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Reduction and aggregation of silver ions in aqueous citrate solutions

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ABSTRACT

Radiolytic reduction of Ag^+ ions and the subsequent formation of Ag clusters were studied in aqueous citrate solutions. Pulse-radiolysis studies show that the presence of citrate in the solution affects the early processes, via complexation of Ag^+ ions with the carboxyl moieties of the citrate. The ratio of citrate to Ag^+ determines the kinetic consequences of the reduction and agglomeration processes. The complexation reduces somewhat the rate of reduction by hydrated electrons. However, when all the ions are complexed to the citrate, the surface plasmon absorption band becomes broader, albeit small, but nevertheless it provides extreme stability to the formed nanoparticles.

1. Introduction

Recently an extensive research has been focused on the physical and chemical properties and potential applications of metal nanoparticles. In this respect, coinage metals such as silver and gold have been explored extensively. The main reason for this is due to the fact that they exhibit strong surface plasmon resonance absorption located in a convenient part of the spectrum ~400 nm for Ag and ~520 nm for Au [1–5]. The other significant reason is that they are relatively unreactive in nature, and the ease with which their nanoparticles can be synthesized. These properties have encouraged the researchers to explore the applications of silver and gold nanoparticles in various areas such as solar cell enhancement [6], biosensing [7], surface-enhanced Raman spectroscopy (SERS) [8,9], etc.

To stabilize the nanoparticles various surfactants, polymers, ligands, etc. have been used to prevent the aggregation [1–5]. Similarly, various methods for reducing metal ions have been reported in literature [1–6,10–13]. In this context, the citrate reduction of $HAuCl_4$ in hot water, initially developed by Turkevich et al. [11] and later refined by Frens [12] is the most commonly used method to synthesize quasi-spherical Au nanoparticles with controlled sizes in the range of 10 to 40 nm, depending on the ratio of citrate to $HAuCl_4$. Similarly, method developed by Lee and Meisel [13] is commonly used for citrate stabilized Ag nanoparticles. In these methods, citrate serves the dual purpose, as a reducing agent and a stabilizer. Very recently, the role of citrate ions in controlling the morphology of the particles has been discussed [14–19].

As mentioned above, many experiments have shown the growth of silver nanocrystals in solution using either citric acid or sodium citrate in which citric acid, (or citrate) is used as a reductant and as a stabilizer. However, the exact role of citrate ions still remains debatable. For instance, in photo illumination by visible light it is demonstrated that the citrate ions act as stabilizers [20,21] for generating monodispersed silver nanoprisms. Also, using γ-irradiation of $AgClO_4$ solutions it was shown that citrate ions do not act as reducing agents but solely as stabilizers of the colloidal particles [22]. It is also demonstrated that citrate ions influence the particle growth by complexing with positively charged Ag_2^+ dimers [23] and nanoparticles [14]. Very recently, the role of citrate in the formation of anisotropic particles is investigated [24]. It has been suggested that citrate is not the crucial component in the evolution of Ag nanoplates. Inspired by the work we have made an attempt to study the effect of rate of reduction on the formation and stability of the particles in the presence of citrate. Radiolysis is a clean method where, reduction can be carried out without adding any reductant from outside. In this study, we systematically investigate the role of citrate ions in the complexation as well as in the stabilization of silver nanoparticles. Functions of citrate ions in the formation and growth of silver clusters and eventually to the nanoparticles were probed using time resolved kinetic spectrophotometry, UV–vis spectrometry and by transmission electron microscopy (TEM) techniques. The possible mechanisms in the formation of silver nanoparticles are finally discussed. The novelty of this study is that using faster rate of reduction it is shown that the small and nearly monodisperse Ag particles can be prepared using citrate.

