be found in United States Patent 4,539,041 to M. Figlarz et al. that has been known as the "polyol process" using a glycol or polyol solvent and transforming metal salts into metal nanoparticles by heating. In this case, the solvent also acts as a reducing agent, while stabilizer in the form of protective polymer may be added to the reaction mixture as shown in the publications of P. Y. Silvert et al. (1996) "Preparation of Colloidal Silver Dispersions by the Polyol Process. Part 1- Synthesis and Characterization" *J. Mater. Chem.*, vol. 6(4) pp. 573-577; and P. Y. Silvert et al. (1997) "Preparation of Colloidal Silver Dispersions by the Polyol Process. Part 2-Mechanism of Particle Formation" *J. Mater. Chem.*, vol. 7(2) pp. 293-299. Similar but more elaborate processes are described in United States Patents 7,749,299 and 7,824,466 to K. Vanheusden et al. that are able to better control the resulting particle size. Numerous other processes are known in the art for making silver

nanoparticles as described, for example, in a review by A.Y. Olenin and G.V. Lisichkin (2011) "Metal Nanoparticles in Condensed Media: Preparation and the Bulk and Surface Structural Dynamics" *Russian Chemical Reviews*, vol. 80(7) pp. 605-630. This review lists approaches including the selection of stabilizer (e.g. sodium citrate, laponite, sodium dodecylsulphate, polyethyleneimine, polyacrylic acid, oleic acid, polyvinylpyrrolidone), silver salts, and reducing agents (e.g. sodium citrate, aldehydes, NaBH_4 , hydrazine, hydroquinone). The medium of silver nanoparticle synthesis may be in organic solvent or in water. A method of organic amine stabilized particle preparation in organic solvent is provided in United States Patent 7,867,316 to B.-H. Jun et al. while a similar approach is described by S. Parashar et al. in United States Patent 7,968,008 relying on alkylamine stabilizer and inclusion of glycol, alcohol or toluene solvent. It is also possible to make silver nanoparticles without dedicated solvent as described by P. Liu et al. in United States Patent 8,057,849 utilising alkylamine stabilisers that take the place of solvent and varied reducing agents such as hydrazines and related compounds.

United States Patent 7,645,318 to D. Anderson et al. describes the use of a pre-formed and suspended polymer for the formation of metal nanoparticles that are incorporated into the polymer particle. Similarly, United States Patent 7,718,094 to P. Alexandridis and T. Sakai teaches the use of polymeric species to stabilize and reduce metal ions and protect the resulting metal nanoparticles.

Although many methods are known to fabricate silver nanoparticles, a majority of them have certain disadvantages. Most notably, the use of organic solvents in most preparations increases both costs and environmental impact. Additionally many methods provide only limited control over the size and size distribution of the particles formed. Thus, there is a need for improved methods of silver nanoparticle preparation that do not use solvents while the control of particle size can be achieved.

Since silver nanoparticles are frequently used as surface coatings or components in surface coatings, methods are also needed to anchor the particles to the surface or coating. Such methods are known. For example, United States Patent 6,121,298 to T. Sakamoto and T. Sato describes the use of organopolysiloxanes as the matrix of silver nanoparticles, prepared in organic solvents. United States Patent 7,648,762 to H.S. Sohn et al. describes the preparation of silver nanoparticle containing hard coating that provides antibacterial and antistatic effect. The method uses unspecified silane coupling agent to coat an insulating layer on the nanoparticle for the incorporation of the particle into the coating layer. United States Patents 7,799,432 and 7,279,173 to C. Becker-Willinger et al. suggest the use of solvent based sol-gel

derived coatings for antibacterial purposes that incorporate silver nanoparticles and complexing/dispersing agent of aminosilanes. Although these methods have useful application areas, they suffer from complex coating preparation process as well reliance on organic solvents.

An alternative method in United States Patent 7,344,773 to K.M. Subramanya and I. Yeo teaches the preparation of nanoparticle layers through the functionalisation of the substrate by varied molecules including alkylsiloxane or alkylsilane followed by the attachment of nanoparticles. In a similar approach disclosed by United States Patent Application 2007/0003603 by B.M. Karandikar et al. to adhere silver nanoparticles on surfaces treated with aminosilanes. In this case, the preparation of adherent nanoparticle layers is relatively simple but requires the treatment of the substrate first. This is acceptable when coatings are prepared in a factory environment but not so useful when nanoparticles must be attached to surfaces that are varied in nature and cannot be pre-treated for some reason. Similarly, nanoparticles can be grown onto surfaces with the help of aminosilane coupling agents as described J. Sun et al. (2006) "Toward Monodispersed Silver Nanoparticles with Unusual Thermal Stability" *J. Am. Chem. Soc.*, vol. 128 pp. 15756-15764; and D.V. Quang et al. (2011) "Preparation of Silver Nanoparticle Containing Silica Micro Beads and Investigation of Their Antibacterial Activity" *Applied Surface Science*, vol. 257 pp. 6963–6970. However, this approach also requires very close control of substrate that is not practical in many applications.

