Journal of Molecular Liquids xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Silver nano-disks: Synthesis, encapsulation, and role of water soluble starch

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ARTICLE INFO

Article history:
Received 26 May 2014
Received in revised form 11 August 2014
Accepted 23 September 2014
Available online xxxx

Keywords:
Nano-disks
Morphology
Capping agent
CTAB

ABSTRACT

Silver nano-disks have been synthesized by using starch as reducing- and stabilizing agent for the first time. UV–visible spectroscopy, transmission electron microscopy (TEM) and iodometric techniques were used to monitor the quantitative growth, and morphology of Ag-nanoparticles. The polyhedral nano-disks with an average diameter of 500 nm contain a large number of truncated triangular nanoplates, spherical, quantum dots, and irregularly shaped nanosilver were formed with starch. The silver nanodisks with an average diameter 500 nm contain a large number of truncated triangular and spherical nanoplates and quantum dots, and irregularly shaped nanosilver were formed with starch. The cetyltrimethylammonium bromide (CTAB) markedly enhanced the reaction path and changed the morphology (size, shape and distribution). This environmental friendly method of biological silver nanoparticle production provides the use of starch as a capping agent.

1. Introduction

Nanoparticles are of great scientific interest as they are, in fact, a bridge between bulk materials and atomic or molecular structures. A bulk material should have constant physical properties regardless of its size, but at the nano-scale size-dependent properties are often observed [1,2]. Nanoparticles often possess unexpected optical properties as they are small enough to confine their electrons and produce quantum effects [3]. Over the last decades silver nanoparticles have found applications in catalysis, optics, electronics and other areas due to their unique size-dependent optical, electrical and magnetic properties [4]. Currently most of the applications of silver nanoparticles are as antifungal agents in biotechnology and bioengineering, textile engineering, water treatment, and silver-based consumer products [5]. Silver nanoparticles have gained more attention owing to their broad spectrum of antimicrobial activity and low cost of manufacturing. There is also an effort to incorporate silver nanoparticles into a wide range of medical devices, including but not limited to bone cement, surgical instruments, surgical masks, and wound dressings. Silver nanoparticles have been used as a cathode in a silver-oxide battery. There are several wet chemical methods for the synthesis of silver nanoparticles. Typically, they involve the reduction of a silver salt with a reducing agent like sodium borohydride in the presence of suitable colloidal stabilizers. Bakshi et al. [6] used bovine serum albumin protein as a reducing-and stabilizing agent to prepare conjugated gold nanoparticles and explore their applications as drug delivery vehicles in systemic circulation. These workers also reported that the sulfur-, oxygen- and nitrogen-bearing groups mitigate the high surface energy of the nanoparticles during their reduction. Lee and his co-workers [7] developed a facile method to prepare a magnetic-silver nano-composite which possesses a high antimicrobial activity against the model microbes *Escherichia coli* and *Bacillus subtilis*. The hydroxyl groups on the cellulose are reported to help in stabilizing the particles. Polydopamine-coated magnetic-bacterial cellulose contains multifunctional groups, which acts as a reducing agent for in situ preparation of reusable antibacterial Ag-nanocomposites [8]. A novel wet chemistry method used to create silver nanoparticles took advantage of D-glucose as a reducing sugar and starch as the stabilizer and also cellulose molecular chain is applied to employ the reducing and stabilizing features of cellulose to synthesize nanosilver [9].

Sulfur-, oxygen-, and nitrogen-containing strong and weak reducing agents have been used with polymers, surfactants, lipids, proteins, starch and cellulose as stabilizing agents [10]. Starch is a biodegradable natural polymer of α-D-glucose produced by many plants as a source of stored energy. Starch can be separated into two fractions—amylose and amylopectin. Among natural and synthetic polymers, the use of starch (fully biodegradable, consists 10–20% amylose forms a colloidal dispersion in hot water and amylopectin 80–90% completely water insoluble). The structure of amylose consists of long polymer chains of glucose units connected by an alpha acetal linkage. Amylose in starch is responsible for the formation of a deep blue color in the presence of iodine–potassium iodide reagents. The iodine molecule slips inside of the amylose coil. If starch amylose is not present, then the color will stay orange or yellow. Starch amylopectin does not give the color, nor does cellulose, nor do disaccharides such as sucrose in sugar.

