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Short communication

# Large scale synthesis and formation mechanism of silver nanoparticles in solid-state reactions at ambient temperature

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ABSTRACT

A one-step strategy for preparing Ag nanoparticles (AgNPs) on large scale is demonstrated successfully, based on solid-state reactions at ambient temperature. The environmentally friendly synthesis can be achieved by simply grinding $AgNO_3$ and ascorbic acid (AA) for about 30 min without adding any solvent and organic protectors. The size of AgNPs can be readily controlled by adjusting the reaction parameters such as $AgNO_3$/AA molar ratio and reaction time. The nanostructures of AgNPs and their formation mechanism have been also investigated with XRD, FTIR, FESEM, HRTEM and HPLC–MS. It was found that AA can reduce $Ag^+$ into $Ag^0$ to form AgNPs directly in accompanying with its first oxidation into 2,3-diketogulonic acid (2,3-DKG) and then a series of fragmentary species of 2,3-DKG.

## 1. Introduction

In recent years, noble metal nanomaterials such as gold, silver and palladium have drawn immense attention due to their potential applications as catalysts [1–4], optoelectronic nanodevices [5–7], substrates for surface-enhanced Raman spectroscopy (SERS) [8–10], chemical/biological sensors [11,12] and biomedicine materials [13,14]. Among various metals, silver nanoparticles are of particular interest because of their remarkable antimicrobial and localized surface plasmon resonance properties, which render them unique applications such as broad-spectrum antimicrobial [15,16], surface-enhanced Raman scattering substrates (SERS) [17–20], optical sensor [21,22], biomarker [23,24] and so on.

Numerous methods, such as chemical reduction [25–27], thermal decomposition [28,29], electrochemical reduction [30–32], chemical and photo reduction [33,34], and biosynthesis [35,36], have been reported for the synthesis of silver nanomaterials so far. Chemical reduction is one of the most applied methods for the preparation of AgNPs colloidal dispersions in water or organic solvents [37–39]. In recent years biological synthesis of Ag nanoparticles has received attention over the physical and chemical synthesis as a clean, non-toxic and eco-friendly approach [40–42]. Also, various shape-controlled Ag nanostructures including quasi-spheres [43], decahedrons [44], cubes [45], prisms [46], rods [47], wires [48], tubes [49], branches [50], sheets [51], plates [52] and belts [53] have been reported. However, to the best of our knowledge, there is no report concerned with AgNPs synthesis based on solid state reactions at ambient temperature so far.

Based on solid-state reactions at ambient temperature, our groups have prepared successively several metal and metal oxide nanoparticles [54–58]. In this paper, we would like to report a method for producing silver nanoparticles on a large scale based on solid-state reactions at ambient temperature for the first time. The reaction was accomplished by grinding $AgNO_3$ and AA for about 30 min without any other agent. The growth of the AgNPs can be terminated by washing the products with water and ethanol, respectively, to remove AA. It was found that the size and shape of the as-prepared silver nanomaterials depend closely on molar ratio of the reactants and reaction time. The dynamic growth of the AgNPs was investigated carefully with XRD, FTIR, FESEM, HRTEM and HPLC–MS to reveal the formation mechanism of AgNPs.

## 2. Experimental

### 2.1. Reagents

Silver nitrate ($AgNO_3$) and ascorbic acid (AA) were purchased from Shanghai Chemical Industrial Co. Ltd. (Shanghai, China). All chemicals were of analytical grade and used without additional

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purification. Double distilled ultrapure water (>18 MΩ cm) was used for all solution preparation. Phosphate buffer solution (PBS, pH 6.94) was made up from $Na_2HPO_4$ and $NaH_2PO_4$.

### 2.2. Preparation and characterization of AgNPs

$AgNO_3$ and ascorbic acid, with molar ratio of 1:1 (0.1699 mg and 0.1762 mg), 1:2 (0.1699 mg and 0.3524 mg) and 1:3(0.1699 mg and 0.5286 mg), were mixed and ground in air for 30 min at ambient temperature. Then the precursor mixture was kept in a vial in air for 4 h, 8 h and 24 h, respectively. The product was washed with distilled water, treated in an ultrasonic bath for 15 min, and centrifuged at 8000 rpm for 10 min. This process was repeated several times until the supernatant became clear. The obtained AgNPs were then dried in air at 60 °C for 24 h.

X-ray diffraction (XRD) patterns were obtained with a D/max-rA rotating anode X-ray diffractometer with Cu Kα radiation ($\lambda = 1.541875$ Å). Fourier transform infrared (FTIR) spectra were recorded by a Nicolet-6700 spectrometer. SEM and TEM images were obtained using a JSM-7001F (JEOL) field emission scanning electron microscopy (FESEM) and a HRTEM-2100 (JEOL) high-resolution transmission electron microscope (HRTEM), respectively.