Particles can also be functionalised with the use of coupling agents, such as organosilanes, as disclosed in United States Patent 7,790,066 to H. Wang et al. as well as in United States Patent 8,071,132 to J.H. Adair et al. that utilises a microemulsion process and suggests the introduction of silanes, among other reactants, for the surface functionalisation. Further, methods are known to produce a coating layer on silver nanoparticles as disclosed in United States Patents 7,824,731 and 8,097,742 to J.Y. Ying et al. by first treating the previously synthesised particle surface with a coupling agent such as aminosilane and then further reacting the modified surface with additional reactants. The functionalisation of metal nanoparticles has also been utilised to aid the deposition and further processing of such particles as disclosed in United States Patent 7,923,110 to J.J. Park et al. that proposes the preparation of metal nanoparticles by reducing the metal ions in organic solvent by sodium borohydride followed by the separation and post-modification of the particles by functionalising their surface using, among other reactants, organosilanes. United States Patent Application 2010/0233361 by N.-X. Hu et al. describes the mixing of nanoparticles with stabilizer and organosilane adhesion

promoter in a solvent to make a composition that can deposit adherent particles on a substrate. Using such functionalised particles may have the advantage of being able to adhere to untreated surfaces as coupling agent is present on the particle. However, their preparation is complex and costly when prepared by methods known in the art, thus precluding areas of applications where cost is a major factor.

A further improvement in the particle synthesis process was achieved by using the adhesion promoting coupling agents as a stabilising material for nanoparticles. This way various aminosilane stabilised silver nanoparticles can be produced as disclosed in several publications. A methanol solvent based synthesis using bis[3-(trimethoxysilyl)-propyl]ethylenediamine to stabilise the silver nanoparticles and reduce the silver ions was described by Y.J. Choi, and T.-J. Luo (2009) "Self-Assembly of Silver – Aminosilica Nanocomposites through Silver Nanoparticle Fusion on Hydrophobic Surfaces" *Applied Materials and Interfaces*, vol. 1(12) pp. 2778-2784, and by Y.-J. Choi et al. (2009) "Spontaneous Formation of Silver Nanoparticles in Aminosilica" *J. Sol-Gel Sci. Technol.*, vol. 51 pp. 124-132. Although this approach is relatively simple, it utilises toxic methanol as the reaction medium. Additionally, the procedure requires an excess of stabilizer. Silver:bis[3-(trimethoxysilyl)-propyl]ethylenediamine = 1:3 to 1:4 molar ratios were recommended to obtain stable sols. The presence of such large amount of stabiliser can have the effect of covering the silver surface excessively and thus reducing certain activities such as conductivity or potentially antibacterial action. Other silane species have also been proposed for the preparation of silver nanoparticles such as by I. Pastoriza-Santos, and L.M. Liz-Marzan (1999) "Formation and Stabilisation of Silver Nanoparticles through Reduction by N,N-Dimethylformamide" *Langmuir*, vol. 15 pp. 948-951; S. Bharathi et al. (1999) "Direct Synthesis and Characterisation of Gold and Other Noble Metal Nanodispersions in Sol-Gel Derived Organically Modified Silicates" *Langmuir*, vol. 15 pp. 1929-1937; S. Devarajan et al. (2005) "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.*, vol. 290 pp. 117-129; and S. Harish et al. (2011) "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.*, vol. 127 pp. 203-207. However, all these methods suffer from the requirement of organic solvent (N,N-dimethylformamide or methanol) and large molar excess of aminosilane stabiliser used. The need for adherent silver nanoparticles that are produced in water in a simple and cost effective process had not been met in the prior art.

SUMMARY OF THE INVENTION

The present invention provides methods to prepare functionalised silver nanoparticles with control of particle size in a cost effective and environmentally friendly way. The methods use aqueous reaction medium, organosilanes that function both as a particle stabiliser and adhesion promoting surface modification to anchor the particle onto surfaces that the particle comes in contact with during its use, and optional reducing agent. The nanoparticle dispersion may, in addition, optionally contain surfactants and surface modifying agents. The optional surfactant may be added before or after the formation of nanoparticles. The surface modifying agents may be added after the formation of the nanoparticles.

The inventor has found, through experimentation, that an aqueous solution of silver ions (from a silver salt or from a silver complex), in the presence of aminosilanes, can form stable silver dispersions without introducing excessive amounts of stabilisers that is advantageous in various applications, for example in antimicrobial preparations. The preparation relies on forming an amine complex of silver ions using aminosilanes, such as aminopropyltrimethoxysilane, aminoethyl-aminopropyl-trimethoxysilane and others in water and allowing the reduction of the silver ions by the aminosilanes. This reaction may take place slowly. In order to increase the rate of particle formation, a reducing agent, such as an aldehyde, can be introduced into the solution, together with an optional base to increase pH when acid is produced as part of the reaction products of the silver reduction. The rate of silver reduction can be further increased by increasing the temperature above room temperature.

