Green synthesis of highly concentrated aqueous colloidal solutions of large starch-stabilised silver nanoplatelets

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ABSTRACT

A simple, environmentally friendly and cost-effective method has been developed to prepare a range of aqueous silver colloidal solutions, using ascorbic acid as a reducing agent, water-soluble starch as a combined crystallising, stabilising and solubilising agent, and water as the solvent. The diameter of silver nanoplatelets increases with higher concentrations of $AgNO_3$ and starch. The silver nanoparticles are also more uniform in shape the greater the diameter of the nanoparticles. Colloidal solutions with a very high concentration of large, flat, hexagonal silver nanoplatelets (~230 nm in breadth) have been used to deposit and fix an antibacterial coating of these large starch-stabilised silver nanoplates on commercial cotton fibres, using a simple dip-coating process using water as the solvent, in order to study the dependence of the antibacterial properties of these nanoplatelets on their size.

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1. Introduction

Noble metal nanoparticles have attracted strong interest for their potential applications as catalytic, electronic, optical, environmental and biomedical materials [1–5]. Silver is one of the most studied noble metal elements due to its attractive physical properties and wide potential applications [6–12]. Various chemical methods have been developed to prepare silver nanoparticles with different sizes and shapes, such as spherical nanoparticles, nanobelts, nanowires, nanocubes and nanoplates [13–26]. However, these procedures suffer from a range of disadvantageous features: undesirable reagents, such as hydrazine hydrate, as the reducing agent; volatile organic chemicals such as the solvent; surfactants and/or polymer stabilising agents; the production of powders or colloidal solutions with only relatively low concentrations of silver nanoparticles and, as a result, unsuitability for large-scale production.

Therefore, it is important to develop "green chemistry" approaches [27] to prepare silver nanoparticles of the desired size, shape, and aspect ratio as stable aqueous colloidal solutions with a high concentration for practical applications, such as in antibacterial coatings for bedding, wound dressings, hospital uniforms, etc. Generally, three aspects should be considered for a green method to prepare silver nanoparticles:

environmentally friendly solvent medium and reducing agent and a non-toxic material for the stabilization of the nanoparticles. When water is used as the solvent, polysaccharides often serve as a reducing reagent or a capping reagent or, in some cases, as both a reducing and a capping reagent [28–32]. Starch-capped silver nanoparticles with particle sizes below 25 nm have been prepared in aqueous solution by ultrasound-mediated, glucose reduction, [33] or normal thermal reduction [34,35]. Khan et al. has reported the preparation of silver nanoparticles using ascorbic acid and starch as reducing and stabilising agents, respectively [36]. Starch as a combined reducing and stabilising agent has also been used to prepare silver nanoparticles (10 nm ≤ d ≤ 34 nm) in an autoclave [37].

Silver ions and silver compounds have been extensively utilised for their anti-septic and anti-microbial activity for more than 100 years, due to their toxic effect on some bacteria, viruses, algae and fungi [4,8,38,39]. Recently there has been much renewed interest in using silver as a broad-spectrum antimicrobial agent due to the increasing prevalence of anti-microbial resistant infections such as MRSA, especially in hospitals. Recent examples include the application of an antimicrobial gel containing silver nanoparticles in the size range of 7–20 nm in the treatment of burn and wound victims [40]. Several devices containing silver nanoparticles have recently been proposed for use in the fields of dental implantology, periodontology, and alveolar bone regeneration, for example, membranes for guided tissue regeneration (GTR) and guided bone regeneration (GBR) applications, scaffolds for bone regeneration, and dental implant coatings [41].

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Although small, spherical silver nanoparticles (4 nm ≤ d ≤ 40 nm) synthesised by green chemistry methods have been reported recently by us and other authors to show good antibacterial activity [42,43], there appear to be no reports of the synthesis and evaluation of the antibacterial properties of large, anisotropic silver nanoparticles (d ≥ 200 nm), i.e., nanoplatelets, and of their deposition on substrates for practical applications. One of the main reasons for this lack of information is the fact that it is difficult to prepare relatively stable colloidal solutions of large size silver nanoparticles. In order to study the antimicrobial properties of large silver nanoplatelets, we have developed a novel green chemistry method, using ascorbic acid as the reducing agent in water, for the preparation of highly concentrated, aqueous colloidal solutions of large, starch-stabilised, silver nanoplatelets with a controlled size, shape and aspect ratio. These aqueous colloidal solutions can then be used in a very simple, but efficient, water-based, non-impact, dip-coating process, based on our previous work, [42] to deposit *and* fix a coating of silver nanoplates on the surface of cotton fibres, without the use of chemical binders, surfactants, dispersants, a post-deposition curing step, etc. [44]. These highly concentrated solutions of silver nanoplatelets of a defined size, shape and aspect ratio could also facilitate the study of the quantum-confined physical properties of such silver nanoplatelets, such as surface plasmon resonance (SPR).

2. Experimental

2.1. Materials

Silver (I) nitrate ($AgNO_3$, 99 + %, product number 0696) and sodium borohydride ($NaBH_4$, 96%, product number 71321) were purchased from Lancaster and Fluka, respectively. Potato starch (product number S2004) and ascorbic acid (reagent grade, product number A7506) were sourced from Sigma-Aldrich. The cotton string fibres (diameter 1.2 mm, product number: 719.504) are from Lyerco, Telford, UK. Ultrapure water with a specific resistance of 18.2 MΩ cm was obtained by reverse osmosis followed by ion-exchange and filtration (UPQ PS system, ELGA, USA).

