Size-controlled and large-scale synthesis of organic-soluble Ag nanocrystals in water and their formation mechanism

Yu-yuan SHI, Bin SUN, Zhe ZHOU, Yong-tao WU, Mei-fang ZHU

State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Material Science and Engineering, Donghua University, Shanghai 201620, China

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Abstract: Organic-soluble Ag nanocrystals (NCs) with tunable sizes in the range from 5.4 to 22.1 nm were synthesized by a facile, reproducible and easily scaled up route using water as solvent in the presence of oleic acid and an alkylamine. The synthetic Ag NCs exhibits excellent hydrophobicity and can be well re-dispersed in various non- or weak-polar media. The tunable sizes of the Ag NCs were achieved by simply adjusting the initial precursor AgNO₃ concentration. Large-scale synthesis of the Ag NCs was realized at a high AgNO₃ concentration (0.4 mol/L). As much as 16.2 g highly uniform organic-soluble Ag NCs with 5 nm average diameter can be readily synthesized at low cost in a single reaction only using 400 mL water as solvent, which is adaptable to the industrial scale production. The structure of the obtained Ag NCs was investigated in detail by X-ray diffractometry, transmission electron microscopy, Fourier transform infrared and thermal gravimetric analysis measurements. The results reveal that the surface of the organic-soluble Ag NCs is coated with the monolayer surfactants consisting of oleic acid and the alkylamine. In addition, on the basis of the sufficient evidences, a proposed mechanism based on the “bilayer surfactant-controlled reaction” successfully demonstrates the formation of high quality organic-soluble Ag NCs in the aqueous solution.

Key words: organic-soluble Ag nanocrystals; large-scale; size-controlled; synthesis; formation mechanism

1 Introduction

The development of metal nanocrystals (NCs) has been intensively pursued, not only for their fundamental scientific interest, but also for various technological applications [1]. Ag NCs display unique properties, such as chemical stability, excellent electrical and thermal conductivity, catalytic activity, antibacterial effects, surface-enhanced Raman scattering (SERS) and nonlinear optical behavior [2−6]. These special properties have led to tremendous applications of Ag NCs in the areas like catalysis [7], antimicrobial products [8], optical sensors [9], printed electronics [10, 11], SERS substrates [12] and nanofluids for heat transfer [13, 14].

Oleic acid, a fatty acid containing a head of carboxyl group and a C₁₇ alkyl chain tail is commonly employed for aiding the synthesis of various organic-soluble metal NCs such as Ag [15, 16], Fe₃O₄ [1, 15], Cu [17] and Pt [18], and even controlling the NCs shapes owing to the strong interaction between the carboxyl group and metal NCs. The synthesis of the organic-soluble Ag NCs using oleic acid as capping agent has attract much interest owing to their versatility in terms of applications. For example, the organic-soluble Ag NCs capped with oleic acid can be used as a catalyst for the organic reactions in the non-polar media [19], exhibit outstanding antibacterial activity [20] and possess an interesting surface mediated phase transfer property due to their changeable surface properties from hydrophobic to hydrophilic [21]. Besides, they also have been found to be a good oil-based nanofluid for heat transfer [14] and an excellent candidate as low-cost high-conductivity elements for printable Ohmic contacts for high-mobility organic thin-film transistors (OTFT) due to their excellent electrical conductivity (2−4×10⁴ S/cm) [10].

A variety of methods to produce organic-soluble Ag NCs capped with oleic acid have been reported in the literatures, such as the thermolysis of suitable precursors in the presence of oleic acid [6, 22], chemical reduction [10], photochemical synthesis [20], green chemical
synthesis [23], ionic liquid method [24], and solvent exchange method. Unfortunately, most of the methods reported so far commonly require low precursor concentrations, high temperatures, long reaction time, organic solvents (because oleic acid is completely insoluble in water, resulting in the difficulty of forming the homogenous system, i.e., single phase system), special chemicals such as catalyst, expensive precursors rather than cheap Ag NO₃ (due to its insolubility in organic solvents) or toxic chemicals such as phenyl hydrazine. For instance, LIN et al [22] have described that the thermal reduction of silver trifluoroacetate (expensive precursor) in isooamy ether (high boil point organic solvent) in the presence of oleic acid produced monodisperse Ag NCs with diameter in the range of 7–11 nm at 160 °C. WU et al [10] developed a synthesis using an organic hydrazine to convert silver trifluoroacetate to oleic acid-stabilized silver nanoparticles in about 60% yield in tetrahydrofuran (THF) at 60 °C. It is undoubtedly that the large-scale synthesis of organic-soluble Ag NCs capped with oleic acid is indispensable to their practical applications in industry. However, those rigorous conditions extremely restrict extending the processes for the large-scale synthesis of organic-soluble Ag NCs coated with oleic acid. Therefore, up to date, it is still a great challenge to produce high quality (i.e., size-controllable and highly uniform) organic-soluble Ag NCs capped with oleic acid using a simple cost-effective method that can yield reproducible results on a large scale.