It was found advantageous to limit the amount of aminosilane in comparison to the silver in order to obtain preparations with stronger antimicrobial effect. In the prior art, aminosilanes were used in organic solvent at high molar ratio, in excess of aminosilane:silver=100:1 molar ratio. However, high levels of aminosilane may reduce the antimicrobial activity of silver nanoparticles. Even the aminosilane:silver=1:1 molar ratio (particles prepared according to the present invention) was found to reduce the effectiveness of silver nanoparticles against bacterial growth as compared to preparations that contained a lower amount of aminosilane. On the other hand, the presence of aminosilane can help to anchor the silver nanoparticles to surfaces as known from the prior art. This phenomenon can be utilised to obtain longer lasting effects when silver nanoparticles are used on surfaces through improved adhesion of the particles to the surface. Thus, an optimum level of aminosilane should be used within the range of aminosilane:silver=0.01:1 to aminosilane:silver=2:1 molar ratios. Apart from adhesion of particles to extraneous surfaces, the presence of aminosilane can also induce the controlled

and at least partially reversible aggregation of silver nanoparticles. Such aggregation can increase the apparent particle size, resulting in quicker sedimentation. This sedimentation then can be utilised for the purification of particles, even without the use of centrifuging, by decanting the suspending liquid from the sedimented particles.

Further to the optimisation of the aminosilane:silver molar ratios, the particle size can be controlled according to the present invention. This can be achieved by first preparing small primary nanoparticles using the aminosilane-silver complex and then supplying additional silver ions at a controlled rate to deposit additional metal onto the previously formed particles. The supply of silver ions can be achieved by the addition of silver salt solutions or silver complex solutions. The amount of silver added in this growth step, relative to the amount of silver used in the formation of primary particles, determines the particle size of the silver.

Once the silver nanoparticles are formed, they can be used for various purposes known in the art, including control of microbial growth, conductive coating preparations, incorporation into coatings as additives, and using the particles in various detectors. In order to use the nanoparticles of the present invention in a wide range of applications, the nanoparticles may require additional surface modification by contacting the particles with modifying agents such as stabilizers, additives; or the particles can be separated from the suspending medium through centrifuging, sedimentation or filtration for the purpose of purification or concentration.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows Extinction spectra of nanoparticle dispersion of Example 1 measured at 10 ppm silver concentration by UV-Vis spectroscopy at two different times during storage: (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).

Figure 2 shows Extinction spectra of silver nanoparticle dispersions of Example 2. Spectra were measured at 10 ppm silver concentration by UV-Vis spectroscopy after storage of the dispersions at 1000 ppm silver concentration for 1 day and diluted to 10 ppm silver concentration just before measurement. The extinction spectra were normalised such that the maximum value is set to 1 for each measurement. The lines correspond to the following dispersions: (1) Example 2A, (2) Example 2B, (3) Example 2C.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The general method of silver nanoparticle synthesis described above as a brief description can be implemented with a range of conditions. These conditions can include the variation of silver concentration in the reaction mixture, the amount of aminosilane used in relation to the silver, the application of reducing agents other than aminosilane, the further growth of the primary particles by controlled addition of silver ions, and the modification of the synthesised particles to change their surface characteristics.

The formation of silver nanoparticles is achieved by first providing an aqueous solution of at least one aminosilane with the preferred chemical structure of $\text{H}_2\text{N}-(\text{CH}_2-\text{CH}_2-\text{NH})_n-(\text{CH}_2)_m-\text{Si}(\text{OR})_3$ where n is an integer between 0 and 10, m is an integer between 1 and 12, while R is an alkyl group including methyl, ethyl, propyl, isopropyl, butyl, isobutyl, and *sec*-butyl. The Si-OR alkoxy functional group is capable of hydrolysis in aqueous solution and thus can improve the solubility of the species by forming silanol groups (Si-OH) when contacted with water. Aminosilanes of other structures can be used in the present invention as well. Suitable aminosilanes include silanes which contain at least one alkoxy group per molecule capable of undergoing hydrolysis to form silanol groups in water. Suitable silanes may also contain more than one silicon atom linked either through siloxane (Si-O-Si) groups or organic groups (Si-CH₂-R'-CH₂-Si) where R' is an organic group. The aminosilane selected must have solubility in water to achieve at least 0.001% (10 ppm) concentration in the solution. Most suitable aminosilanes are N-(2-aminoethyl)-3-(aminopropyl)trimethoxysilane, N-(2-aminoethyl)-3-(aminopropyl)triethoxysilane, 3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, N-[N'-(2'-aminoethyl)-2-aminoethyl]-3-aminopropyltrimethoxysilane, and N-[N'-(2'-aminoethyl)-2-aminoethyl]-3-aminopropyltriethoxysilane but other examples of aminosilanes conforming to the structure and description specified above can also be employed. Aminosilanes containing at least two nitrogen atoms are especially preferred.

