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A novel one-pot 'green' synthesis of stable silver nanoparticles using soluble starch

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Abstract—Stable silver nanoparticles have been synthesized by using soluble starch as both the reducing and stabilizing agents; this reaction was carried out in an autoclave at 15 psi, 121 °C for 5 min. Nanoparticles thus prepared are found to be stable in aqueous solution over a period of three months at room temperature (~25 °C). The size of these nanoparticles was found to be in the range of 10–34 nm as analyzed using transmission electron micrographs. The X-ray diffraction analysis revealed the face-centred cubic (fcc) geometry of silver nanoparticles. Iodometric titration confirmed the entrapment of silver nanoparticles inside the helical amylose chain. These silver nanoparticles embedded in soluble starch produced a typical emission peak at 553 nm when excited at 380 nm. The use of environmentally benign and renewable materials like soluble starch offers numerous benefits of eco-friendliness and compatibility for pharmaceutical and biomedical applications.

Keywords: Amylose–iodine complex; Green chemistry; Photoluminescence; Silver nanoparticles; Soluble starch

1. Introduction

Over the past decade, increasing awareness about the environment has led researchers to focus on 'green chemistry'. Utilization of nontoxic chemicals, environmentally benign solvents and renewable materials are some of the key issues that merit important consideration in a green synthesis strategy.[1–3] Nanomaterials have wide-ranging implications in a variety of areas, including physics, chemistry, electronics, optics, materials science and the biomedical sciences. In spite of the novel properties exhibited by the metal nanoparticles due to quantum size effects, their synthesis protocol poses a major environmental problem.[4–6] Most of the synthetic methods reported to date rely heavily on the use of organic solvents and toxic reducing agents like sodium borohydride and *N*,*N*-dimethylformamide. All these chemicals are highly reactive and pose potential environmental and biological risks. With the increasing interest in minimization/elimination of waste and adoption of sustainable processes through green chemistry, the development of biological, biomimetic and biochemical approaches is desirable. In earlier reports where natural polymers like starch[3] and chitosan[7] are reported to stabilize silver nanoparticles, separate reducing agents were used.

Recently, researchers have begun using biological molecules as templates for generation of inorganic structures and materials. Biological systems form sophisticated mesoscopic and macroscopic structures with tremendous control over the placement of nanoscopic building blocks within extended architectures.[8] Since the more immediate applications of nanoparticles will be in medical diagnosis and therapeutics like detection of genetic disorders by using gold nanoparticles,[9,10] colour-coded fluorescent labelling of cells using semiconductor quantum dots[11] and cell transfection for gene therapy and drug delivery,[12] the use of biologically compatible materials for nanoparticles synthesis and stabilization will undoubtedly play a crucial role.

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The concept of green nanoparticles preparation using β-D-glucose as the reducing agent was first reported by Raveendran et al.[3] where starch played the role of stabilizer. In the present work, silver nanoparticles are prepared using soluble starch acting as both the reducing and stabilizing agents. Soluble starch, the amylose component of starch, is a linear polymer formed by the α-(1→4) linkages between D-glucose units and adopts a left-handed helical conformation in aqueous solution. Despite its slight branching, amylose behaves essentially like a linear polymer, forming films and complexes with ligands.[13] In this report, the aldehyde terminal of soluble starch is used to reduce silver nitrate while the starch itself stabilized the silver nanoparticles.

2. Materials and methods

2.1. Materials

Soluble starch ($\overline{M}_w = 2200$; $\overline{M}_n = 950$; polydispersity index = 2.3) and silver nitrate were obtained from HiMedia® Ltd (India). All chemicals were of analytical grade and used without further purification. All aqueous solutions were made using ultrahigh purity water (18 MΩ cm resistance) purified using a Milli-Q® Plus system (Millipore Co.).

2.2. Preparation of silver nanoparticles

In a typical one-step synthesis protocol, 1.0 g of soluble starch was added to 100 mL of deionized water and heated in microwave oven. After complete dissolution, 1 mL of a 100 mM aq solution of silver nitrate was added and stirred well. This mixture was kept in an autoclave at 15 psi pressure, 121 °C for 5 min. The resulting solution was clear yellow in colour indicating the formation of silver nanoparticles.

2.3. UV–visible spectral analysis

The UV–vis spectrum of the silver nanoparticles embedded in soluble starch was recorded in Specord 50 ANALYTIKJENA® spectrophotometer, from 200 to 900 nm. A solution containing 1.0% soluble starch was used as the blank.

2.4. Transmission electron microscopy and electron diffraction

For transmission electron microscopy (TEM), a drop of aqueous solution containing the silver nanoparticles embedded in soluble starch was placed on carbon-coated copper grids and dried under infrared lamp. Micrographs were obtained using a Philips® EM208 TEM operating at 200 kV. The electron diffraction pattern was also recorded for the selected area.

2.5. Iodimetric titration

The stabilization of silver nanoparticles by soluble starch was analyzed by iodimetric titration. The silver nanoparticles prepared in soluble starch solution (100 mL) was titrated with 0.1 N iodine solution (I_2/KI). At regular intervals, the change in colour was monitored by recording the UV–vis spectrum as mentioned above. Once the stable blue colour was obtained due to the amylose–iodine complex, 50 mL of the nanoparticles solution stabilized with soluble starch was added, and the spectrum was recorded again.

2.6. X-ray diffraction analysis

The aqueous solution of soluble starch embedded with silver nanoparticles was spray dried in a JISL LSD48 Mini Spray Drier at 100 °C, and the brown-coloured powder obtained was used for X-ray diffraction (XRD) analysis. The powder X-ray diffraction was performed using a Phillips® PW 1710 X-ray Diffractometer with nickel filtered Cu Kα ($\lambda = 1.54$ Å) radiation and analyzed using APD (automatic powder diffraction) software. The diffracted intensities were recorded from 10° to 65° 2θ angles.

2.7. Photoluminescence analysis

Photoluminescence spectra were recorded in Perkin–Elmer LS55® Spectrofluorimeter using 90° illumination. Initially, prescan was performed[14] to find out the excitation and emission maxima for the silver nanoparticles. Based on the excitation maxima, emission scans were carried out in the range of 500–700 nm. The excitation and emission slit widths were kept at 2.5 and 5.0 nm, respectively, to get the maximum signal-to-noise ratio. The entire scanning was done at the speed of 100 nm/min. The data were analyzed using the FL Winlab® software.

3. Results and discussion

It is well known that solutions of polymers can be used for the synthesis and stabilization of nanoparticles. Linear as well as dendritic polymers have been successfully used for nanoparticle synthesis. Polyhydroxylated macromolecules present interesting dynamic supramolecular associations facilitated by inter- and intra-molecular hydrogen bonding resulting in molecular level capsules, which can act as templates for nanoparticle growth.[3] Though heparin has been evaluated both as reducing and protecting agent for the preparation of silver