An Improved Approach for Synthesis of Positively Charged Silver Nanoparticles

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Positively charged silver nanoparticles capped by cetyltrimethyl ammonium bromide (CTAB) are prepared in aqueous solution. The structure of capping agents on Ag particles is systematically characterized by Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), and thermal gravimetric analysis (TGA). It suggests that CTAB molecules form a bilayer shell on Ag surface with a 1:5 rough ratio of inner/outer molecules.

In the past decades, nanoparticles (NPs) have been the focus of intense research activities not only because of its unusual behavior compared to the bulk materials but also for its wide applications in the practical world.[1] Silver NPs are of great interest in photography, catalysis, electrode, surface enhanced Raman spectroscopy, and chemical analysis.[2] For their synthesis, many surfactants have been utilized as either stabilizers or templates. They decrease the surface energy, control the growth and shape of the particles, and act against aggregation. Among them, anionic surfactants are widely used to prepare negatively charged NPs.[3] However, only few researchers use cationic surfactants to get positively charged silver particles, probably because of undesired precipitate of silver halides as halogens are often employed as counterions. Yonezawa et al. utilizes bis[2-(11-trimethylammonioundecanoylamino)ethyl]disulfide dibromide, a complex and specially designed cationic surfactant, to produce monodisperse positively charged silver NPs.[4] Though the resulted particles keep stable, it can not be a general manner because of the unavailability of such capping agent. For more extensive application, a common cationic surfactant CTAB, has been used as a stabilizer to fabricate positively charged silver particles by Pal et al., but the formation of silver bromide will affect the product purity, and result in many aggregates, with a wide size distribution between 25 and 75 nm.[5] Recently, Chen et al. reported a seed-mediated growth of silver nanodisks in an aqueous CTAB solution, in which silver NPs capped by sodium citrate are used as seeds, but AgBr is also found being formed on silver surface.[6] To explore a more effective way of producing Ag NPs with positive charge, we adopt a classical method here to change silver nitrate to diamminesilver ion to avoid AgBr formation. Such produced Ag NPs are steady and monodisperse for more than one month, owing to the dense shell of CTAB.

In a typical experiment, an aqueous solution containing 2×10^{-3} M $AgNO_3$ and 0.4 M NH_3 is prepared firstly, then CTAB is added to a concentration of 5×10^{-4} M. Another solution comprises 8×10^{-3} M $NaBH_4$ and 5×10^{-4} M CTAB. Yellow silver colloidal dispersion is obtained by mixing these two solutions of equal volume drop by drop with vigorously stirring at ice-cold temperature for 4 h. The mixture was heated to drive out remanent NH_3 and decompose the excess $NaBH_4$. By transferring the solution into an U-shaped tube and applying an electric field, we observe the color deepening near the cathode, which indicates that NPs are positively charged.

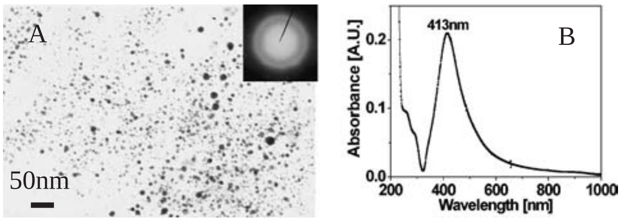

Figure 1. TEM image (A) and UV–vis absorption spectrum (B) of Ag nanoparticles hydrosols. The inset in (A) is ED pattern of NPs.

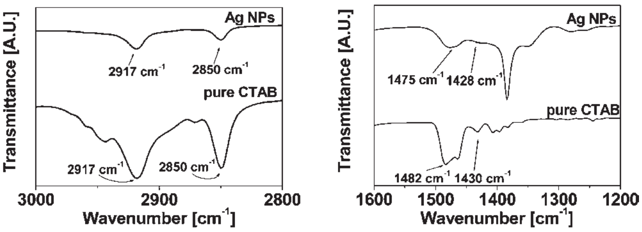

Figure 2. FTIR spectra of CTAB and Ag NPs.

Figure 1 shows the transmission electron microscopy (TEM) image, electron diffraction (ED) pattern (inset), and UV–vis spectrum of silver NPs. The TEM image indicates monodisperse but not aggregated particles, which are in amorphous state with little face-centered cubic (fcc) crystal lattice as confirmed by ED pattern. The well-defined surface plasmon band with a maximum absorbance at 413 nm also implicates a monodisperse Ag NPs sol. The measured average particle size is 13.5 ± 3.3 nm.