The second step in forming the nanoparticles is the introduction of silver ions into the aqueous aminosilane solution to allow the formation of silver-aminosilane complex. This is achieved by mixing an aqueous solution of a silver salt or silver complex into the aminosilane solution. Suitable silver salts and silver complexes are those that are soluble in water, including sparingly soluble salts and silver oxide, to form a silver concentration of 0.001% (10 ppm) or higher. Non-limiting examples of such silver salts are silver nitrate, silver perchlorate, silver sulphate, silver citrate, silver lactate, silver acetate, silver carbonate, silver nitrite, as well as silver complexes with ammonia, boric acid, thiocyanate ions, sulphite ions, sulphate ions, fluoride ions, and

chloride ions. Further, complexes with organic nitrogen containing compounds, amines, organic acids, amino acids and low molecular weight peptides are useful. Non-limiting examples of such complex forming materials are: aminoethanol, ethylenediamine, trimethylenediamine, 1,3-diamino-2-propanol, 1,2,3 –triaminopropane, triethanolamine, 2,2' bipyridyl, oxalic acid, acetic acid, glycolic acid, citric acid, glycine, L-2-aminopropionic acid, 3-aminopropionic acid, aspartic acid, glutamic acid, glycylglycine, 2-aminobenzoic acid, ethylenediamine tetraacetic acid, and semicarbazide.

The aminosilane complex of silver is capable of forming silver nanoparticles through oxidation of the amine functional groups by the silver ions. However, the reaction tends to be slow. It is advantageous to increase the rate of reaction by adding a second compound to reduce the silver ions. There are many reducing agents for silver known in the art, including aldehydes, amines, ascorbic acid, citric acid, hydrazine and hydrazine derivatives, and sodium borohydride. With the addition of reducing agents, the reaction can be greatly accelerated and the necessary amount of aminosilane reduced as it is no longer needed for reducing the silver ions.

The reduction step can be done at room temperature but it is advantageously carried out at elevated temperature in the range of 25 °C to 100 °C, or more preferably in the range of 30 °C to 70 °. The increase in temperature improves the reduction rate while it also promotes the formation of more uniform particles.

Once the silver is reduced and primary particles are formed, the particles can be further grown by introducing additional silver ions in the presence of a reducing agent. By controlling the rate of addition and the quantity of the silver ions, the particle size can be controlled in a wide range. Suitable materials to introduce silver ions are aqueous solutions of silver salts or silver complexes as described above, in the preparation of primary silver particles, with the additional option of using silver-aminosilane complex as the source of additional silver ions.

At the end of the growth process, either when primary particles are grown and used without further growth, or when the primary particles are further grown in size, the particles are suitable for use. However, if desired, the synthesised particles can be further treated to enhance their compatibility with various materials or to improve their stability. Such treatment may consist of adding a surfactant or surface modifying agent. Surfactants and surface modifying agents are known in the art as described for example in a review by A.Y. Olenin and G.V. Lisichkin (2011) "Metal Nanoparticles in Condensed Media: Preparation and the Bulk and Surface Structural Dynamics" *Russian Chemical Reviews*, vol. 80(7) pp. 605-630. Non-limiting examples of such

materials are sodium dodecylsulphate, polyvinylpyrrolidone, citric acid, alkylthiols, alkylamines, and polyimines.

In the preparation of the nanoparticles, specific proportions of the materials should be maintained. In the first step of preparing the aminosilane complex, the aminosilane:silver molar ratio should be in the range of 0.01:1 to 2:1, more preferably in the range of 0.05:1 to 1:1. Higher amounts of aminosilane tend to produce smaller, more stable and more adherent particles but potentially lower functionality such as diminished antimicrobial effect or reduced conductivity. The total amount of silver may vary between 0.001% (10 ppm) to 1% (10000 ppm). More preferably the silver content can be between 0.01% (100 ppm) to 0.2% (2000 ppm). Although silver concentrations below 10 ppm could be used, low silver content is not advantageous as many of the silver nanoparticle applications require higher concentrations and thus a concentrating step would be needed to achieve the desired concentration if the synthesis takes place at low silver content. On the other hand, very high silver concentration may promote excessive particle aggregation during synthesis that can result in the undesired precipitation of silver particles.

If reducing agents other than the amino groups of the aminosilane are used, the proportion of silver and reducing agent is optimum at the stoichiometric level. For example, when aldehydes are used and oxidised to carboxylic acids by the silver, an aldehyde:silver=0.5:1 molar ratio is optimum. However, if the produced acid is further oxidised by silver ions (e.g. at high reaction temperature) a lower amount of aldehyde is sufficient to achieve the stoichiometric ratio. Higher concentrations of reducing agents, above the stoichiometric ratio) can be used to accelerate the reaction. However, the unreacted reducing agent will remain in the silver particle dispersion and may contribute as an unnecessary contamination. Using reducing agents below the stoichiometric level is also possible. In this case, some of the reduction may be facilitated by the amines in the solution. However, if the total amount of amines and other reducing agents are insufficient to fully reduce the silver ions, then the conversion of silver ions into metallic nanoparticles will be limited.

