Kinetically controlled seed-mediated growth of narrow dispersed silver nanoparticles up to 120 nm: secondary nucleation, size focusing, and Ostwald ripening

Ruilong Zong, Xiaolong Wang, Shikao Shi and Yongfa Zhu

A facile synthesis method was developed based on the seed-mediated growth to get the narrow dispersed silver nanoparticles with controllable sizes ranging from 20 nm to larger than 120 nm. Environmentally friendly glucose acts as a reducing agent. Because of its weak reducing ability, the secondary nucleation is prevented in the seed-mediated growth, and the size of silver nanoparticles can be tuned continuously by the continuous addition of reactants. Controlling the supersaturation level is critical to suppress both the nucleation and Ostwald ripening, which can be realized by carefully controlling the addition rate of the reactants. We also set up a convenient method to determine the size and size-distribution of silver nanoparticles from the size-dependent absorption spectra of the colloids, and optimize the growth parameters using this method to get narrow dispersed silver nanoparticles.

Introduction

The size-dependent properties are always the central problem in the research of nanomaterials. The fundamental physical and chemical properties of nanomaterials can be dramatically changed by tuning their size, which significantly affects their performances in different applications such as catalysis, analytical chemistry, and biology. Moreover, nanoparticles with narrow size distribution are the basic building blocks for the construction of the self-assembled structures that can exhibit collective properties as well as the size-effect of the individual nanoparticle. Hence, it is critical to develop new methods to get the nanomaterials with controllable size and narrow size distribution.

Noble metal nanoparticles have been intensively studied in recent years, not only because of the fundamental scientific interest, but also because of their many different technological applications. For example, a 0.5 nm bilayer gold cluster supported on iron oxide demonstrated the highest catalytic activity for carbon monoxide oxidation at ambient temperature. In particular, colloidal gold ranging from 3 nm to 30 nm had been used in biotechnology as a useful marker for transmission and scanning electron microscopy. And, gold nanoparticles in the size range of 120–135 nm showed the highest SERS activity at the 632.8 nm excitation wavelength. The particle size determines their physical and chemical properties as well as the different applications.

The colloidal chemical synthetic method is the most popular process to synthesize uniform nanocrystals with a controlled particle size and shape. In 1993, Murray, Norris, and Bawendi reported the synthesis of uniform cadmium chalcogenide nanocrystals in nonaqueous solvents using the “hot injection” method, which was a landmark work in the synthesis of monodisperse nanocrystals using the colloidal chemical method. These semiconductor nanocrystals showed an apparent quantum size effect, and their band gaps decreased with the increase of size leading to the continuous red-shifts of their emission peaks. Monodisperse noble metal nanoparticles, protected by the appropriate thiol ligands, could also be prepared in nonaqueous solvents. The above processes were not ideal from the viewpoint of the green chemistry, and the size ranges of these methods were limited to a few nanometers.

Monodisperse gold nanoparticles with different sizes had been prepared in aqueous solutions by using different reducing agents, such as NaBH₄, hydrazine, and sodium citrate. Peng X. G. et al. had synthesized the nearly monodisperse gold nanocrystals in the range of 20–40 nm by simply varying the concentration of sodium citrate or the pH values. However, in these processes the adjustable range of sizes was normally small, and got a broad size distribution when the particle deviated from the optimized size range due to difficulties in avoiding formation of new nucleation sites during the growth stage.

© the Owner Societies 2014
Natan and Murphy groups had developed a seed-mediated growth method of Au nanoparticles using mild reducing agents and obtained particle sizes with a wide tunable range.\textsuperscript{21,22} In the seed-mediated process, the nucleation and growth stages were separated by controlling the reaction parameters, so the new nucleation could be avoided during the growth, which prevented the size broadening. Moreover, under the conditions of diffusion controlled growth, the size distribution of particles further narrowed with increasing size since smaller particles grow faster than larger ones.\textsuperscript{23–25} Recently, Victor Puntes \textit{et al.} prepared gold nanoparticles with different sizes from 10 nm to 200 nm through the seeding growth synthesis using citrate.\textsuperscript{26} Similar to the method of Murphy, Ag nanoparticles with narrow size distribution had been prepared by seed-mediated growth using modified Frens and Lee–Meisel methods.\textsuperscript{27–29} Chumanov G. and his coworkers prepared size-controlled chemically clean silver nanoparticles using hydrogen gas as a reducing agent.\textsuperscript{30,31} However, this process needed relatively complex installation and hazardous instruments, such as the use of hydrogen gas, high temperature and pressure as well as filtration and centrifugation to get the final product with special size and shape. Compared with the preparation of Au nanoparticles under the similar conditions, the size and the size distribution of Ag nanoparticles were difficult to control because of their high sensitivity to the reaction parameters.