2. Materials and methods

2.1. Materials

Silver perchlorate (Aldrich), *tert*-butanol (Sisco, India) and sodium citrate (S.D. Fine Chemicals, India) were used as received. IOLAR grade N_2 gas (purity ≥99.99%) used for purging solutions was

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obtained from Indian Oxygen Limited. All solutions were prepared just before the experiments, wrapped with aluminum foil and kept in the dark to avoid any photochemical reactions. Water purified through a Millipore system was used.

2.2. Methods

In a typical synthesis, 1 mL of $AgClO_4$ solution (0.01 M) and 50 mL of sodium citrate solution (0.1 M) were added to the volumetric flask. The mixture turned to a light white suspension immediately, indicating the formation of a poorly soluble Ag–citrate complex (solubility 0.029 g/L at room temperature). Then, the solution was diluted to 100 mL using Millipore purified water. The complex dissolved completely and all the ratios of [citrate]/[Ag^+] were prepared accordingly.

Electron pulse radiolysis experiments were performed at the Bhabha Atomic Research Centre Laboratory with the 7 MeV electron linear accelerator [25]. Briefly, samples were irradiated in a 1 cm × 1 cm suprasil quartz cuvette kept at a distance of approximately 12 cm from the electron beam window, where, the beam diameter was approximately 1 cm. Upon generation of transient species, their absorption spectra and/or kinetics were measured using a pulsed Xe lamp as the light source. The absorption changes were measured using a monochromator-photomultiplier tube arrangement while the photomultiplier output was collected with a digital oscilloscope and then stored on a computer for further analysis. An aerated 10^{-2} M KSCN solution was used for dosimetry, and the $(SCN)_2^{\bullet -}$ radical was monitored at 475 nm. The absorbed dose per pulse was calculated [26] assuming $G\varepsilon\,[(SCN)_2^{\bullet -}] = 2.6 \times 10^{-4}$ $m^2\,J^{-1}$ at 475 nm. Absorbed doses per pulse were of the order of 6 Gy (1 Gy = 1 J kg^{-1}, for aqueous solution, 1 Gy corresponds to 1 J L^{-1}). For practical purposes, the *G*-unit rather than the SI-unit for radiation chemical yields is used. The *G*-unit denotes the number of species formed or converted per 100 eV of absorbed energy in aqueous solution; $G = 1$ corresponds to 0.1036 μM per 1 J of absorbed energy in aqueous solution [27].

The radiolysis of water produces reactive free radicals, hydrated electrons, OH radicals and H atoms, and molecular products H_2O_2 and H_2, according to the stoichiometry [28,29] as shown in reaction (1).

$$H_2O \rightsquigarrow e_{aq}^-(0.28),\ {}^\bullet OH(0.28),\ {}^\bullet H(0.06),\ H_2(0.05),\ H_2O_2(0.07),\ H_3O^+(0.27) \quad (1)$$

where, the numbers in parentheses represent the radiolytic yields, *G*-values, the quantity of species formed per Joule of energy deposited at pH 7 in μmol J^{-1}. Depending on the experimental conditions, one can get exclusively either reducing or oxidizing conditions by purging the solution either with N_2 or N_2O gas, respectively. In general, alcohols are added to the N_2-bubbled media to scavenge ${}^\bullet OH$ radicals and ${}^\bullet H$ atoms, to get the reducing conditions. Hence, to isolate hydrated electron reactions, solutions were bubbled with N_2 in the presence of *tert*-butanol as the *tert*-butanol radical produced (reaction 2) is inert and reduction proceeds via e_{aq}^- reaction only. The dose absorbed by the aqueous solution was kept low (dose = 6 Gy, total radical concentration = 1.6 μM per pulse) to minimize radical–radical reactions.

$$^\bullet OH/^\bullet H + (CH_3)_3COH \rightarrow H_2O/H_2 + {}^\bullet CH_2(CH_3)_2COH \quad (2)$$

2.3. Characterization of Ag nanoparticles

UV–vis extinction spectra were collected on Jasco-650 spectrophotometer. Particle sizes were determined by TEM using a Zeiss-Carl, Libra-120 instrument. Specimen for TEM analysis was prepared on Lacey Formvar/carbon-coated 200 mesh copper grid from Ted-Pella. The 20 μL droplet of the sol was put on the grid and put on filter paper to remove excessive solution. The TEM image was taken by air-drying of the nanoparticles.