When the primary particles grown through the reduction of silver ions in the aminosilane complex are further grown in size with the addition of silver ions, the size of the final particles will depend on the ratio of silver in the primary particles and the silver added to the primary particles. If the additional silver is introduced at a sufficiently slow rate, the additional silver can deposit onto existing particles in a uniform manner and the ratio of the mass of the final particle to the mass of the primary particle will be near to the ratio of the amount of all silver used to the

silver used in making the primary particles. The ratio of total silver to the silver in the primary particle can be in a wide range, limited only by the excessive growth of the particles beyond the “nano” range (approximately 1nm to 200 nm, more preferably 1nm to 100 nm). In case when the particles are further grown from the primary particles according to the method described in this invention, the total concentration of the silver should be maintained in the 0.001% (10 ppm) to 1% (10000 ppm). More preferably the silver content should be between 0.01% (100 ppm) to 0.4% (4000 ppm) in order to maintain useful particle concentrations but avoid excessive particle aggregation at high concentration.

At the completion of the nanoparticle synthesis, the obtained dispersion can be used for various purposes such as deposition onto surfaces as an adherent antimicrobial treatment, use as a conductive additive in coatings, preservative in various formulations, or use as an antimicrobial coating additive for paints, and others. However, certain applications may require particle properties that are not immediately achieved during the synthesis but can be achieved by treating the nanoparticles with specific chemical species. For example, if the particles are to be used in an organic phase, such as a solvent based paint, the compatibility of the particles can be improved by treatment of the particles with long chain alkylamines or long chain alkylmercaptanes of the general formula of $\text{H}_2\text{N}-(\text{CH}_2-\text{CH}_2-\text{NH})_n-(\text{CH}_2)_m-\text{CH}_3$ and $\text{HS}-(\text{CH}_2-\text{CH}_2-\text{S})_n-(\text{CH}_2)_m-\text{CH}_3$, respectively, where n is an integer in the range of 0 to 6 and m is an integer in the range 2 to 17. The surface treatment can be achieved by introducing the alkylamines or alkylmercaptanes into the particle dispersion, thus inducing the precipitation of the nanoparticles from the aqueous dispersion and re-dispersion of the separated particles in the organic phase. Similarly, if long term storage of the particle dispersion is desired, additional stabilizing agents can be added to the dispersion. Many useful stabilizing agents are known in the art including polyvinylpyrrolidone, citric acid, polyamines, surfactants, and polyimines. These stabilizing agents can be readily introduced into the aqueous dispersion to provide additional particle stabilisation.

In some applications, metal particles with low amounts of contaminants are desired. The nanoparticles of the present invention can be purified by the methods of sedimentation (in normal gravitational field or through the application of a centrifuge as required by the silver particle size) or by filtration and the separation of supernatant solution that carry most of the contaminants. These purification methods are especially suitable for the particles described in the present invention since the particles contain aminosilanes that are able to cause reversible aggregation of the silver particles. Since the aggregated particles tend to settle easier, the

sedimentation step can be carried out in normal gravitational field instead of by centrifugation. Alternatively, if centrifugation is used, it can be carried out at lower rotational speeds or in shorter duration. Similarly, if filtration is used, the filtration of aggregated particles tends to be far more effective than that of individual nanoparticles. The isolated metal particles then can be further purified by repeated dispersion in water followed by sedimentation (or filtration) if desired. To aid re-dispersion, it is generally useful to add additional stabilizing agents prior to the purification steps. Non-limiting examples of such additional stabilizing agents are polyvinylpyrrolidone, citric acid, polyamines and polyimines.

The preparation of the nanoparticles according to the present invention is further elaborated by the following non-limiting examples. All percentage compositional information is based on the weight of the components. Similarly "ppm" (parts per million) units are also based on weight.

EXAMPLES

Example 1

Preparation of aminosilane stabilised silver nanoparticles with aminosilane:silver=1:1 molar ratio was carried out by first dissolving N-(2-aminoethyl)-3-(aminopropyl)trimethoxysilane in water to obtain a 0.613% solution. An aliquot of 44.67g of this solution was further diluted with 30.03g water and heated to a temperature in the range of 45 °C to 50 °C. An aqueous solution of silver nitrate and formaldehyde was made by first dissolving silver nitrate in water and then adding a 0.37% solution of formaldehyde to obtain a solution with 1.09% silver nitrate and 0.048% formaldehyde content. A 12.90g aliquot of this second solution was added to the warm aminosilane solution prepared in the previous step. Upon addition of silver and formaldehyde, the solution turned dark amber within minutes indicating the formation of silver nanoparticles. At the same time, the solution was heated to 60 °C and kept at that temperature for 10 minutes. The dark dispersion was then left to cool; it was kept at room temperature for 12 days and additional formaldehyde was added (1.69 g of 0.37% solution) to complete the reduction of silver. The resulting dispersion contained 1002 ppm silver (0.1002%). The dispersion was characterised by UV-Vis (Ultraviolet-Visible) spectroscopy by first diluting the dispersion by 100-fold to 10 ppm concentration and recording the spectra. The measurement was done at 6 days and 45 days after the preparation was completed, and the resulting spectra are shown in Figure 1. As seen, there is very little change in the absorption properties of the silver indicating a stable dispersion for a period of over 6 weeks. The extinction peak is centred near 400 nm indicating the presence of surface plasmon resonance, characteristic of silver nanoparticles of small