In this article, a facile green chemical method is firstly reported to prepare the size controllable silver nanoparticles in aqueous solution using a seed-mediated process. The synthesis method is based on the silver mirror reduction, which is a good model system to get insight into the growth mechanism of the seed-mediated growth. Through varying the amount of silver nitrate, the particle sizes can be tuned continuously from 20 nm to larger than 120 nm. In order to understand the growth mechanisms and get nanoparticles with narrow size distribution, we systematically investigated the effect of experimental parameters on the size distribution, such as the addition rate of reagents, pH value, temperature and the amount of poly(vinylpyrrolidone) (PVP). Comparing the peak–FWHM (full width at half maximum) curves deduced from optical spectra, we can get the optimized reaction parameters to prepare Ag nanoparticles with the narrowest size distribution. This work developed a simple method to control the kinetics of the colloidal nanocrystal nucleation and seed-mediated growth through controlling the bulk concentration of silver ions in solution, which realized the preparation of various size Ag nanoparticles with narrow size distribution.

**Experimental**

**Materials**

Silver nitrate was purchased from the Sigma-Aldrich Chemical Co. (St. Louis, MO). Poly(vinylpyrrolidone) (PVP; average molecular weight of 30 000 g mol\textsuperscript{−1}), chloroauric acid, trisodium citrate, sodium carbonate, tannic acid, glucose, ammonium hydroxide, and sodium hydroxide were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All these chemicals were of analytical grade and used as received.

**Methods**

**Synthesis of gold seeds.** All of the glass containers used for the synthesis and storage of silver nanoparticles (Ag NPs) were immersed in 30% nitric acid (v/v) and rinsed with deionized water. Briefly, the 5 nm gold nanoparticles were prepared by tannic acid reduction. First, 10 mg of HAuCl\textsubscript{4} were added to 80 mL of deionized water in a conical flask. After HAuCl\textsubscript{4} was heated to 60 °C, a mixed solution of 4 mL of trisodium citrate (50 mg mL\textsuperscript{−1}), 2 mL of sodium carbonate (3 mg mL\textsuperscript{−1}) and 2 mL of tannic acid (10 mg mL\textsuperscript{−1}) was added into the previous solution. During the reaction, the solution was heated to boiling under magnetic stirring and was maintained at this temperature for 5 min. The solution turned pink immediately after adding the reducing agent, indicating the formation of gold nanoparticles. The seed solution can be used for several months as stored at 7 °C.

**Preparation of growth solution.** Solution 1: 200 mL aqueous solution containing 100 mg glucose and 200 mg PVP was prepared in a conical flask. Different amounts of 1 M NaOH were added in order to adjust the pH of the solution. Solution 2 is Tollens’ reagent: 20 mL of ammoniacal silver nitrate solution was prepared as follows. First, 50 μL of NaOH (1 M) was dropped into aqueous AgNO\textsubscript{3} (45 mg in 10 mL of deionized water), and the solution appeared as a brown precipitate. Then, 5% (v/v) ammonia solution was slowly added (dropwise) under shaking, until the brown precipitate was dissolved. The final volume of the solution was adjusted to 20 mL by adding the deionized water. Both solutions should be freshly prepared just before the reaction.

**Seed-mediated growth.** 0.2 mL of gold seeds were added into the solution 1 with stirring for another 1 min. Next, solution 2 was slowly added (dropwise) into the above solution with different rates while vigorously stirring. The solution turned yellow after adding solution 2, and the color of the solution gradually changed from yellow to brown and red with the addition of solution 2. The adding rate was tuned from 50 μL min\textsuperscript{−1} to 10 mL min\textsuperscript{−1} which was controlled by an injection pump.

