



Molecular insights into sodium dodecyl sulphate mediated control of size for silver nanoparticles

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ABSTRACT

A specific condition directing the formation of silver nanoparticles (AgNPs) with narrow size-distribution in aqueous sodium dodecyl sulphate (SDS) solutions, using trisodium citrate (TSC) is investigated. The peculiar control in distribution of size for AgNPs in presence of 35 mM (~1 wt%) aqueous SDS solution as stabilizing agent is evident. Water penetration through packed PTFE powder and dynamic surface tension measurements demonstrate formation of stable aggregates at the given condition and accordingly reduced numbers of free SDS monomers diffusing to the growing AgNP interface. The smaller size of AgNPs was also confirmed by TEM images, which illustrates mixed morphologies for the nanoparticles in an aggregated state. The NMR experiments reveal strong hydrophobic interactions between the alkyl chains of SDS molecules adsorbed on AgNPs. These results also indicate that TSC is molecularly distributed in bulk phase without binding to the SDS micellar aggregates. A plausible molecular mechanism is proposed based on diffusion of Ag⁺ ions to the growing AgNP surface along with SDS monomers and submicellar aggregates, subsequently forming bigger size AgNPs. The narrow distribution of size for AgNP in presence of 35 mM SDS is arguably driven by the capping of stable SDS micelles or monomers around growing nuclei and restricted number of SDS monomers and submicellar aggregates responsible for supply of Ag⁺ at the growing AgNP nuclei.

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1. Introduction

Two major challenges involved in application of silver nanoparticles (AgNPs) are (i) formation of smaller size of nanoparticles and (ii) forming stable colloidal dispersions of AgNPs by preventing the aggregation process. The failures in overcoming these challenges lead to the formation of aggregates and concomitant decrease in the antibacterial activity [1,2]. In this perspective, the stability of aqueous AgNP dispersions are mainly achieved by inducing two different forces on the particle-bulk interface, namely steric and electrostatic repulsions [3].

The commonly adopted approach involves introduction of steric repulsion forces, which is governed by a stabilizing effect exerted by the non-ionic surface active agents and polymers, which readily adsorb at the particle surface [4]. The thickness of the adsorbed layer controls the equilibrium between the repulsive and the attractive forces [5]. If

polymer molecules are used as capping agents, the interacting moieties play a crucial role along with the length of hydrophobic chain [6]. Different types of polymers are used as stabilizing agents that include polyvinyl alcohol (PVA), polyvinyl pyrrolidones (PVP) and polyethylene glycol (PEG) [7–10]. Low molecular weight non-ionic surfactants like Triton X-100, Brij-58 and Tween-80 provide best stabilization effects due to specific adsorption on particle surface [11,12].

The second pathway leading to stable nanodispersion relies on electrostatic repulsion approach based on increasing the surface charge of the dispersed particles using ionic surfactants, which consequently inhibit particle growth and aggregation. In this case, the mechanism involving interactions of AgNPs and the ionic surfactants has not been well understood. Various cationic surfactants e.g. cetyltrimethyl ammonium bromide and anionic surfactants e.g. sodium dodecyl sulphate (SDS) are used as electrostatic stabilizers [13–15]. A plausible hypothesis featuring adsorption of SDS molecules around the AgNPs is described by Chen et al. [16]. According to their assumptions, the hydrophilic groups of the SDS molecules get adsorbed on the AgNP surface leaving the hydrocarbon chain facing outside towards bulk medium to form the primary adsorption layer. As the adsorption process continues, a

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secondary layer starts to develop following a tail-tail interaction and hence bilayer of surfactant will appear on AgNP.

Nanoparticle synthesis using tri sodium citrate (TSC) as reducing agent is investigated by various research groups [17–19]. Pillai and Kamat [20] discussed the role of TSC in controlling the size and shape of the AgNPs. The action of TSC ions as a reducing, stabilizing and complexing agent on the size and morphology of AgNPs is deduced by steady-state and pulse-radiolysis experiments. TSC ions modulate the particle growth at initial stage by forming a complex with positively charged Ag_2^+ dimers. The change in TSC concentration simultaneously affects the mechanism of reduction and nucleation process; hence it is very difficult to differentiate their individual contribution. Guzman et al. [21] discussed the role of SDS as stabilizer and hydrazine hydrate + TSC mixture as reducing agent in synthesis of AgNPs. The Ag^+ ions electrostatically interact with the negative OSO_3^- headgroup of SDS in the Stern layer and thereby induce formation of giant Ag ion clusters due to formation of ion-pair [22]. These results demonstrate that concentration of reducing agent and stabilizing agent is extremely important in controlling the size distribution of AgNPs. The concentration of SDS used for most of these articles was 1 wt% (~35 mM), but no scientific explanation was discussed for this specific choice.