diameter well below 100 nm as known from the prior art. Descriptions of the optical properties and extinction spectra of silver nanoparticles as well as dependence of the extinction properties on particle size are found in many published works, for example by D.D. Evanoff, and G. Chumanov (2004) "Size-Controlled Synthesis of Nanoparticles. 2. Measurement of Extinction, Scattering, and Absorption Cross Sections" *J. Phys. Chem. B*, vol. 108 pp. 13957-13962 and D.D. Evanoff, and G. Chumanov (2005) "Synthesis and Optical Properties of Silver Nanoparticles and Arrays" *Chem. Phys. Chem.*, vol. 6 pp. 1221-1231.

Example 2

Silver nanoparticles were prepared by first making primary particles from an aminosilane-silver complex, followed by the growth of the particles by adding additional silver ions in the form of a silver complex. The example demonstrates the method of controlling the size of particles. First, stock solutions of the necessary reactants were prepared. An aqueous solution of aminosilane was made to contain 0.500% N-(2-aminoethyl)-3-(aminopropyl)trimethoxysilane (stock solution 2a). A silver nitrate solution was prepared in water containing 0.332% silver nitrate (stock solution 2b). An ammine complex of silver was prepared by first dissolving silver nitrate in water to obtain a 0.333% solution and mixing it with dilute ammonia solution to obtain final silver nitrate concentration of 0.218% and ammonia concentration of 0.0482%, thus forming an ammine complex of silver ions (stock solution 2c).

(A) Nanoparticles with aminosilane-silver=0.25:1 molar ratio.

First warm aminosilane solution was prepared by using 10.00g stock solution 2a that was further diluted by 19.48g water and heated to 45 °C. A solution of silver nitrate and formaldehyde was prepared by mixing 5.98g of stock solution 2b with 3.84g 0.37% formaldehyde solution, and 15.13 g of this mixture was added to the warm aminosilane solution. Amber colour started developing within a minute. The temperature of the solution was raised to 60 °C in about 5 minutes and 52.47g silver-ammine complex (stock solution 2c) was introduced into the mixture drop by drop over a period of nine minutes. After a further 1 minute heating (at 60 °C) the dispersion was left to cool. The concentrated dispersion had a dark, nearly black, colour. Upon dilution with water, the dispersion revealed a blue colour. As shown in Figure 2, the colour is due to broad absorption in the visible light range indicated relatively large sizes for the particles.

(B) Nanoparticles with aminosilane-silver=0.5:1 molar ratio.

First warm aminosilane solution was prepared by using 20.00g stock solution 2a that was further diluted by 15.52g water and heated to 45 °C. A solution of silver nitrate and formaldehyde was prepared by mixing 23.20g of stock solution 2b with 3.74g 0.37% formaldehyde solution, and 26.62 g of this mixture was added to the warm aminosilane solution. Amber colour started developing within a minute. The temperature of the solution was raised to 60 °C in 5 minutes and 34.94g silver-ammine complex (stock solution 2c) was introduced into the mixture drop by drop over a period of six minutes. After a further 5 minutes heating (at 60 °C) the dispersion was left to cool. The concentrated dispersion had a dark, nearly black, colour. Upon dilution with water, the dispersion revealed a reddish colour. As shown in Figure 2, the colour is due to broad absorption in the visible light range indicated relatively large sizes for the particles but smaller than particles made in Example 2A.

(C) Nanoparticles with aminosilane-silver=1:1 molar ratio.

First warm aminosilane solution was prepared by using 40.02g stock solution 2a that was further diluted by 15.52g water and heated to 45 °C. A solution of silver nitrate and formaldehyde was prepared by mixing 46.31g of stock solution 2b with 3.74g 0.37% formaldehyde solution, and 49.53 g of this mixture was added to the warm aminosilane solution. Amber colour started developing within a minute. The temperature of the solution was raised to 60 °C in about 5 minutes and kept there an additional 6 minutes. No further quantities of silver ions were introduced. The dispersion was left to cool. The concentrated dispersion had a dark, amber, colour. Upon dilution with water, the dispersion revealed a bright amber colour. As shown in Figure 2, the colour was due to a sharp absorption in the blue end of the visible light range and indicated relatively small sizes for the particles.

Comparison of the UV-Vis spectra of the three nanoparticle preparation of Example 2 clearly demonstrates the ability of the invention to produce particles with varied size.