**Characterization**

In order to monitor the kinetics of seed-mediated growth, the silver colloids about 3 mL were collected from the reaction vessel at different reaction times. The optical spectra were measured after 3 hours in order to monitor their size and size distribution, and we got the peak–FWHM curves at different reaction parameters. The UV-vis absorption spectra of the silver nanoparticles were measured using a Hitachi U-3010 spectrometer. If the absorbance has exceeded 3, the solution should be diluted in order to improve the accuracy of the test. Transmission electron microscopy (TEM) images were acquired with a Hitachi HT7700 electron microscope, operating at 100 kV. TEM samples were prepared by placing one drop of the silver nanoparticle colloid, after centrifugation and redispersed in 1 mL ethanol, on a carbon-coated copper grid. The grids were allowed to dry under ambient conditions.
Results and discussion

Continuous size-controllable growth

In this work, the silver mirror reaction was first used in the seed-mediated growth of silver nanoparticles, in which the glucose acted as a reducing agent. Xia Y. N. et al. have prepared silver nanoparticles with dimensions in the range of 20–50 nm through the Tollens’ process. However, the reducing ability of the aldehyde group can be controlled by the reaction conditions, such as the pH value, temperature and other parameters, which ensured a small number of additional nucleations or even no additional nucleation in the seed-mediated reaction. To prove the weak reducing ability of glucose and the crucial role of gold seeds in the reaction, a control experiment was carried out in which the above-mentioned reaction was carried out without the addition of gold seeds. It was observed that there was no color change during the reaction indicating no spontaneous nucleation of silver nanoparticles. We could also easily tune the size of silver particles continuously and precisely by simply changing the amount of ammoniacal silver nitrate while all other parameters were kept unchanged. Especially, we found that the rate of reagent addition strongly affected the final diameter and size distribution. A narrow size distribution could be obtained at an optimized adding rate. Fig. 1 shows typical TEM images of silver nanoparticles with different diameters from about 20 nm to larger than 120 nm. As evident from Fig. 1, these nanoparticles have a relatively narrow size distribution and their relative standard deviation (RSD) is less than 20%. The silver nanoparticles are kept quasi-spherical very well, seldom observing other shapes such as rod, wire, triangle, etc. Actually using this method, we can get silver nanoparticles whose absorption peaks are from 420 nm to larger than 500 nm as shown in Fig. 2. The optical properties more conveniently reveal the size change of silver nanoparticles. The inset establishes a relationship between the nanoparticle size from TEM measurements and their optical absorption peaks that is useful in determining Ag nanoparticle size from optical data.

Fig. 3a shows the UV-vis absorption spectra of silver nanoparticles including the spectrum of the gold seed solution itself, in which the amount of the gold seed solution decreases from 1 mL to 0.2 mL. As shown in the figure, the strong plasmon band of silver particles dominated the optical properties of the core@shell structure. Moreover, their absorption spectra gradually shift to red as decreasing the amount of seeds, suggesting the formation of the particles with larger average diameters. A similar result was also observed in previous studies. As shown in Fig. 3b, when the seed solution was fixed at 0.5 mL, the plasmon bands red-shift from 410 nm to 455 nm upon gradually increasing the amount of the reaction reagent of ammoniacal silver nitrate solution, which also proves the gradual growth of silver nanoparticles. From these UV-vis spectra we can reasonably infer that the seed-mediated autocatalysis reaction dominates the process, which hinders the additional nucleation.

Seed-mediated growth mechanism and kinetically controlled growth

The separation of nucleation and growth is the key problem in the synthesis of monodisperse nanoparticles. Classical studies on the preparation of monodisperse colloids have suggested that the burst nucleation followed by the diffusion-controlled
growth on the existing nuclei is the critical condition to get the monodisperse colloids. In the typical LaMer model, there exist three stages in the reaction: the accumulation of the monomers, the burst nucleation, and the growth stage. However, in the seed-mediated growth process, the homogeneous nucleation, occurring at higher activation energy, can be prevented by introducing the seed in the system because the autocatalysis growth happened at a relatively low concentration and consumed the reaction reagent. And the seeds serving as the nuclear center grow continuously to a desired size. In the growth stage, different growth mechanisms, diffusion-control or reaction-control, can affect the final size distribution too. In order to get the nanoparticles with relatively narrow size distributions, both the nucleation and growth stages should be controlled.

