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# Gamma irradiation route to synthesis of highly re-dispersible natural polymer capped silver nanoparticles

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## ABSTRACT

Aqueous dispersions of highly stable, redispersible silver nanoparticles (Ag NPs) were synthesized using gamma radiolysis with gum acacia as a protecting agent. The formation of nanosized silver was confirmed by its characteristic surface plasmon absorption peak at around 405 nm in UV–vis spectra. The size of the silver nanoparticles can be tuned by controlling the radiation dose, ratio of gum acacia to silver ions and also the ionic strength of the medium. Dynamic light scattering (DLS) measurement of the as-synthesized nanoparticles indicated the size less than 3 nm at higher dose of radiation and this also corroborated the size measurement from the width of the corresponding X-ray diffraction (XRD) peak. The face centered cubic (fcc) crystallinity of the nanoparticles was evident from XRD and high resolution transmission electron microscopic (HRTEM) measurements. Fourier transform infra-red (FTIR) spectroscopic data indicate a bonding of Ag NPs with COO<sup>-</sup> group of acacia through bridging bidentate linkage.

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## 1. Introduction

Unique optical, electrical and excellent catalytic properties of metal nanoparticles have spurred interest in developing different synthetic methodologies for diverse applications. Among these, the silver nanoparticles have attracted considerable attention because of their potential applications in various fields such as oxidative catalysis (Shiraishi and Toshima, 2000), surface enhanced Raman scattering (Kneipp et al., 1983; Débarre et al., 2004; Faulds et al., 2004), nanoelectronics (single-electron transistors, electrical connects) (Sato et al., 1997), conductive coatings (Wuelfing et al., 2001), biosensors (Frederix et al., 2003; Bakker, 2004; Haes et al., 2004), antibacterial activity (Sondi and Salopek-Sondi, 2004), etc. Considering their applications in various fields, many techniques of synthesizing silver nanoparticles have been investigated. Some of them are chemical reduction (Yu, 2007), electrochemical reduction (Liu and Lin, 2004), photochemical reduction (Henglein, 1998), microemulsion (Cai et al., 2004; Taleb et al., 1997),  $\gamma$ -ray irradiation (Henglein, 1979; Meisel, 1979; Mostafavi et al., 1989, 2002; Remita et al., 2005; Temgire and Joshi, 2004), UV irradiation (Cheng et al., 2005), microwave (Tsuji et al., 2007) and ultrasonic (Lei and Fan, 2006).

Over the past decade, there has been an increased emphasis on the topic of green chemistry (Gross and Kalra, 2002). Utilization of

non-toxic chemicals, environmentally benign solvents and renewable materials are some of the key issues in the green synthetic strategy. Enormous quantities of nanomaterials are being synthesized every year due to the rapid development in the areas of material science and nanotechnology. However, their negative effect on the environment has been known in the very recent years. That is why, in the current drive there is a necessity for the development of facile and green technologies in nanomaterial synthesis. The concept of green nanoparticles preparation using  $\beta$ -D-glucose, as the reducing agent was first reported by Raveendran et al. (2003), where starch played the role of a stabilizer. Inspired and improved by the green chemistry, some new approaches appear very recently to prepare metal nanoparticles.

Natural polymers such as sodium alginate (Liu et al., 2009), chitosan (Huang et al., 2004; Wei and Qian, 2008; Chen et al., 2007; Yoksan and Chirachanchai, 2009), natural rubber (Abu Bakar et al., 2007), carboxy methyl cellulose sodium (Chen et al., 2008) and heparin (Huang and Yang, 2004) have been used for the capping of silver and gold nanoparticles. Among the natural polymers, gum acacia (also known as gum Arabic) is a well-known polysaccharide obtained from the stems and branches of *Acacia Sengal* tree. According to recent characterization studies (Renard et al., 2006), it is known to be composed of three main components: (i) the abundant portion by weight (around 88.4% w/w of the total gum) is an arabinogalactan (AG) fraction with a mean molecular weight around  $M_W \sim 2.79 \times 10^5 \text{ g mol}^{-1}$ , (ii) a high-molecular-weight around ( $M_W \sim 1.45 \times 10^6 \text{ g mol}^{-1}$ ) arabinogalactam–protein (AGP) complex fraction and (iii) a third

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minor glycoprotein fraction contributes around 1.2% w/w of the gum. As a whole gum acacia has average molecular weight  $M_w \sim 3.06 \times 10^5$  and number average molecular weight  $M_n \sim 2.44 \times 10^5$  with polydispersity index  $M_w/M_n \sim 1.25$ , whereas degree of polymerization values are 3600 and 1550, respectively, for  $DP_w$  and  $DP_n$ . The radius of gyration ( $R_g$ ) value was found to be in the range 11.3–41.3. The Newtonian flow is up to 40% concentration. The protein content (dry matter %) is 2.42 and the protein to total sugar ratio for the gum is 0.025; 70% of weight of gum is polysaccharide with little or no nitrogenous material (0.29%). Remaining higher molecular weight part has protein as part of its structure (a protein polysaccharide) and this is attached to polysaccharide through hydroxyproline and serine residues. The presence of very low content of uronic acid (16%) in the different components of the gum made this polymer to be considered as a weakly charged polyelectrolyte.

We have chosen gum acacia as the stabilizer for capping silver nanoparticles mainly because of its following advantages: (i) it is a water soluble natural material and non-toxic, (ii) gum acacia stabilised Ag NPs offer compatibility for pharmaceutical and biomedical applications, (iii) the wide spread availability of the naturally occurring polysaccharide makes this process amenable to get large-scale industrial production, (iv) it has excellent emulsifying (Johnson, 2005) and surface-active properties, which would be beneficial for the design of metal nanoparticles and (v) capping action of this long chain natural polymer is non-specific physical adsorption (i.e., which does not involve covalent or ionic interactions).