Example 3

Silver nanoparticles were prepared similarly to Example 2 but the addition of silver during the particle growth step was achieved with the use of an organic amine complex of silver. First, solutions of the necessary reactants were prepared. An aqueous solution of aminosilane was made to contain 0.333% N-(2-aminoethyl)-3-(aminopropyl)trimethoxysilane (stock solution 3a). A silver nitrate solution was prepared in water containing 1.00% silver nitrate (stock solution 3b). An organic amine complex of silver was prepared by first dissolving silver nitrate in water to obtain a 1.00% solution and mixing it with an aqueous solution of trimethylolpropane

tris[poly(propylene glycol), amine terminated] ether (also known as Jeffamine T-403, available from Huntsman Corporation) to obtain final silver nitrate concentration of 0.589% and Jeffamine T-403 concentration of 1.02%, thus forming a complex of silver ions (stock solution 3c).

(A) Nanoparticles with aminosilane-silver=0.125:1 molar ratio.

First warm aminosilane solution was prepared by using 7.34g stock solution 3a that was further diluted by 59.47g water and heated to 45 °C. A solution of silver nitrate and formaldehyde was prepared by mixing 2.03g of stock solution 3b with 3.92g 0.37% formaldehyde solution, and 5.49g of this mixture was added to the warm aminosilane solution. Amber colour started developing within a minute. The temperature of the solution was raised to 60 °C in about 5 minutes and 22.24g silver (stock solution 3c) was introduced into the mixture drop by drop over a period of five minutes. After a further 10 minute heating (at 60 °C) the dispersion was left to cool. The concentrated dispersion had a dark, nearly black, colour. Upon dilution with water, the dispersion revealed an intense blue colour. The blue colour and the slow sedimentation of particles over the course of about one day indicated the presence of relatively large nanoparticles.

(B) Nanoparticles with aminosilane-silver=0.25:1 molar ratio.

First warm aminosilane solution was prepared by using 14.70g stock solution 3a that was further diluted by 54.00g water and heated to 45 °C. A solution of silver nitrate and formaldehyde was prepared by mixing 3.99g of stock solution 3b with 3.82g 0.37% formaldehyde solution, and 7.35g of this mixture was added to the warm aminosilane solution. Amber colour started developing within a minute. The temperature of the solution was raised to 60 °C in about 5 minutes and 19.16g silver complex (stock solution 3c) was introduced into the mixture drop by drop over a period of four minutes. After a further 11 minute heating (at 60 °C) the dispersion was left to cool. The concentrated dispersion had a dark, nearly black, colour. Upon dilution with water, the dispersion revealed a reddish colour.

(C) Nanoparticles with aminosilane-silver=0.5:1 molar ratio.

First warm aminosilane solution was prepared by using 29.40g stock solution 3a that was further diluted by 42.09g water and heated to 45 °C. A solution of silver nitrate and formaldehyde was prepared by mixing 7.77g of stock solution 3b with 3.74g 0.37% formaldehyde solution, and 11.1764g of this mixture was added to the warm aminosilane solution. Amber colour started developing within a minute. The temperature of the solution was

raised to 60 °C in about 5 minutes and 12.69g silver r complex (stock solution 3c) was introduced into the mixture drop by drop over a period of three minutes. After a further 12 minute heating (at 60 °C) the dispersion was left to cool. The concentrated dispersion had a dark, brownish, colour. Upon dilution with water, the dispersion revealed a deep yellow colour indicating the presence of relatively small silver nanoparticles.

Example 4

Silver nanoparticle dispersion was prepared similarly to Example 1 containing aminosilane at the aminosilane:silver=1:1 mol ratio for antibacterial tests.

A 37.28g portion of 0.500% N-(2-aminoethyl)-3-(aminopropyl)trimethoxysilane in water was further diluted with 38.57g water and heated to a temperature in the range of 45 °C to 50 °C. To this solution, 14.26g of an aqueous solution of silver nitrate and formaldehyde was added containing 1.00% silver nitrate and 0.088% formaldehyde; followed by heating the solution to 60 °C and keeping it at 60 °C for 10 minutes. Upon addition of silver and formaldehyde, the solution turned dark amber indicating the formation of small silver nanoparticles. The resulting silver dispersion was left to cool. The silver content was 1000 ppm. The silver nanoparticle dispersion was diluted with water to 500 ppm concentration and sprayed onto ceramic tiles in a thin and uniform layer. The layer was dried and stored for 24 hours. An aliquot of 0.1ml *Staphylococcus Aureus* (ATCC 6538) dispersion containing 10^3 CFU was inoculated onto the coated ceramic tile. In addition, an uncoated ceramic tile was inoculated as a reference. The ceramic tiles were swabbed after 15 minutes with 3M pipette swab and 1ml of the diluted solution was transferred onto 3M petrifilm. The petrifilm was examined for colony formation after incubation for 24 hours at 37 °C. Bacterial growth was 93% inhibited as compared to the reference.

Example 5

The silver nanoparticle dispersion of Example 3B, containing approximately four times less aminosilane than the preparation of Example 4, was used for antimicrobial test according to the procedure described in Example 4. Bacterial growth was 100% inhibited (no growth at all).