To study the capping effect of CTAB, FTIR spectra of Ag NPs and pure CTAB are recorded as shown in Figure 2. The symmetric and asymmetric CH_2 stretching vibrations of pure CTAB lie at 2850 and 2917 cm^{-1}, as well as those of silver NPs. The same CH_2 stretching vibrations indicate equivalent gauche defects for pure CTAB molecules and those adsorbed on Ag NPs.[7] The peaks at 1482 and 1430 cm^{-1} for pure CTAB sample are attributed to asymmetric and symmetric C–H scissoring vibrations of CH_3–N^+ moiety. They change to 1475 and 1428 cm^{-1} for silver NPs, exhibiting Ag cluster's effect on CH_3–N^+ vibration. The characteristic [C–H···metal] vibration, however, hasn't been observed, indicating the absence of C–H binding to metal surface.[8] These results suggest that CTAB molecules are bound to silver cluster with their headgroups, and the broad peak at 1475 cm^{-1} suggests that there may also be some unbound CTAB molecules in NPs sample.

To further characterize the structure of capping molecules on silver surface, DSC and TGA measurements are conducted under the protection by nitrogen, as shown in Figures 3 and 4.

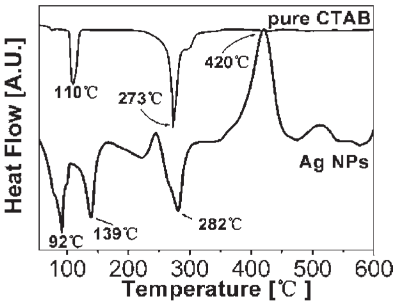

Figure 3. DSC curves of CTAB and Ag NPs.

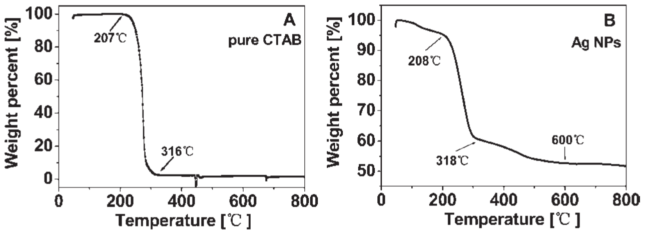

Figure 4. TGA data of pure CTAB (A) and Ag NPs (B).

The DSC curve of pure CTAB has two endothermic peaks at 110 and 273 °C. However, the corresponding TGA curve exhibits only one weight-loss process of ca. 100% around 273 °C in Figure 4a, reflecting the thermal decomposition of CTAB molecules. The plot for Ag NPs displays three endothermic peaks at 92, 139, and 282 °C, and an exothermic peak around 420 °C in Figure 3. The latter is considered as amorphous-to-crystalline transition of Ag clusters, and this transition should result in no weight change.[9] Corresponding TGA curve exhibits three weight losses of 5, 35, and 7% at 100–208, 208–318, and 318–600 °C, respectively (Figure 4b). The last two weight-loss steps in the temperature range of 208 to 600 °C, which are resulted from decomposition of CTAB, reflect two different status of CTAB capped on Ag clusters, suggesting the formation of CTAB bilayer on the metal surface.

It is noted that, however, the sharp DSC peaks for pure CTAB at 110 °C and for Ag NPs at 92 °C are not accompanied by any weight loss. In our opinion, these changes correspond to the melting of ordered regions of hydrocarbon chains in free CTAB and CTAB bilayer, respectively.[10] For the peak at 139 °C, which is concomitant by a less than 5% weight loss, it is believed to be desorption of moisture entrapped between Ag clusters and CTAB bilayer. In the range from 208 to 600 °C, the first sharp step of 35% weight-loss arises within 208–318 °C, and is considered as decomposition of CTAB outer layer. While the second step of 7% weight-loss in 318–600 °C is attributed to CTAB inner monolayer decomposition.[10,11] The ratio of molecules in inner and outer layers is thus roughly estimated as 1:5 by comparing the amount of the weight-losses from these two steps. On the basis of this measured results, the total amount of CTAB molecules both in adsorbed bilayers and in free state, is approximately matchable to the calculated value, according to Ag clusters' size and CTAB headgroup area. Therefore, the capping models of CTAB shell on Ag NP in solution and dry status are established and shown in Figure 5.

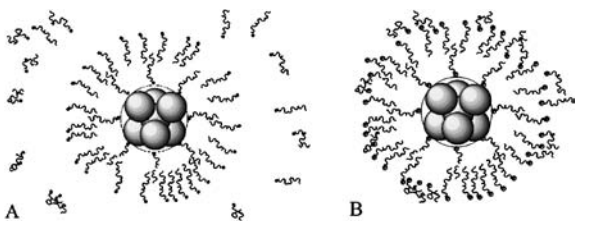

Figure 5. The schematic model for Ag NPs capped by CTAB molecules in the solution (A) and dry sample (B) (in TGA process).

In conclusion, CTAB molecules adsorb on Ag clusters' surface through their headgroups, and orient their tail groups toward solution. Further adsorption results in an increasing number of CTAB molecules to form a bilayer on Ag clusters' surface, with headgroups facing the solution.[11] Such a bilayer capping shell makes Ag NPs positively charged and much stable in aqueous solution. This method, utilizing both complexing and capping effect to prepare Ag NPs, may be extended to other monodisperse NPs' preparation.

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