In this paper, we report on the control in size-distribution of AgNPs during synthesis using TSC in 35 mM aqueous SDS solutions. During preliminary experiments, we noticed a superior size control for AgNPs in presence of 35 mM SDS and 3.5 mM TSC in the reaction mixture. The observations were examined in terms of the concentration of free monomers and submicellar aggregates in aqueous SDS solutions; if the concentration of the monomers and the submicellar aggregates is more in the solution, the AgNPs are of large size with broad distribution. The monomers and the submicellar aggregates were found to be carrier of the Ag⁺ ions adsorbing on the AgNPs to increase their size. At 35 mM concentration of SDS in the solution, the minimal number of monomers and the submicellar aggregates (due to stable micelles) restricted the growth of the AgNPs. In addition, the stable SDS micelles (at 35 mM) capped the AgNPs inhibiting the adsorption of Ag⁺ ions on the AgNPs. The AgNP morphology and molecular interactions leading to peculiar size control are investigated by dynamic light scattering (DLS), UV-visible spectroscopy, dynamic surface tension (DST), water penetration through packed Teflon® powder, nuclear magnetic resonance (NMR) spectroscopy, zeta potential, small angle neutron scattering (SANS) and Transmission electron microscopy (TEM). Based on these results, we also describe a plausible molecular mechanism for the formation of AgNPs with narrow size distribution in 35 mM aqueous SDS solutions.

2. Materials and methods

The chemicals used for the AgNP preparation, namely silver nitrate (AgNO_3), tri sodium citrate (TSC) and sodium dodecyl sulphate (SDS) were obtained from Sigma-Aldrich, USA. Milli-Q water obtained from Millipore® water filter was used for the preparation of all sample solutions. The samples for NMR experiments were prepared in D_2O . The Teflon® powder with average particle size of 300 nm was used for the wettability experiments.

2.1. Synthesis for silver nanoparticles

The aqueous SDS solutions (as capping agent) in different concentrations (5 mM, 35 mM and 100 mM) were added in a round bottom flask. A required volume of AgNO_3 solution (0.5 mM and 2 mM) was then added with continuous stirring for 10 min and heated under reflux condition at 90 °C. Then, desired volume of TSC (reducing agent) in three different concentrations (1.75 mM, 3.5 mM and 5.25 mM) was added drop-wise with constant stirring to control the numbers of nuclei formation. This will facilitate the diffusion and adsorption of SDS monomers/micelles on the growing nuclei surface and accordingly control particle size. With faster addition of TSC the numbers of uncapped

nuclei increases and hence the particle size. The reaction mixture (50 ml) was heated at 90 °C for 1 h. Subsequently, colour of reaction mixture changed from faint yellow to reddish yellow indicating formation of AgNPs. The formation of AgNPs in the absence of capping agent was also investigated at different concentrations of TSC in range of 0.5 to 10 mM.

2.2. Instrumental methods of characterization

2.2.1. Dynamic light scattering (DLS) and zeta potential

DLS experiments were performed at a fixed scattering angle of 173° using a Malvern Zetasizer instrument (# Nano-ZS 4800, UK) equipped with a He-Ne laser operating at a wavelength of 633 nm at 25 °C. Each measurement system for the measurement of size distribution was repeated five times, and average values were considered. The same instrument was used to measure the zeta potential under the effect of applied potential.

2.2.2. UV-visible spectroscopy

The surface plasmon spectrum for AgNPs was recorded using UV-VIS-NIR (Agilent, UK) spectrophotometer at wavelength range of 300–800 nm. The characteristic surface plasmon for the AgNPs was observed between 390 and 450 nm.

2.2.3. Dynamic surface tension (DST)

Dynamic surface tension measurements were carried out using a bubble tensiometer (Biolin, model # BPA-800P) at 25 °C using maximum bubble pressure method as a function of bubble lifetime.

2.2.4. Water penetration in packed powders

Water penetration through packed PTFE powder is measured using Attension surface tensiometer (Biolin, model #Sigma 700). 1 g PTFE powder was filled in metal cylinder hanged to a sensor that measures the change in weight as a function of time. One end of this cylinder was allowed to dip in surfactant solution for 15 min. at a constant depth of 3 mm, and the resultant weight gain due to absorption of water was noted. The measurements were repeated three times in order to ensure reproducibility.

2.2.5. Transmission electron microscopy (TEM)

The AgNPs synthesized in various solution conditions were analyzed using transmission electron microscope (Philips techno 20:200 kV) at sophisticated instrumental centre for applied research and testing (SICART), V.V. Nagar, India.

2.2.6. Nuclear magnetic resonance (NMR)

The ^1H NMR studies of the micellar solutions, prepared in D_2O , were carried out to reveal the molecular interactions of the SDS molecules in the micelles and with the TSC. This was investigated using NMR facility (Advance DPX 200 Bruker) at Central Salt and Marine Chemical Research Institute (CSMCRI), Bhavnagar, India.

2.2.7. Small angle neutron scattering (SANS)

In SANS one measures the differential scattering cross-section per unit volume ($d\Sigma/d\Omega$) as a function of scattering vector Q . For a system of charged interacting

micelles $d\Sigma/d\Omega$ is given by [23].

$$\frac{d\Sigma}{d\Omega} = nV^2(\rho^m - \rho^s)^2 \left[\langle F(Q)^2 \rangle + \langle F(Q)^2 \rangle (S(Q) - 1) \right] + B$$

where n denotes the number density of the micelles, ρ^m and ρ^s are, respectively, the scattering length densities of the micelle and the solvent and V is the volume of the micelle. $F(Q)$ is the single particle form factor and $S(Q)$ is the interparticle structure factor. B is a constant term that represents the incoherent scattering background. The single particle

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