Example 6

An aliquot of nanoparticle dispersion of Example 3B was left to sediment and formed a well-defined layer of dark precipitate and a clear supernatant. Most of the supernatant was removed, and replaced by deionised water. The resulting nanoparticle dispersion was shaken vigorously. This mild treatment was able to re-disperse the particles. In addition, the particle sedimentation was noticeably slower after the purification.

Comparative Example 1

Nanoparticle preparation was attempted according to the method described in Example 3B but N-(2-aminoethyl)-3-(aminopropyl)trimethoxysilane was replaced Jeffamine T-403.

A solution of 1.0% Jeffamine T-403 was prepared in water. A 1.70g portion of this solution was further diluted with 18.81g water and warmed to 60 °C. To this amine solution, 3.86g of a mixture consisting of 0.256% silver nitrate and 0.179% formaldehyde in water was added. Within minutes, a grey precipitate of silver formed instead of nanoparticles unlike in Example 3B where an aminosilane was used to complex the silver prior to reduction.

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United States Patent Applications

2007/0003603 by B.M. Karandikar et al.
2010/0233361 by N.-X. Hu et al.

WHAT IS CLAIMED IS:

1. The method of making silver nanoparticles in an aqueous medium by mixing at least one aminosilane and silver ions.
2. The method of modifying the size of nanoparticles by first preparing nanoparticles according to Claim 1 and then growing the particles to a larger size by supplying additional silver ions to a nanoparticle dispersion of Claim 1 at a controlled rate, in the presence of reducing agents.
3. The methods of Claims 1 and 2 where the silver ions are supplied to the aqueous medium from a water soluble silver salt or water soluble silver complex to provide silver ion concentration above 0.001%.
4. The method of Claim 1 where the aminosilane is selected from the group of compounds containing at least one amine or imine functional group per molecule linked to a silicon atom through at least one carbon atom.
5. The aminosilane of Claim 4 where the aminosilane further contains at least one alkoxy functional group linked to the silicon atom.
6. The method of Claim 1 where the aminosilane is provided in the concentration of 0.001% to 2%, and the initial silver ion concentration is independently selected in the range of 0.001% to 1%, and the aminosilane:silver molar ratio is maintained in the range of aminosilane:silver=0.01:1 to aminosilane:silver=2:1.
7. The methods of Claims 1 and 2 where the aqueous mixture optionally includes an additional reducing agent where the reducing agent is selected from the group of aldehydes, aldoses, hydroquinones, hydrazine, hydrazine derivatives, hydroxylamine, hydroxylamine derivatives, phenols, ascorbic acid, sodium tetrahydroborate, and amines including aminosilanes.

8. The method of Claim 7 where the aqueous mixture optionally includes an acidity controlling agent where the acidity controlling agent is a base, selected from the group of alkali metal hydroxides, alkali earth metal hydroxides, organic amines, ammonia, salts of alkali metals with weak acids, salts of alkali earth metals with weak acids.
9. The methods of Claims 1 and 2 where the aqueous mixture of silver ions and aminosilane are optionally reacted at elevated temperature between 25 °C to 100 °C.
10. The method of Claim 7 where the aqueous mixture of silver ions, aminosilane and the additional reducing agent are optionally reacted at elevated temperature between 25 °C to 100 °C.
11. The method of Claim 8 where the aqueous mixture of silver ions and aminosilane, the additional reducing agent, and additional acidity controlling agent are optionally reacted at elevated temperature between 25 °C to 100 °C.
12. The method of purifying the nanoparticles of Claims 1 and 2 by sedimentation, either natural or aided by centrifuging, or by filtration and removing at least a portion of the suspending solution
13. The method of purifying the nanoparticles according to Claim 12 where the presence of aminosilane on the nanoparticles promotes reversible or partially reversible aggregation of the particles, thus enhancing the sedimentation or filtration of the nanoparticles.
14. The method of re-suspending the nanoparticles of Claims 12 and 13 in a liquid medium by mixing the nanoparticles with the liquid medium followed by agitating the mixture.
15. The method of functionalising the nanoparticles of Claims 1, 2, 12, 13, and 14 by the addition of stabilizing agents that interact with the nanoparticles.
16. The use of nanoparticles of Claims 1, 2, 12, 13, and 14 as antimicrobial constituents, disinfectants, and coatings made with the nanoparticles.
17. The use of nanoparticles of Claims 1, 2, 12, 13, and 14 as antimicrobial additives in paints, coatings, textile treatments, disinfectants, and disposable diapers.

18. The use of nanoparticles of Claims 1, 2, 12, 13, and 14 as preservatives in formulated products including paints, coatings, soaps, liquid cleaning detergents, personal care products, beauty care products, household cleaning products.
19. The use of nanoparticles of Claims 1, 2, 12, 13, and 14 in conductive inks, decorative inks, and sensors.
20. The use of nanoparticles according to Claims 16, 17, 18, and 19 where the nanoparticle adhesion to surfaces treated by the nanoparticles is enhanced by the presence of aminosilane in the silver nanoparticle preparation.