In this work, high quality organic-soluble Ag NCs capped with oleic acid have been successfully synthesized at low cost using water as solvent in the presence of oleic acid and an alkylamine. The structure and properties of the synthesized Ag NCs were investigated, and on the basis of the sufficient evidences, a mechanism based on the “bilayer surfactant-controlled reaction” was proposed to describe the formation of organic-soluble Ag NCs capped with oleic acid in our synthesis.

2 Experimental

2.1 Materials

Silver nitrate was supplied by Shanghai Chemical Corporation, China. Oleic acid, n-propylamine, ascorbic acid, and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. All the reagents employed in this work were of analytical grade and were used as received. Aqueous solutions were prepared using deionized water.

2.2 Synthesis of organic-soluble Ag NCs

In a typical procedure, a mixture of oleic acid and n-propylamine along with 40 mL 0.1 mol/L AgNO₃ aqueous solution was added into a three-neck round-bottom flask equipped with a condenser and a stirring bar, and then heated to 50 °C using a water bath under continuous stirring at a speed of 400 r/min until the solution became transparent. Both oleic acid and n-propylamine were in a largely stoichiometric excess with respect to AgNO₃. The pH value of the solution was measured to be 11 with a pH meter. Ascorbic acid solution was quickly added to the resulting solution, and the reaction was allowed to proceed for 2 h to produce the colloidal Ag NCs in the original reaction solution before cooling down to room temperature. Subsequently, ethanol was added to the original reaction solution to precipitate the crude Ag NCs. The crude Ag NCs were isolated by filtration, washed twice with acetone, and vacuum-dried at room temperature to afford the final products in the form of blue-gray powders.

A large-scale synthesis of the Ag NCs was also carried out at a high AgNO₃ concentration. In this case, 400 mL 0.4 mol/L AgNO₃ aqueous solution along with proper amounts of oleic acid and n-propylamine were used. The synthetic procedures were the same as described above. The resulted powder product with about 80% Ag content is about 16.2 g in about 75% yield.

2.3 Characterization of Ag NCs

The structure, size and morphology of the Ag NCs were investigated by a JEOL−2100F transmitting electron microscope (TEM). All TEM samples were prepared by placing a drop of the silver colloidal dispersion in n-heptane onto an amorphous carbon coated copper grid. The particle size distribution was analyzed based on TEM micrographs using Image-Pro Plus 6.0 software, from which the average size and standard deviation of Ag NCs were also obtained. X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max−2550 PC wide-angle X-ray diffractometer with monochromatized Cu Kα radiation (λ=1.540 5 Å). The Fourier transform infrared (FTIR) spectra were collected on a Fourier transform infrared spectrophotometer (NEXUS−670) in the wavenumber range 500−4000 cm⁻¹. The samples were prepared in the form of pellets together with KBr. Thermal gravimetric analysis (TGA) was performed on a thermogravimetric analyzer (NC88-TG 209 F1 Iris) at heating rate of 10 °C/min in N₂.

3 Results and discussion

3.1 Size-controlled synthesis of organic-soluble Ag NCs

Narrowly distributed surfactant-capped Ag NCs with tunable sizes were synthesized by the reduction of precursor AgNO₃ with ascorbic acid in the presence of oleic acid and n-propylamine in aqueous solution. Although oleic acid is fully insoluble in water, the
resulting mixture forms a homogenous and light yellowish solution. This is due to the formation of the oleic acid-amine (OA-RNH$_3^+$) complex with better hydrophilicity by reacting oleic acid with the amine, as described in Fig. 1. The Ag NCs could precipitate out from the original reaction solution by adding ethanol to yield the final products in the form of powders after filtering and vacuum-drying, which is greatly beneficial to storage and application. The as-synthesized Ag NCs exhibit excellent hydrophobicity and could be well re-dispersed in various non- or weak-polar organic solvents, such as cyclohexane, n-heptane, hexane, toluene, chloroform, THF, etc., even after prolonged storage in air. Figure 2 shows the photographs of the as-synthesized Ag NCs re-dispersed in cyclohexane (samples a–d) and a mixture (e) of cyclohexane and water (1:1 by volume). Samples a–d in Figure 2 with different contents of Ag NCs show stable and homogeneous dispersions, and display different color from light yellow to dark-brown with increasing concentration of Ag NCs due to the light absorption and scattering in the visible region based on the plasmon resonance [25]. As clearly shown in Fig. 2(e), the obtained Ag NCs are completely dispersed in the cyclohexane (upper) rather than in water (bottom) in the mixture of cyclohexane and water, suggesting that the synthesized Ag NCs are strongly hydrophobic. The long hydrocarbon chains of the surfactant capped on the Ag NCs are responsible for the hydrophobicity. The size-controlled synthesis of the organic-soluble Ag NCs was achieved by simply adjusting the initial precursor AgNO$_3$ concentrations instead of utilizing the complicated changes of the proportions among oleic acid, alkylamine and AgNO$_3$.