2.2. Synthesis of starch-protected silver seeds

Seeds of starch-protected, silver nanoparticles were prepared by a procedure similar to that developed by Zou et al. [25]. A 2.95 M $AgNO_3$ solution (0.5 cm^3) was added to a 0.5% aqueous starch solution (99 cm^3). Then a 0.5 M $NaBH_4$ solution (1.0 cm^3), which had been aged for 2 h, was added all at once. The resultant solution was stirred for 1 h and then aged for 24 h at room temperature to give a stable yellow silver colloidal solution (S_0). The solution exhibits a SPR band at 400 nm on the UV–vis spectrum. The silver seeds are nearly spherical with a diameter of 8.8 nm $\pm$ 2.0 nm according to analysis using transmission electron microscopy (TEM).

2.3. Stepwise seed-mediated synthesis of silver nanoparticles

2.3.1. Method 1
Silver nanoparticles with different sizes and shapes were prepared using a stepwise, seed-mediated, growth strategy using ascorbic acid as a mild reducing agent in a dilute aqueous solution of soluble starch. Eight samples were prepared in total. A fresh $AgNO_3$–0.5% starch solution (29.5 mM) was prepared by dissolving $AgNO_3$ (0.50 g) in an aqueous 0.5% starch solution (100 cm^3). For the first reaction step, a portion of the S_0 silver nanoparticle seed solution (5.0 cm^3) and a freshly prepared 1.0 M ascorbic acid solution (0.6 cm^3) were added to a 0.5% aqueous starch solution (15 cm^3). A freshly prepared aqueous $AgNO_3$–0.5% starch solution (10 cm^3) was then added dropwise to the resultant silver-seed/starch/ascorbic acid reaction solution under strong stirring. A clear brown solution (S_1) was

obtained after stirring at room temperature for 1 h. For the following steps, S_n samples were prepared by adding a portion of the S_{n-1} solution (10 cm^3) and ascorbic acid solution (0.6 cm^3) into a 0.5% starch solution (10 cm^3) followed by dropwise adding of a freshly prepared 0.5% $AgNO_3$–starch solution (10 cm^3). All the reactions were carried out by stirring at room temperature for 1 h. Each of these experiments was repeated three times.

2.3.2. Method 2
A fresh $AgNO_3$–0.5% starch solution (29.5 mM) was prepared as described in method 1. For the first reaction step, a freshly prepared 1.0 M ascorbic acid solution (0.6 cm^3) was added to the S_0 silver nanoparticle seed solution (5.0 cm^3) and then a freshly prepared aqueous $AgNO_3$–0.5% starch solution (10 cm^3) was added dropwise to the resultant silver-seed/ascorbic acid reaction solution under strong stirring. A clear brown solution (S_1) was obtained after stirring at room temperature for 1 h. For the following steps, S_n samples were prepared by adding ascorbic acid solution (0.6 cm^3) to a portion of the S_{n-1} solution (10 cm^3) followed by dropwise adding of a freshly prepared 0.5% $AgNO_3$–starch solution (10 cm^3). All the reactions were carried out by stirring at room temperature for 1 h.

2.4. Coating of silver nanoparticles on cotton fibres

A thin film of silver nanoparticles was coated and fixed on the surface of cotton fibres (diameter: 1.2 mm) by a simple immersion procedure, e.g., cotton fibres (0.23 g) were immersed in one of the S_0–S_8 colloidal solutions of silver nanoparticles (15 cm^3), prepared according to the method described above, for 4 h at room temperature. The resultant silver-coated fibres were then washed carefully with copious amounts of water, with no observable loss of silver nanoparticles, and then dried under vacuum overnight.

2.5. Characterization methods

UV–vis spectra were recorded in the range between 300 and 700 nm using a PerkinElmer Lambda 25 spectrometer. The aqueous silver colloidal solutions, prepared as described above, were diluted by a factor of 100 so that their absorption could be measured in a quartz cuvette with a 1 cm optical path. Scanning electron microscopy (SEM) images were obtained using Carl Zeiss SMT 'EVO60' SEM operating at 20 kV and EDX data were obtained using an Oxford Instruments 'INCA' Energy Dispersive X-ray Spectrometer. TEM images were collected using a Jeol 2010 TEM instrument running at 200 kV. Images were recorded using a Gatan Ultrascan 4000 digital camera. The liquid sample for TEM analysis was mixed well in a vial and then a 5 μL aliquot was placed on a hydrophilic carbon coated copper grid and allowed to dry in air. Fourier Transform Infrared spectroscopy (FT-IR) for silver powder samples were recorded on a Nicolet Magna-500 FTIR spectrometer. X-ray powder diffraction (XRD) analyses were either performed using a SIEMENS D5000 instrument for analysing silver powder samples or a Bruker AXS D8 Discover with GADDS detector for analysing silver-coated cotton fibres. The silver powder samples for FTIR, XRD and SEM were obtained by centrifugation (Sigma Laborzentrifugen 2-15 Howe in combination with Fisher oak ridge 28 mL centrifuge tubes) at 10,000 rpm for 15 min, washing (×3) with water and then drying under vacuum overnight. The concentration of the silver nanoparticles present on the surface of the fibres was determined using an inductively coupled PerkinElmer plasma 40 emission ICP instrument. The solutions for ICP were prepared by dissolving the samples (100 mg) in 3 ml concentrated nitric acid (Romil Ltd, Cambridge UK, SpA grade) then heated to 200 °C in a sealed Teflon digestion vessel (CEM Xpress vessels) and, when cool, they were diluted to 15.0 g.