

Solvothermal synthesis of silver nanoparticles from thiolates

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Abstract

A new solvothermal method for the synthesis of thiol-protected silver nanoparticles starting from silver thiolates is reported. The method has been tried with thiols of different chain length, such as octane and octadecane thiols, and the particle size was found to be nearly the same for both molecules. The synthesis was dependent on heating conditions and the best results were obtained when the temperature was between 180 and 200 °C. Addition of complexation agents such as acetyl acetone or triethylamine to the solvent did not change the product distribution significantly.

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1. Introduction

Since the preparation of alkanethiolate-stabilized gold nanocrystals [1], there have been intense research efforts on various aspects of soluble metal particles [2] and their aggregates. Important advantages of this thiol protection methodology are the narrow size distribution of the particles and the synthetic flexibility the method offers to make variously functionalized materials. Several other methodologies of solution chemistry have been reported pertaining to the synthesis of nanocrystal noble metal particles, the most recent being the reduction by amines [3]. In all these solution chemistry approaches, the procedure is often elaborate, involving postsynthesis steps such as solvent-selective precipitation and chromatography, if one is interested in a narrow size distribution. The synthetic methods involve reduction of an ionic salt in an appropriate medium in the presence of a surfactant [1]. The procedure is conducted in an organic medium, necessitating the use of a phase transfer reagent. These procedures are time consuming and one has to use reducing agents and phase-transfer agents, which are expensive. We have been thinking of a simple, one-step method avoiding the use of expensive chemicals that are not part of the final product. Many of the metals forming clusters make stable thiolates, and we thought of using these directly for

the synthesis. This approach finally took us to solvothermal synthesis. Although the objectives stated above were not fully achieved, and additional efforts are needed to realize them, a set of studies on silver thiolates [4–9] is now complete, which we are reporting here.

2. Materials and methods

Octadecane and octane thiols were purchased from Aldrich and were used without purification. Silver nitrate was purchased from Qualigens Fine Chemicals, India. The solvents used were all obtained from Ranbaxy chemicals, India, and were used after distillation.

Silver thiolate was prepared using a two-phase method [4]. A toluene solution of alkane thiol was added drop-wise to a vigorously stirred aqueous solution of silver nitrate. The stirring was continued for about 3 h and the thiolate formed was collected by centrifugation and washed with toluene, water, and ethanol, in that order, and vacuum dried. The aqueous solution was tested for the absence of Ag^+ ions, which was confirmed by the addition of Cl^- ions. About 0.3 g of the prepared silver thiolate was taken in a Teflon-coated hydrothermal bomb made of 316 stainless steel and about 5 ml of toluene was added. There was no free airspace left in the bomb (this is important). After being tightened, the bomb was heated overnight at 200 °C and gradually cooled, and the contents were extracted by sonication in toluene. About 10% by weight of the material was toluene-soluble,

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giving a brown solution. The residue could be digested with acetone to extract more material (about 30%). Both the fractions were essentially the same.

UV/Vis spectra were recorded with a Perkin–Elmer Lambda 25 spectrometer and FT-IR spectra were recorded with a Perkin–Elmer Spectrum One instrument using 5% (by weight) KBr pellets. Drop-cast films on carbon-coated grids were imaged by transmission electron microscopy (Philips CM12, 120 keV as well as JEOL 300 keV). Powder X-ray diffraction data were collected with a Shimadzu XD-D1 diffractometer with Cu $K\alpha$ radiation (30 kV, 20 mA).

3. Results and discussion

Fig. 1 shows the UV/Vis absorption spectra of the toluene-soluble reaction product of silver octanethiolate and silver dodecanethiolate obtained at 200 °C. The spectra show the characteristic surface plasmon excitation feature of silver, which occurs around 420 nm.

Both samples show this feature at 423 nm, which is slightly red shifted from the normal value and shows a large background. The product obtained contains two kinds of particles, one larger and another smaller in dimension (which is clear from the TEM image). The larger particles are agglomerated, while the small particles are arranged in an organized manner. The background is attributed to the agglomeration of the particles [10]. The inset in Fig. 1 shows the peak obtained for silver octanethiol at a reaction temperature of 190 °C; all three curves are almost the same, suggesting that the method holds good for temperatures between 180 and 200 °C for different chain-length thiols. The amount of particles extracted varies with the preparative conditions and a quantitative recovery of silver in the form of clusters was not achieved. Total dissolvable silver particles was 40% of the original thiolate. Selective precipitation by increasing the polarity of the solvent could remove most of the large

