Size controllable synthesis of ultraine silver particles through a one-step reaction

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1. Introduction

Silver particles with ultraine and uniform size are currently of considerable use in electronics [1], catalysis [2], non-linear optics [3], photonic crystals [4], and surface-enhanced Raman spectroscopy (SERS) [5]. For their application, the morphology and size play a key role. For example, when silver particles are used to enhance the photoluminescence (PL) intensity of dyes nearby, larger silver particles show much better enhancement while quenching often takes place for smaller particles [6]. The different performance arises from the size-dependent scattering and absorption cross-section of silver particles. In SERS application of silver particles, the particle size determines the area of “hot spot” locating at the junction of neighboring particles. Moreover, the catalytic efficiency for the reduction of certain organic dyes [7], and the non-linear optical properties of silver particles also correlate with their size [8].

Generally, silver particles are produced by physical or chemical methods. Physical methods usually produce particles with uneven sizes and irregular shape. As a result, chemical methods are commonly adopted. The most frequently used chemical methods are reduction of silver salt by one of two reduction agents: NaBH₄ [9] or citrate sodium [10,11]. Although sodium borohydride can be used to produce small particles (<10 nm), synthesis of larger particles is difficult. Silver particles produced by citrate sodium often have non-uniform size and shape. To produce large particles (>100 nm), the primary approach is based on a two-step reduction method, which comprises seeding and growth section in separated solutions [12]. However, this method consumes much time and suffers from low efficiency caused by the low concentration of reactants in the growth solution.

Here, a simple one-step reduction method was developed to controllably synthesize silver particles of different size. Though the Polyvinylpyrrolidone (PVP) assistant reduction method has been used [13], there was no report of systematic tuning of the reaction parameters to control the size of silver particles in a large region. In our experiment, uniform particles with size of 40 nm–2 μm can be obtained.

2. Materials and methods

All the reagents were analytically purified and used without further purification. In a typical synthesis, PVP (k30) and AgNO₃ were dissolved in 50 mL water, then 1 mL 37% CH₂O was added, and concentrated ammonia (28%) was lastly injected to initiate the reaction. Upon the addition of ammonia, the mixture turned yellow or gray in a few minutes. The reaction mixture was stirred for 30 min before it was centrifuged.

The morphology of silver particles was examined by a scanning electron microscope (SEM, S-4800; Hitachi). X-ray diffraction (XRD) test was performed on a Rigaku D/max-ga X-ray diffractometer with the graphite monochromatized CuKa radiation.

3. Results and discussion

Through tuning the reaction parameters, silver particles of different size were obtained. Fig. 1 gives several typical examples. With 0.25% PVP and 0.5 mM AgNO₃, the silver particles have an average diameter of about 40 nm as shown in Fig. 1a. The particles have a narrow size-distribution and good dispersion. When the concentration of AgNO₃ was raised to 2.5 mM and 10 mM, the...
particles with an average diameter of 70 nm and 2 μm were obtained, as shown in Fig. 1b and f. Obviously, the large particles in Fig. 1f are aggregates of small particles. Spherical particles with the size in the range of 100–200 nm were obtained by raising the reaction temperatures and the amount of ammonia. At 30 °C, the silver particles of about 100 nm as shown in Fig. 1c were obtained when the amount of ammonia was increased to 2.4 mL. The silver particles of about 160 nm were obtained at 40 °C by slightly decreasing the PVP concentration. Moreover, the large particles of about 200 nm were obtained by further raising the amount of ammonia to 12 mL and raising the temperature to 60 °C. Usually, such large particles could be obtained through a two-step growth, but here were obtained through a one-step reaction in our experiment.

The XRD pattern of a product is shown in Fig. 2. The four peaks in the spectrum can be designated to (111), (200), (220) and (311) planes of silver with an FCC phase structure, which suggests that the high purity of the silver crystals and no silver oxide or reaction residue is detectable.

Fig. 3 depicts the growth process of silver particles. First, the solution is supersaturated with silver atoms after the redox reaction, then primary particles form through a burst-nucleation step. For the growth of primary silver particles, there are two kinds of growth modes: diffusional growth and aggregation. In a limited time, the former mode produces smaller particles, and the aggregation mode easily produces larger particles [14]. In our experiment, the above two modes may also proceed together, and then the reaction parameters determine the detailed growth route. Moreover, metal particles formed through an aggregation mechanism are mostly spherical and polycrystalline, as shown in Fig. 1f.

In our experiment, the change of AgNO₃ concentrations which determine the total amount of silver atoms influences the Ag particle size, as the molar ratio of Ag atoms to PVP influence the growth mode. When AgNO₃ concentration is low, there is enough PVP to coat the Ag particle surface [15]. In this condition, silver particles grow up through diffusional growth, and then smaller silver particles about 40 nm as shown in Fig. 1a were obtained when 0.5 mM AgNO₃ was used. With the increase of concentration of AgNO₃, silver particles become larger due to more silver atoms deposited onto the nuclei. As shown in Fig. 1b, when 2.5 mM AgNO₃ was used, the particle size was raised to 70 nm. When the AgNO₃ concentration was further raised to 10 mM, there were not enough PVP molecules to stabilize the particles and aggregation mode took place, resulting in the large particles of 2 μm as shown in Fig. 1f.
The reaction rate is highly dependent on temperatures. When the reaction was carried at 25 °C with 1% PVP, it took several minutes to form nuclei. If the temperature was lifted to 50 °C, the color of the reaction solution changed immediately. The final size of the particles obtained at these two temperatures is different. As shown in Fig. 4a, large aggregates of about 300 nm formed when the reaction was carried at 50 °C, as the reaction was so fast that PVP could not effectively coat primary particles, which aggregated into larger particles. When the reaction temperature was lowered to 25 °C, the dispersed silver particles as shown in Fig. 4b with the size around 50 nm were obtained. Obviously, the reaction temperatures influence the production rate of silver atoms and further the growth mode.

In our experiment, ammonia was added to start the reaction. It was found that the amount of ammonia influenced the number of primary particles, which would affect the aggregation degree. As shown in Fig. 4c, when the amount of NH₃·H₂O was changed from 2.4 ml to 0.6 ml while keeping the other reaction parameters the same as that in Fig. 1c, the average particle size was changed from 160 nm to 80 nm. According to the discussion above, the 160 nm silver particles are aggregations of primary particles. When 12 mL NH₃·H₂O was used, the particles of about 200 nm were obtained, as shown in Fig. 1e. So it can be inferred that aggregation takes place more easily at higher pH value.

4. Conclusion

In conclusion, through a simple one-step reaction, uniform silver particles of diameters 40 nm–2 μm were controllably synthesized. The reaction parameters control the nuclei number, the growth rate and the growth mode (diffusional growth or aggregation) which determines the final size. The silver particles of such well controlled sizes could be used in electronic and photovoltaic industry.

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