In the present study, starch coated silver nano-disks and/or nanoparticles were synthesized and characterized by UV/Vis spectroscopy.

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http://dx.doi.org/10.1016/j.molliq.2014.09.041
0167-7322/

This paper intends to give a clear overview of starch-capped silver nanoparticles preparation, characterization, morphology, and shape-controlling activity of CTAB. Eco friendly starch coated silver nanoparticle could provide a simple chemical-reduction method for the synthesis of silver nano-disks and prevent the spreading and persistence of endodontic infections.

2. Experimental

2.1. Materials and preparation of solutions

Deionized double distilled, CO_2 and O_2 free water used as the solvent for the preparation of stock solutions of all reagents. All glassware was washed with aqua regia (3:1 HCl and HNO_3), rinsed with water, and drying before use. Silver nitrate ($AgNO_3$, Merck India, 99.99%), CTAB (99%, Fluka), potassium iodide (KI, Merck India, 99%) and iodine (I_2, Merck India, 99.9%) were used as received. Potatoes were purchased from a local market near to the campus of Jamia Millia Islamia, New Delhi. The 0.1 N KI–I_2 reagents was prepared by dissolving the required amounts in required water, stored in an amber colored glass bottle and used to detect the presence of starch in the potato water extract. Iodine is not very soluble in water; therefore the iodine reagent is made by dissolving iodine in water in the presence of KI. This makes a deep blue complex with starch and/or triiodide ion and iodine molecules. The triiodide ion slips into the coil of the starch causing an intense blue-black color.

2.2. Preparation of potato starch aqueous extracts (PSE)

The 15.0 g of potato was rinsed with deionized water, chopped into fine pieces, soaked in 250 ml water, heated for 30 min on water bath at 60 °C, allowed to cool, stand for 24 h at room temperature, and the supernatant was filtered with Whatman paper No. 1. The filtrate was used to the reduction of Ag^+ ions into Ag^0. The resulting PSE contains mainly water soluble starch which has been confirmed by the addition of iodine-potassium iodide reagents (wide infra). In order to see the presence of reducing sugars (monosaccharides) in the PSE, spot tests were negative with PSE and Benedict reagent indicating that PSE does not contain any monosaccharides.

2.3. Green synthesis and characterization of Ag-nanoparticle using PSE

In the present studies, an aqueous PSE was used as reducing agent to the bio-reduction of Ag^+ ions into Ag^0. To synthesize Ag-nanoparticles, PSE from 2.0 cm^3 to 10.0 cm^3 were added in an aqueous 10.0 cm^3 of 0.01 mol dm^{-3} of $AgNO_3$ solution. As the reaction proceeds, the colorless reaction mixture turned yellow to orange, indicating the formation of nanoparticles [11]. Preliminary observations showed that the appearance of color was very fast and reaction completed within ca. 40 min at room temperature. In all experiments, PSE was added in the required [Ag^+]. UV–visible Spectrophotometer (model UV-260 Shimadzu) with 1 cm light path quartz curette was used to monitor the progress of the reaction under different experimental conditions. The transmission electron microscopy (TEM) images were obtained on a JEOL, JEM-1011; Japan, transmission electron microscope operating at 160 kV. The samples for TEM were prepared by drop-casting one drop of the prepared silver sols onto carbon-coated copper grids and then drying in air.