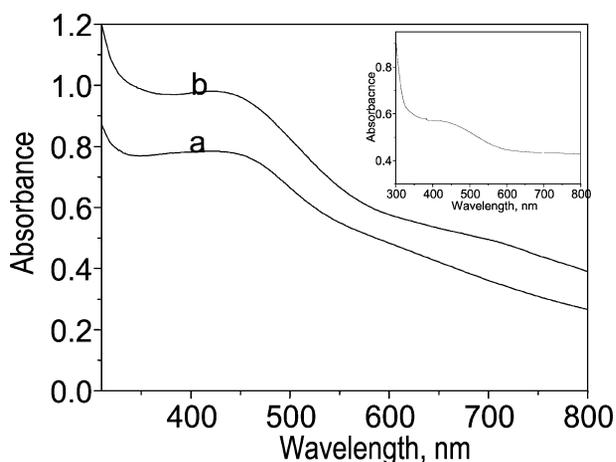


Fig. 1. UV/Vis absorption spectrum of (a) Ag-octanethiolate and (b) Ag-dodecanethiolate in toluene at 200 °C. Inset shows the absorption spectrum of Ag-octanethiolate at 190 °C in toluene.

particles [11]. Selective precipitation was done by adding different solvents such as acetone to the toluene solution of the nanoparticles.

The particles could be dried and resuspended repeatedly. The temperature stability was poor, unlike the thiolate-protected clusters made by the two-phase synthesis route [12]. We tried to synthesize nanoparticles having medium size and monodispersity by the same method at different temperatures between 180 and 200 °C. The product obtained was small in size from 180 to 195 °C and those obtained at 200 °C was a mixture of both small- and large-sized particles. Above 200 °C we obtained very large particles, which do not come in the nano regime. We believe that the particle surface is contaminated with minor impurities not detected by spectroscopic analysis, which reduced thermal stability.

As a result of the presence of the large particles, the XRD pattern of the as-prepared sample was narrow in width. XRD showed all the standard features of bulk silver and none of the features of thiolates, which show characteristic $(0k0)$ reflections [8]. Absence of peaks in the small angle region suggests that there is no superlattice formation in the bulk; but short-range periodicity is clear from the TEM image (see below).

In order to check the nature of the passivating layer, an infrared spectrum of the cluster solid was taken. The spectrum shows characteristic hydrocarbon structures and is identical to a thiolate-protected silver cluster, which we have been investigating in the laboratory for some time [12]. The spectrum (Fig. 2) shows all the characteristic features of an organized hydrocarbon chain, with pronounced progression bands and characteristic features occurring at the solid-state positions [12]. The C–H stretching region shows characteristic features at 2849 and 2916 cm^{-1} corresponding to symmetric and antisymmetric modes. Apart from this the spectrum also shows two peaks, at 600 and 718 cm^{-1} , due to C–S stretching; the latter is also mixed up with the methyl-rocking mode.

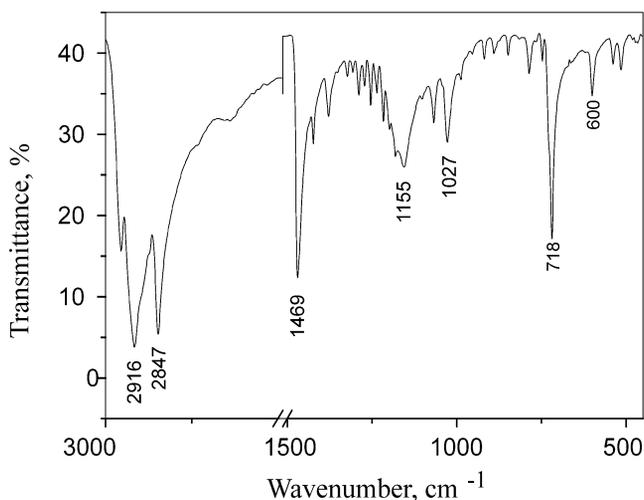


Fig. 2. Infrared spectrum of the residue. Important features are marked. The featureless 2500 to 1500 cm^{-1} region is not shown.