The TEM images recorded for the Ag NCs synthesized by varying precursor AgNO$_3$ concentration from 0.02 to 0.2 mol/L are shown in Fig. 3. From Fig. 3, it can be seen that the Ag NCs in all samples are well-defined spherical particles and narrowly distribute, and each NCs is well separated from the neighbour NCs, indicating that the Ag NCs are well surface passivated by stabilization action of oleic acid and alkylamine and possessed excellent organic solvent dispersity. The self-assembled Ag NCs with hexagonal networks can also be observed, as shown in Fig. 3(f), indicative of their high uniformity in size [6, 22]. It is noted that the small Ag NCs (<10 nm) are obtained at the high precursor AgNO$_3$ concentrations (>0.1 mol/L). Plot of the average size and standard deviation of the as-synthesized Ag NCs against precursor AgNO$_3$ concentration is shown in Fig. 4. The average size decreases dramatically from 22.1 to 8.7 nm with the increase of AgNO$_3$ concentration from 0.02 to 0.1 mol/L, and then slightly decreases from 8.7 to 5.4 nm with AgNO$_3$ concentration further increasing to 0.2 mol/L. Additionally, as the precursor concentration increases, the size distribution becomes narrower, and the obtained Ag NCs at 0.2 mol/L AgNO$_3$ concentration are highly uniform. Hence, it is evident that simply changing the precursor AgNO$_3$ concentration is favorable for the size and size distribution control of the organic-soluble Ag NCs.

3.2 Large-scale synthesis and structure characterization of organic-soluble Ag NCs

The feasibility of large-scale synthesis of the organic-soluble Ag NCs was examined at a high AgNO$_3$ concentration (0.4 mol/L), and as much as 16.2 g highly uniform Ag NCs with 5 nm average diameter can be readily synthesized in about 75% yield in a single reaction only using 400 mL water as solvent. The structure of the as-synthesized Ag NCs in large-scale was characterized by XRD, HRTEM, FTIR and TGA measurements. Figure 5 shows the XRD pattern of the obtained Ag NCs in large-scale. All the diffraction peaks are clearly distinguished and broadened in Fig. 5. There are four diffraction peaks with 2θ values of about 38.1°, 42.1°, 64.5°, and 77.5° in agreement with the literature [21] values for a face-centered cubic (FCC) crystal structure corresponding to (111), (200), (220), and (311) lattice planes, respectively. It is well known that the broadness of the diffraction peaks in the XRD patterns reflects the size of the Ag NCs, and that smaller NCs tend to show broader XRD patterns. Calculated over the (111) reflection using the classical Debye-Scherrer
Fig. 3 TEM images of Ag NCs synthesized at various precursor AgNO$_3$ concentrations: (a) 0.02 mol/L; (b) 0.05 mol/L; (c) 0.10 mol/L; (d) 0.15 mol/L; (e, f) 0.20 mol/L.

Fig. 4 Variation of size and size distribution with AgNO$_3$ concentration for as-synthesized Ag NCs
equation, the average diameter of the Ag NCs was calculated as 4.8 nm from the width of the diffraction peak.

The TEM image and the size distribution histogram (inset) of the as-synthesized Ag NCs in large-scale are shown in Fig. 6(a). As shown in Fig. 6(a), the Ag NCs synthesized in large-scale are highly uniform, with an average size of approximately $(5.0\pm1.5)$ nm in diameter, which was nearly consistent with the result from XRD (4.8 nm). High-resolution transmission electron microscopy (HRTEM) measurement was also used in order to further investigate the crystal structure of the Ag NCs, which gives a fringe spacing (0.24 nm) that agrees well with the spacing (0.236 nm) of the (111) lattice planes of silver crystals calculated from the XRD pattern using the Bragg’s equation. The corresponding fast Fourier transform (FFT) of the HRTEM image indicates a set of six-fold rotational symmetry spots (inset in Fig. 6(b)), suggesting that the basal plane of the Ag NCs is actually presented by (111) lattice planes. In addition, it is worth noting that the Ag NCs are twinned or penta-twinned crystals, which is indicated by the lattice spacings and angles between crossed lattices in the HRTEM image.