There are some reports of chemical synthesis of silver nanoparticles with gum acacia as a capping agent (Velikov et al., 2003; Mohan et al., 2007). Even synthesis of single-wall carbon nanotubes (SWNTs) is also possible with this natural polymer (Bandyopadhyaya et al., 2002). In the present study, we have adopted  $\gamma$ -radiolysis route for reduction of silver ions because of its several important advantages: (i) controlled reduction of metal ions can be performed without using an excess of a reducing agent or producing any undesired oxidation products from the reductant, (ii) reducing agent is generated uniformly in the solution, (iii) the method provides metal nanoparticles in fully reduced, pure and highly stable state, (iv) no interfering impurities like metal oxides are introduced, (v) the method is highly reproducible and (vi) synthesis can be carried out at ambient conditions.

In this paper, we report single pot aqueous synthesis of highly stable and densely dispersed silver nanoparticles stabilized with gum acacia by  $\gamma$ -radiolytic reduction method. Silver nanoparticle dispersions prepared by this method are stable for more than five months. The present method of synthesis is carried out in aqueous medium at neutral pH at room temperature without involving toxic, carcinogenic materials.

## 2. Experimental

### 2.1. Materials

Gum Arabic (gum acacia) (> 99% of purity),  $\text{AgNO}_3$ , 2-propanol and  $\text{K}_2\text{SO}_4$  of analytical reagent quality were purchased from Merck. Milli-Q water was used for all preparations. All the reagents used were as received without any further purification.

### 2.2. Synthesis of silver nanoparticles capping with gum acacia

Solutions of four different concentrations (0.01, 0.05, 0.1 and 0.5 wt%) of both silver nitrate and gum acacia were prepared in water. In a typical synthesis, 0.2 ml of aqueous  $\text{AgNO}_3$  (0.1 wt%) solution was mixed with 2 ml of gum solution (0.01 wt%) and

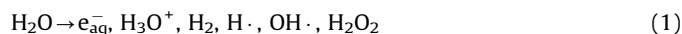
in the resulting mixture, 0.25 ml of 2-propanol (13 M) was added. The whole solution was then deaerated by bubbling with pure nitrogen gas for 15 min to remove oxygen and irradiated with  $^{60}\text{Co}$   $\gamma$  at a dose rate 6 kGy/h for different time intervals; 2-propanol was added in each sample to avoid oxidation due to the oxidizing species, namely, hydroxyl radical, produced in the radiolysis of water. In order to look into the effect of ionic strength on the formation of silver nanoparticles,  $\text{K}_2\text{SO}_4$  was added in the reaction mixture.

### 2.3. Instrumentations

UV-vis spectra of as-prepared silver nanoparticles were recorded on a UV-1601 PC (Shimadzu) spectrophotometer. Unirradiated solution was taken as the blank and all samples were diluted six times before taking the measurements. The size distribution and zeta potential of silver nanoparticles capped with gum acacia were determined by dynamic light scattering (DLS; Model DLS-nano ZS, Zetasizer, Nanoseries, Malvern Instruments). The commercially available software installed in the instrument determines the average particle size in an ensemble based on Stokes-Einstein equation using cumulants analysis or distribution analysis. The zeta potential was calculated from the electrophoretic mobility using the Smoluchowski equation with the help of commercial software. For Fourier transform infra-red spectroscopy (FTIR), silver colloidal solution was freeze-dried and pelletized along with KBr. The FTIR spectra of the samples were recorded on Perkin-Elmer spectrometer (Spectrum GX) with a resolution of  $2 \text{ cm}^{-1}$  over a scan range  $4000\text{--}400 \text{ cm}^{-1}$ . X-ray diffraction (XRD) measurements were carried out in the reflection mode on a Rigaku diffractometer ULTIMA-III (Tokyo, Japan) operated at 40 kV voltages and a current of 30 mA with  $\text{CuK}\alpha$  radiation ( $\lambda = 0.1546 \text{ nm}$ ). The particles size was calculated from Ag (1 1 1) reflection using a scan rate of  $2^\circ/\text{min}$  in the  $2\theta$  range  $20\text{--}90^\circ$ . For XRD measurement also, the freeze-dried sample was used. The morphology and particle sizes were also determined by transmission electron microscopy (TEM). The TEM images were taken on JEOL-2010 model transmission electron microscope with an accelerating voltage of 200 kV. A drop of as-prepared sample was placed on a carbon copper grid and dried before putting it into the TEM sample chamber.

## 3. Results and discussion

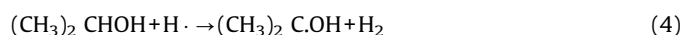
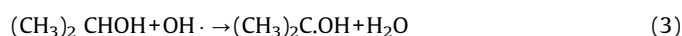
When aqueous solutions are subjected to  $\gamma$ -radiolysis, it produces the following species (Spinks and Woods, 1990):



The solvated electrons and  $\text{H}\cdot$  atoms are strong reducing agents:  $E^0(\text{H}_2\text{O}/e_{\text{aq}}^-) = -2.87 \text{ V}$  (NHE) and  $E^0(\text{H}^+/\text{H}) = -2.3 \text{ V}$  (NHE) and can reduce  $\text{Ag}^+$  ions to neutral  $\text{Ag}^0$  atoms:



The reduction of  $\text{Ag}^+$  ions is the main process for the formation of nanoparticles under  $\gamma$ -radiolysis. So, the oxidizing  $\text{OH}\cdot$  radicals produced in radiolysis of water (Eq. (1)) should be scavenged and it can be done efficiently by adding 2-propanol. Besides,  $\text{H}\cdot$  radicals are also scavenged by these molecules:



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