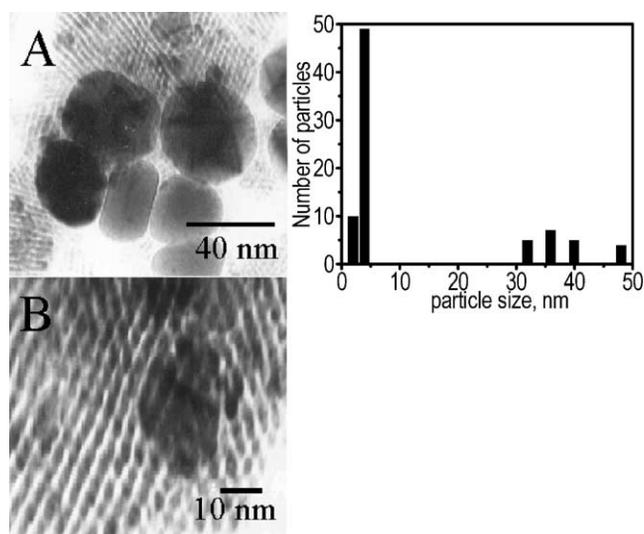


Fig. 3. Transmission electron micrograph of the particles, drop-cast from solution. (A) A larger area image with two kinds of particles and (B) the self-assembly of the smaller clusters. On the right is the histogram showing the size distribution of the nanoparticles obtained at 200 °C.

A TEM image of the drop-cast solution is shown in Fig. 3. A large area image is shown in Fig. 3A and an expanded view of one of the regions is shown in Fig. 3B. Two size distributions are seen in the figure: the larger particles are of nonuniform size and shape, while the smaller particles have a narrow size distribution. The latter particles form regular patterns on the grid, indicating the fact that their size distribution is uniform; an area is expanded in Fig. 3B, where this pattern is clearly evident. This tendency for aggregation may be manifested in the UV/Vis spectrum (Fig. 1) in the form of interparticle interactions [13–15]. The size of the smaller particles observed is 4 ± 0.5 nm, and the interparticle length is 1.4 ± 0.2 nm; this is smaller than twice the octanethiol chain length, indicating interdigitation of the chains [16].

Isolated particles were also imaged by a higher resolution instrument (JEOL 300 keV). An image is shown in Fig. 4 and the particles have well-defined morphology and average diameter is 4 ± 0.7 nm. Here again the particle dimension is highly uniform. These two TEMs (Figs. 3 and 4) are from two separate preparations, suggesting that the method is reproducible. While particles of Fig. 3 were prepared at 200 °C, those of Fig. 4 were prepared at 180 °C. These two samples were prepared by taking the same amount of thiolate and heating for the same time period at two different temperatures. A histogram showing the particle size distributions is shown together with the TEM image. It shows both small-sized and large-sized particles with small particles in large numbers. These two TEM images clearly show that the method is sensitive to the temperature conditions. The best results were obtained in the temperature range of 180–200 °C. Below this temperature range, no clusters were observed. At higher temperatures (>200 °C), only large particles were seen. Larger thiolate concentrations also led to the formation of larger clusters. Addition of complexation

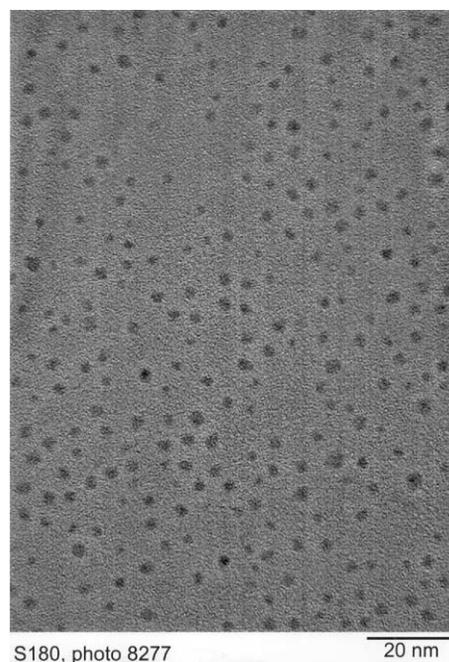


Fig. 4. TEM image of the isolated particles.

agents such as acetyl acetone or triethylamine to the solvent (expected to reduce the growth rate and thereby result in a more uniform size) did not change the product distribution very much.

4. Summary

We have reported a novel method for the synthesis of silver nanoparticles by the solvothermal route, which is inexpensive and requires only simple precursors. The nanoparticles were characterized by UV/Vis, IR, and TEM. UV/Vis spectra show the characteristic plasmon absorption peak for the silver clusters, with a large background suggesting the presence of two kinds of particles, which was confirmed by TEM. While the larger particles are nonuniform in size, the smaller particles are uniform and they form short-range arrays on the grid. The signature of aggregation is evident in the solution state as well. Two different chain-length thiols gave similar data. The method was found to be very much temperature sensitive, giving the best results between 180 and 200 °C. Above this temperature, no clusters were found. Alkyl chains on the surface of these particles are well organized with solid-like features.

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