Figure 7 shows the FT-IR spectra of the pure oleic acid and the organic-soluble Ag NCs capped with surfactants. For the typical IR spectrum of the pure oleic acid, the broad feature between 3500 and 2500 cm$^{-1}$ was undoubtedly due to the O—H stretching of the carboxylic acid and the three IR bands at 3005, 2925 and 2855 cm$^{-1}$, which were superimposed on the O—H stretching, were attributed, respectively, to the C—H stretching adjacent to a double bond, the asymmetric C—H stretching and the symmetric C—H stretching of CH$_2$ groups [6, 21, 26]. The intense peak at 1710 cm$^{-1}$ was derived from the existence of the C=O stretching and the band at 1285 cm$^{-1}$ exhibited the presence of the C—O stretching [26, 27]. The O—H in-plane and out-of-plane bands appeared at 1462 and 937 cm$^{-1}$, respectively. In the IR spectrum of the surfactant-capped Ag NCs, the asymmetric CH$_2$ stretching and the symmetric CH$_2$ stretching shifting to 2919 and 2850 cm$^{-1}$, respectively, were observed. The surfactant molecules in the adsorbed state were subject to the field of the solid surface. As a result, the characteristic bands shifted to a lower frequency region [28] and indicate that the hydrocarbon chains in the monolayer surrounding the Ag NCs are in a close-packed, crystalline state [26]. It is worth noting that the C=O stretching band of the carboxyl group (—COOH), which is present at 1710 cm$^{-1}$ in the IR spectrum of pure liquid oleic acid and the characteristic band of the outerlayer oleic acid in the bilayer oleic acid-coated structure, is absent in the spectrum of the surfactant-capped Ag NCs, indicating the monolayer surfactant-capped structure of the synthesized Ag NCs. Instead, a new band at 1561 cm$^{-1}$ observed in the IR spectrum of the Ag NCs should be attributed to the asymmetric —COO$^-$ stretching of the acid-base complex (—COO$^-$/NH$_3^+$) which was formed by reacting oleic acid with the alkylamine during the synthesis [6]; the bands at about 3450, and 1631 cm$^{-1}$ were attributed to the NH stretching and the NH$_2$ scissoring mode [6, 29, 30], and the intense band at 1101 cm$^{-1}$ were ascribed to C—N stretching [31]. Thus, on the basis of the comprehensive analysis above, it is reasonable to consider that the synthesized Ag NCs were capped by the monolayer surfactants consisting of oleic acid and the
amine (i.e., OA-RNH$_3^+$ complex).

TGA measurement could also be used to characterize the existence of whether bilayer or monolayer surfactant on the fatty acid-capped metal NCs surfaces as a proof. For monolayer surfactant-coated NCs, the mass profile only exhibits a single-step decrease till constant mass. While, for bilayer surfactant-coated NCs, the heating curves are characterized by mass losses with two distinct steps, revealing a different pattern from that observed for the monolayer surfactant-coated NCs. To further examine the chemical structure of the synthesized Ag NCs, TGA measurement was carried out on the Ag NCs, as shown in Fig. 8. Only a one-step mass loss process was observed mainly in the temperature range from 200–400 °C corresponding to the decomposition of the monolayer oleic acid (or OA-RNH$_3^+$ complex) capped on the Ag NCs. In addition, the metal Ag content of the as-synthesized Ag NCs obtained from the TGA data is about 80%.

### 3.3 Formation mechanism of organic-soluble Ag NCs in aqueous solution

As discussed above, the developed protocol was confirmed to be a facile, size-controlled, reproducible and easily scaled up route suitable for large-scale synthesis of organic-soluble Ag NCs capped with oleic acid (or OA-RNH$_3^+$ complex). A mechanism based on the “bilayer surfactant-controlled reaction” was proposed to describe the formation of the narrowly distributed Ag NCs with the surfactants, as illustrated schematically in Fig. 9.