In the seed-mediated process, the most important problem is how to prevent the secondary nucleation, which is critical for getting the silver nanoparticles with improved monodispersity. Because the energy barrier of spontaneous homogeneous nucleation is extremely high, the nucleation is difficult when compared with the seed-mediated growth. But, some new nuclei maybe generated in this process at a critical supersaturation condition that lower the spontaneous homogeneous nucleation because of the catalysis of the seeds. In order to suppress the secondary nucleation, a mild reducing agent is the basic requirement for the seed-mediated growth. Sodium citrate, NH₄OH and ascorbic acid have been used to fabricate monodisperse gold nanoparticles using the seed-mediated process. However, it is difficult to prevent the secondary nucleation using these reducing agents because of their relatively strong reducing ability. The problem can be partly solved by adding a surfactant, such as the cetyltrimethylammonium bromide (CTAB) forming the metal–surfactant complexes to enhance the stability of Ag⁺, but it is difficult to control the particle shape and discard the CTAB.

The glucose, being a very weak and green reducing agent, cannot reduce the silver salt in this reaction without the seeds. We did not notice any color change in the reaction without gold seeds. But, in the seed-mediated growth as shown in Fig. 4, when the adding rate of reaction reagents was so fast that the consumed reagents were less than the added reagents, the bulk concentration would be increased even larger than the critical concentration of secondary nucleation and caused the new nucleation. So controlling the adding rate of reaction reagents can effectively suppress the additional nucleation.

Even if without the secondary nucleation in the seed-mediated growth, the size distribution can be widened for the reaction-controlled growth, which comes from a kinetic process related to the Gibbs–Thomson effect that is the well-known Ostwald ripening process. During the growth stage, two oppositional processes occur in the reaction, namely precipitation and dissolution. According to the mechanism of LaMer, there exists a critical size for a given concentration, in which the precipitation and dissolution have the same rate. Those particles, smaller than the critical size, will be dissolved at the critical concentration. Generally, the Ostwald ripening widens the size distribution because the smaller particles are swallowed by larger particles in this process.

However, the size distribution will spontaneously narrow or focus in a diffusion-controlled growth condition, which is the opposite process of the Ostwald ripening. This process had been predicted more than 50 years ago by Howard Reiss that the small particles will grow more rapidly than larger ones if the concentration is sufficiently high. At the high reagent concentration, the growth rate is controlled by the diffusion-controlled growth, in which the reagent’s diffusion is the rate-determining step. In this case, the reagents are transported from the bulk solution and precipitated immediately onto the surface of the particles. This diffusion-controlled growth, called the size focusing process, normally occurred at higher concentration just below the concentration of nucleation.

In the seed-mediated process, the solution of ammoniacal silver nitrate was added into the reaction solution with different adding rates from 50 μL min⁻¹ to 10 mL min⁻¹. The concentration of the bulk solution would gradually increase with the increase of the adding rate. Actually, the growth mechanism and the size distribution can be tuned by controlling the adding rate of reaction reagents. When the rate is slow, the reaction mechanism was a reaction-controlled process and caused an Ostwald ripening process. By increasing the rate, the reaction will be controlled by a continued diffusion-controlled growth that leads to size focusing and produces uniform nanocrystals at the relatively high concentration. But when the concentration...
is higher than the critical concentration at some adding rate, the additional nucleation will occur in the solution.

**Peak–FWHM standard curve**

As well known, the determination of the size distribution of nanoparticles is not as trivial as it may sound. Normally, the TEM method was used to calculate the size distribution through counting a large amount of nanoparticles. But the method is time consuming and easily affected by the sample preparation. Except the TEM method, the analytical ultracentrifugation (AUC), dynamic light scattering (DLS), asymmetric flow field flow fractionation (aF-FFF) measurements, X-ray diffraction (XRD), and the optical spectra method can be used to determine the size distribution of nanoparticles. But, just as discussed by Dieckmann Y. and his co-workers, there is no “absolute” or “best” method for determining nanoparticle size distributions that is applicable to all situations.36