2.4. Experimental evidence to the complete reduction and kinetic measurements

It has been well known that the morphology (shape, size and the size distribution) of the silver nanoparticles depend on the experimental conditions such as [reactants], reduction potentials of reactants, [stabilizers], temperature, reaction time, order of mixing and PH. Therefore, in order to establish the role of [Ag^+], [CTAB], [extract], and reaction time, a series of experiments were performed under different experimental conditions. In a typical experiment, 5.0 cm^3 (0.01 mol dm^3) NaCl was added in a reaction mixture containing PSE extract (10.0 cm^3) + $AgNO_3$ (10.0 cm^3 of 0.01 mol dm^{-3}) + CTAB 5.0 cm^3 of (0.01 mol dm^3) after appearance of the perfect transparent yellow orange color silver sol. We did not observe the white precipitate and/ or turbidity of AgCl indicating the complete reduction of Ag^+ ions to Ag^0. It was also observed that atmospheric oxygen and or nitrogen gas has no significant effect on the nucleation and growth of silver nanoparticles. These observations are in good agreement to our previous result regarding the formation of silver nanoparticles by using ascorbic acid and CTAB as reducing and stabilizing agents, respectively [12].

The kinetic measurements were carried out in a three necked reaction vessel fitted with a double surface condenser to check evaporation by adding the required concentrations of $AgNO_3$, CTAB and water (for dilution maintained). The progress of the reaction was followed spectrophotometrically by adding the required concentrations of leaves extract. The absorbance of the appearance of yellowish-brown color sol was measured at 475 nm at definite time intervals. Apparent rate constants were calculated from the initial part of the slopes of the plots of ln (a / (1 − a)) versus time by a fixed time method (vide infra). The results were reproducible to within ± 5% with average linear regression coefficient.

3. Results and discussion

3.1. Morphology of Ag-nanoparticles

In the first set of experiments, a solution of PSE (3 cm^3) was added to a $AgNO_3$ solution (0.01 mol dm^{-3}; 10.0 cm^3, total vol. 40 cm^3). Reduction of the Ag^+ ion to Ag^0 by PSE extracts could be followed by color change. Fig. 1 show the UV–vis spectra recorded from the reaction medium as a function of different experimental conditions. It is interesting to note that a broad band begins to develop in the whole visible region instead of a peak very slowly (Fig. 1; ▼). It has been established that CTAB has strong influence on the morphology of silver and gold nanoparticles [13–16]. To increase the nucleation rates, the effect of shape directing [CTAB] (from 2.5×10^{-4} to 15.0×10^{-4} mol dm^{-3}) was studied at different [PSE] and fixed [Ag^+] = 25.0×10^{-4} mol dm^{-3}. The spectra of resulting colored silver sols are given in Fig. 1. The most interesting features of the present observations are the fast appearance of color with

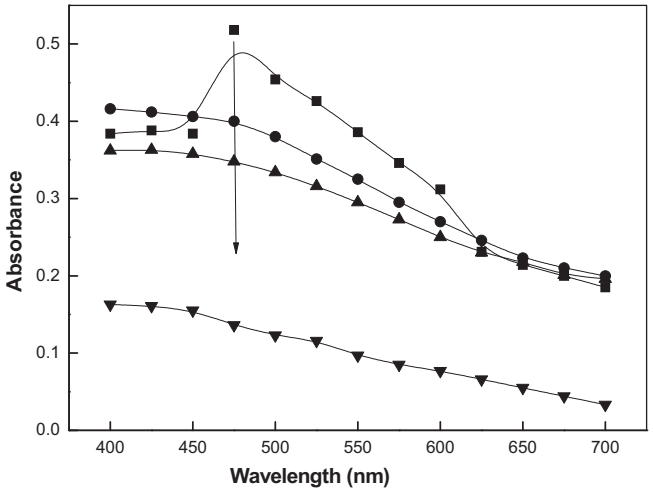

Fig. 1. Spectra of starch capped Ag-nanoparticles at different [CTAB]. *Reaction conditions*: [Ag^+] = 25.0×10^{-4} mol dm^{-3}, [CTAB] = 0.0 (▼), 2.5 (▲), 10.0 (●) and 12.5×10^{-4} mol dm^{-3} (■), [PS] = 5.0 (▲, ●, ■) and 10.0 cm^3 (▼).

Please cite this article as: O. Bashir, Z. Khan, Silver nano-disks: Synthesis, encapsulation, and role of water soluble starch, J. Mol. Liq. (2014), http://dx.doi.org/10.1016/j.molliq.2014.09.041