HPLC–MS spectrometry was carried out using an Accela UPLC (Thermo Fisher Scientific, San Jose, CA, USA). The mobile phase consisted of 0.1% (v/v) formic acid in water (eluent A) and ACN (eluent B). The analysis was held with 5% of eluent A during 2 min. The flow rate was 0.40 mL/min and the column temperature was set at 20 °C. The UHPLC system was coupled to a single stage Orbitrap mass spectrometer (ExactiveTM, Thermo Fisher Scientific, Bremen, Germany) operating with a heated electrospray interface (HESIII, Thermo Fisher Scientific, San Jose, CA, USA), in negative ionization mode (ESI−) using the following operational parameters: spray voltage, −2.5 kV; skimmer voltage, −20 V; capillary voltage, −60 V; tube lens voltage, −120 V; sheath gas ($N_2$, >95%), 40 (adimensional); auxiliary gas ($N_2$, >95%), 10 (adimensional); heater temperature, 150 °C; and capillary temperature, 350 °C. The mass spectra were acquired using an acquisition functions: full MS, ESI−, mass resolving power is 25,000 FWHM; mass range is 100–2000; scan time is 0.25 s.

## 3. Results and discussion

### 3.1. Synthesis and characterization of AgNPs

In order to determine the best parameters for the formation of AgNPs, the morphology of the silver nanoparticles synthesized under different conditions was investigated using SEM as shown in Fig. 1. The images in the columns reveal the molar ratio effect of $AgNO_3$ to AA on the formation of Ag nanoparticles, and those in the rows show the influences of reaction time. When the molar ratio was 1:1, AgNPs were about 100–500 nm and irregular, and there is no too much difference in the size and shape of the particles after prolonging the reaction time. After increasing the amount of AA to 1:3 in the reaction, the nanoparticles became smaller and more uniform. The mean particle sizes of *ca.* 40.92 nm, *ca.* 134.54 nm, *ca.* 142.50 nm for 4 h, 8 h and 24 h respectively are obtained, and the corresponding size distributions are shown in Fig. S1. But adding more AA was not always better. When the molar ratio was adjusted to 1:5 and 1:8, it was found that the size of the AgNPs increased again. This could be attributed to the enhanced formation rate of AgNPs with excess amount of AA. On the other hand, the morphologies of samples prepared at 1:3 changed from spherical shape to polyhedron after performing the reaction for different time. It can be concluded that the growth of AgNPs in solid-state reactions can be controlled by adjusting the molar ratio of $AgNO_3$ to AA and the reaction time conveniently. More uniform and smaller AgNPs can be produced by performing the reaction at molar ratio of $AgNO_3$ to AA at 1:3.

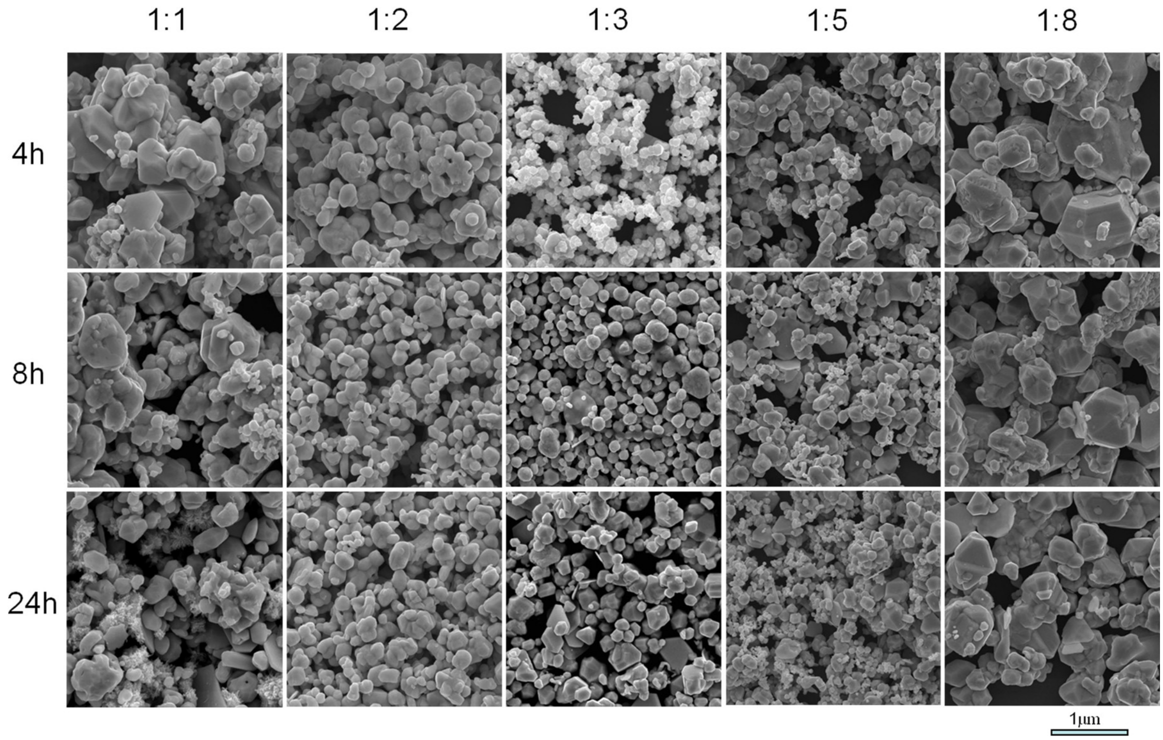

**Fig. 1.** FESEM images of AgNPs as-synthesized. The columns present samples produced from different molar ratio of $AgNO_3$ to AA, and the rows show materials obtained at different reaction time.