The intrinsic property of oleic acid is fully insoluble in water; however, it has been reported the conversion of oleic acid into sodium oleate by the interaction between oleic acid and sodium hydroxide resulted in forming a two-phase oil/water system (i.e., normal microemulsion) [32, 33]. In our case, we consider the similar principle. The transparent oil-in-water microemulsion formed after oleic acid together with the amine were added, which was due to the transform of the carboxyl group in oleic acid from $-\text{COOH}$ to $-\text{COO}^-$ by reacting oleic acid with the amine. The mean size of the micelles in the normal microemulsion was about 3 nm, detected by a particle size & zeta potential analyzer (Nano ZS). When silver cations existed in the solution, they were absorbed around the oil core due to the electrostatic attraction between Ag$^+$ and OA-RNH$_3^+$ complex [34], as illustrated in Fig. 9(a). As the reductant ascorbic acid was added, the Ag$^+$ was reduced by ascorbic acid to form Ag atom. The initially formed silver atoms self-nucleated to form a number of seeds at the beginning of the reaction, and the crystals then continued to grow by diffusion-driven deposition of silver atoms. During this process, the bound OA-RNH$_3^+$ complexes were still adsorbed on the crystal seeds or ripened Ag NCs due to the strong covalent interaction between the OA-RNH$_3^+$ complex and the Ag atom. Simultaneously, the free OA-RNH$_3^+$ complexes and the OA-RNH$_3^+$ complexes binding to Ag atoms interpenetrated through the hydrophobic/hydrophobic interaction between the long alkyl chains to form the structured surfactant bilayer on the surface of Ag NCs [8, 35], as shown in Fig. 9(b), which helps to control the size of the Ag NCs and stabilize the colloidal Ag NCs in the aqueous solution. The bilayer surfactant-capped structure could not only make the colloidal Ag NCs stable in original reaction solution but also control their size and size uniformity. The structured surfactant bilayer surrounding the Ag NCs is similar to a “micelle”, which makes the crystal growth to be performed inside the “micelle” cores, and Ag NCs have nearly uniform size and shape due to the confinement of the “micelles”. When the precursor AgNO$_3$ concentration is increased, the number of the formed seed at the beginning of the reaction is also increased, then leading to the increase in the number and the decrease in size of the “micelles”. As
a result, higher concentrations of silver precursor give smaller crystals. Finally, ethanol was added to destroy the bilayer surfactant-capped structure to make the Ag NCs precipitate from the stable colloidal system. This is because ethanol is better solvent for OA-RNH$_3^+$ complex compared with water, resulting in the outlayer OA-RNH$_3^+$ complexes in bilayer overcoming the hydrophilic/hydrophobic interaction to enter into ethanol phase. As a result, only the monolayer surfactants remained on the Ag NCs, which led to the precipitation of the Ag NCs from the original reaction solution due to the altered surface properties from hydrophilic to hydrophobic. The precipitated Ag NCs were filtered and vacuum-dried to afford the final products in the form of blue-gray powders, as shown in Fig. 9(c), which could be well re-dispersed in common organic solvents. The precipitated Ag NCs were coated with the monolayer surfactant consisting of oleic acid and the amine (i.e., OA-RNH$_3^+$ complexes), which has been confirmed by a combination of FTIR and TGA measurements previously. Hence, the interpretation for the entire synthesis process is reasonable.

4 Conclusions

1) Narrowly distributed organic-soluble Ag NCs with tunable sizes in the range from 5.4 to 22.1 nm were synthesized using a facile, reproducible and easily scaled up route in water in the presence of oleic acid and n-propylamine by simply varying the precursor AgNO$_3$ concentration. The precursor AgNO$_3$ concentration plays an important role in determining the size and size distribution of the Ag NCs. The smaller and more narrowly distributed Ag NCs were obtained at higher precursor AgNO$_3$ concentration. The Ag NCs are able to be isolated from the original reaction solution by precipitation with ethanol and dried to yield a blue-gray powder product, which possess excellent hydrophobicity and can be well re-dispersed in the common organic solvents.

2) Large-scale synthesis of the Ag NCs has been carried out at 0.4 mol/L AgNO$_3$ concentration, and a reaction yielding as much as 16.2 g of highly uniform organic-soluble Ag NCs with 5 nm average diameter was performed in 400 mL water in about 75% yield. This can supply large quantities of high quality organic-soluble Ag NCs for catalytic, electrical, and biological applications.

3) The surface of the organic-soluble Ag NCs was capped with the monolayer surfactants consisting of oleic acid and the amine. The proposed mechanism based on the “bilayer surfactant-controlled reaction” successfully demonstrates the formation of the organic-soluble Ag NCs in aqueous solution. The formed bilayer surfactant-capped structure on the colloidal Ag NCs in original reaction solution is crucial for the stabilization of the colloidal Ag NCs and for controlling their size and size uniformity.
References