3. Results and discussion

3.1. Effect of citrate ions

Citrate generally acts as a reducing agent for metal ions (Ag^+ and Au^{3+}) only at high temperature [11–13]. In radiolytic method, it is possible to initiate reduction of metal ions by primary species; hence, the role of other additives in the reaction mixture can be partitioned (or alienated) based on kinetic parameters. This helps in understanding the actual reaction mechanism and the role played by additives in the formation of nanoparticles. In order to investigate the role of citrate ions as a stabilizer and reductant, if any at room temperature, in the synthesis of silver nanoparticles, the molar ratio of [citrate]/[Ag^+] was varied from 5 to 15, 50 and 500 and other parameters were kept constant.

Fig. 1 shows the effect of citrate on the decay of e^-_{aq} for the reaction with Ag^+ at constant concentration. It can be seen that the decay of e_{aq}^- decreases as the concentration of citrate increases due to the complexation of Ag^+ with the citrate. To get the molar ratio of citrate/Ag^+ at which nearly complete complexation of Ag^+ occurs the variation in the bimolecular rate constant of e_{aq}^- with Ag^+ at different citrate concentration was plotted. It can be seen from Fig. 2 that nearly complete complexation occurs at molar ratio ≥500.

The equilibrium constant for Ag^+ with citrate can be determined as follows. The observed rate of formation of Ag^0 can be expressed as Eq. (1)

$$k_{obs}\left[Ag^+\right]_0 = k_f\left[Ag^+\right]_f + k_b\left[Ag^+\right]_b \quad (1)$$

where, $[Ag^+]_0$ is the initial Ag^+ concentration, k_{obs} is the observed rate constant, and subscripts f and b denote free and citrate-bound species, respectively. From Fig. 2, we obtain $k_f = 2.2 \times 10^{10}$ and $k_b = 1.1 \times 10^{10}\ M^{-1}\ s^{-1}$. The fraction of bound Ag^+ is given by

$$f = \left[Ag^+\right]_b / \left[Ag^+\right]_0 \quad (2)$$

which can be rearranged to give

$$f = (k_{obs} - k_f)/(k_b - k_f). \quad (3)$$

Assuming a simple equilibrium for binding Ag^+ to citrate, the equilibrium constant can be estimated from the results in Fig. 2 and using Eq. (4).

$$1/f = 1 + 1/\{K[\text{citrate}]\} \quad (4)$$

These results shown in Fig. 2 agree well with Eq. (4). The slope of the line yields $K = 50\ M^{-1}$. The binding of Ag^+ with citrate was further

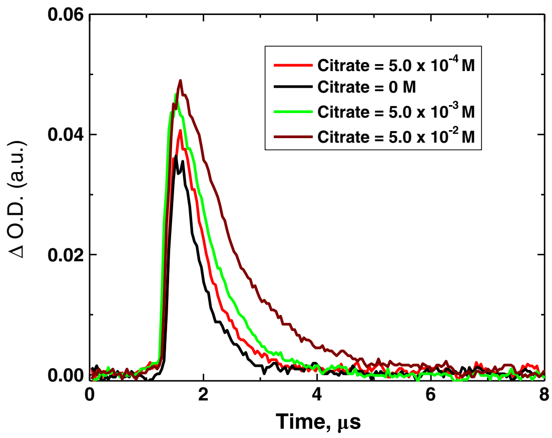

Fig. 1. Decay traces of e^-_{aq} in N_2-bubbled aqueous solution containing 1×10^{-4} M $AgClO_4$, 0.1 M tert-butanol and various concentrations of citrate.