In the study of the size distribution of semiconductor quantum dots, the relative standard deviation (RSD) of the semiconductor nanocrystals could be approximately represented by the FWHM of the photoluminescence (PL) spectra expressed in wavelength, which is independent of the emission peak position or the average size of the nanocrystals. In above method it is assumed that the particles with different sizes have the same emission efficiency. Similar to the semiconductor quantum dots, the noble metal nanoparticles also presented the size-dependent optical spectra and the localized surface plasmon resonance (LSPR) spectra, whose UV-vis spectra had been directly used to determine their size and concentration.37 Generally, it is reasonable to assume that there is a positive correlation between the FWHM of the absorption spectra and the size distribution. However, in the LSPR spectra, there exists an intrinsic broadening that the FWHM of the optical spectra widened with the increase in the particle size. That is to say, the FWHM of LSPR spectra is not only dependent on the size distribution of the noble metal nanoparticles but also on their average size. The extinction spectra of monodisperse silver nanoparticles, diameters ranging from 10 nm to 100 nm, are calculated using Mie theory. And the relationship between the peak position and its FWHM, called as the peak–FWHM curve, is shown in Fig. 5a. Obviously, different from the case of semiconductor quantum dots, it is difficult to determine the size distribution from the FWHM of absorption spectra of noble nanoparticles.

In this work, the peak–FWHM curve acted as a standard to optimize different reaction parameters in order to get a narrow size distribution. Because of the effect of the intrinsic broadening, it is difficult to deduce the size distribution of silver nanoparticles from the independent parameter of FWHM, similar to the system of semiconductor quantum dots. Nonetheless, we can determine the size distribution of silver nanoparticles according to their peak–FWHM curves because the effect of the intrinsic widening has been eliminated at one specific peak position. So the optimized preparation parameters could be got easily through comparing their peak–FWHM curves. Fig. 5b shows the peak–FWHM curve at different adding rates, in which the rate of 200 μL min⁻¹ gives the narrowest FWHM at the same peak position. Moreover, as shown in Fig. 5b, when the rates are larger than 2 mL min⁻¹, the peak positions are apparently shorter than the sol prepared with slow rates. It proves that the fast addition caused the additional nucleation and the final small average particles. And when the rates are slower than 200 μL min⁻¹, the absorption peaks displayed apparently red-shift upon adding the same amount of reactant and wide FWHM at the same peak position, which is the evidence of Ostwald ripening. So size focusing can be got at the optimized parameter window in which the diffusion becomes the rate limiting step.

We also systematically studied the effect of other reaction parameters, such as the amount of NaOH added and the temperature, in which the adding rate of the reagent was fixed at the optimized 200 μL min⁻¹. At the optimized rate, the effect of the other parameters has been shown in Fig. 6. The pH values (the amount of NaOH added) have a great influence on the reaction. The increase of the pH values will decrease the energy barrier of the nucleation and increase the reaction speed of the seed-mediated growth. The lower pH values will hinder the additional nucleation, but as discussed in the seed-mediated mechanism the relatively slow growth rate will cause the Ostwald ripening and broaden the size distribution. We got an optimized amount of NaOH. When the pH is higher than the optimized pH value, the additional nucleation caused the small final particle size and large size distribution. The temperature has a relatively small effect on the reaction under ambient conditions as shown in Fig. 6b.

The fitting curve of peak–FWHM under optimal conditions (200 μL min⁻¹, 180 μL NaOH, and at 30 °C) is shown in Fig. 7. For any quasi-spherical silver nanoparticle prepared in the research, we can easily characterize its UV-vis absorbance spectrum, and get

**Fig. 5** (a) Mie theory calculated peak–FWHM relationship of different size silver nanoparticles and (b) the effect of adding rate on the peak–FWHM relationship.

**Fig. 6** Effects of (a) different amounts of NaOH and (b) temperature on the FWHM of absorbance spectra.
its peak position and FWHM. Through comparing the experimental results with the calculated FWHM from the fitting curve, we can determine its relative size distribution quickly.

**Conclusion**

Utilizing the weak reducing ability of glucose and the controllable silver ion concentration, we can easily control the nucleation and growth of silver nanoparticles in the seed-mediated growth method. The relatively high supersaturation, just below the critical supersaturation of nucleation, can prevent the additional nucleation and lead to the size focusing to produce narrow dispersed nanoparticles. We can determine the size and size-distribution from the optical spectra of silver nanoparticle colloids according to the absorbance peaks and peak–FWHM curves. The size of silver nanoparticles with narrow size distributions (RSD less than 20%) can be continuously tuned from 20 nm to 120 nm.

**Acknowledgements**

This work was supported by the National Natural Scientific Foundation of China (21075076).

**References**