

# Silver Nanoparticles from Ultrasonic Spray Pyrolysis of Aqueous Silver Nitrate

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Silver particles less than 20 nm in diameter were synthesized by pyrolysis of an ultrasonically atomized spray of highly dilute aqueous silver nitrate solution at temperatures above 650°C and below the melting point of silver. Feed solution concentration and ultrasound power applied to the atomizer were found to have a significant impact on the particle size of the silver nanoparticles. Average particle size was found to be controllable in the range of 20 nm to 300 nm by varying the solution concentration and the ultrasound power to the atomizer.

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## 1. INTRODUCTION

Ultrasonic spray pyrolysis may be employed to generate an aerosol from a dilute aqueous metal salt solution, resulting in the production of particles with a narrow size distribution. A review by Messing et al. (1993) has shown that spray pyrolysis has been used for the synthesis of particles of micron size, producing various metal powders. Tsai et al. (2004) used ultrasonic spray pyrolysis and observed that uniform particles of 90 nm can be synthesized from smaller droplets whereas larger droplets generated porous particles. Pluym et al. (1993) used three types of aerosol generators in synthesizing solid, spherical, micron-sized silver metal particles. It was observed that the effect of precursor concentration on the particle size was weak and mostly dependent on the aerosol droplet size.

Ultrasonic spray pyrolysis has been most used to synthesize fine powders by aerosol decomposition. Ogihara et al. (1999) synthesized powders of barium titanate to study the effect of temperature on the structure of the particles. According to Xia et al. (2001), the conventional method of spray pyrolysis was

only capable of producing sub-micron to micron sized particles. This limitation was overcome by adding salt to the precursor solution through ultrasonic aerosol decomposition in synthesizing single nanosize crystals of CeO<sub>2</sub> in the size range of 20–120 nm. Yuan et al. (1998) used flame-assisted ultrasonic spray pyrolysis technique to synthesize ceramic powders in micron and sub-micron size range by controlling the concentration of precursor solution. According to the study of Jokanović et al. (1996), the influence of aerosol droplet formation was the main control parameter in the particle size distribution of the Al<sub>2</sub>O<sub>3</sub> powders synthesized by ultrasonic spray pyrolysis.

The effect of feed solution concentration on the size of the particles produced was studied by Kozhukharov et al. (2003), who used an ultrasonic spray pyrolysis method to synthesize ceramic powders of spherical sub-micron particles. Kim et al. (2005) synthesized hollow spherical silica particles using ultrasonic flash pyrolysis by adding a small amount of urea to the sodium silicate solution. Taniguchi and Kuang (2001) synthesized fine particles of spinel lithium manganese oxide from aqueous lithium nitrate using an ultrasonic spray pyrolysis method. Lenggono et al. (2000) used an electrospray technique to prevent agglomeration and produce monodisperse particles of ZnS.

In this work, the effects of feed solution concentration and ultrasonic atomization on the synthesis of nanoparticles of silver using a spray pyrolysis technique were studied. In the thermal processing technique employed, reduction of silver ion was achieved by heating the material above the pyrolysis temperature in an oxygen-free environment. This processing technique was examined as a direct route for silver nanoparticle synthesis. While the effect of concentration on the particle size has been studied, a particle size of less than 20 nm has not been reported. Size distribution characterization of particle samples obtained by spray pyrolysis of an aerosol generated by ultrasonic atomizer has not been reported for feed concentrations on the order of 10<sup>-7</sup> kmol/m<sup>3</sup>.

## 2. EXPERIMENTAL

In this work, silver nanoparticles are produced by flash pyrolysis of a liquid feed solution of silver nitrate (Sigma-Aldrich, 204390-50G), nebulized by an ultrasonic atomizer and power

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supply (SONO•Tek Models 06-05108 and 06-05112, respectively) at a feed rate of  $6 \times 10^{-10} \text{ m}^3/\text{s}$  ( $1 \times 10^{-4} \text{ ml/s}$ ). The reaction was carried out in an oxygen-free environment using argon as a carrier gas to avoid oxide formation and to assure reduction to metal occurs in the high temperature reaction zone. Argon is fed at constant flow rate, manually controlled with a valve and rotameter. The operating partial pressure of the gas stream was  $2 \times 10^5 \text{ Pa}$ . Across a frequency range ( $f$ ) of 20 to 120 kHz, the number mean diameter ( $d_{mn}$ ) varies from 84 to  $24 \mu\text{m}$ , while number median diameter ( $d_{md}$ ) is in the range of 19 to  $67 \mu\text{m}$  for this atomizer. Regression of number mean diameter data obtained from the atomizer user manual resulted in the relationship  $d_{mn} = 1.0 \times 10^3 / f^{0.79}$  with a correlation coefficient of 0.99. This result differs somewhat from that of Lang (1952), where the exponent on frequency was presented as  $-2/3$ .

Silver nanoparticles were generated by flash pyrolysis using the design illustrated in Figure 1. Aqueous silver nitrate solution is gravity fed from a burette to an atomizer, and the atomized spray is discharged into the reaction chamber that is maintained above  $650^\circ\text{C}$  with a tube furnace. Silver nanoparticles are deposited on the substrate placed in the flow path, while the water vapor and off-gases are discharged through an exhaust line. A vacuum pump was used to put the reactor under slight vacuum to discharge the water vapor and exhaust gases to vent. Thermocouples were inserted near the surface of the atomizer, the surface of the reactor, and the sample holder location to record an axial profile of temperature within the reaction chamber.

The spray atomizer, shown schematically in Figure 2, was connected to an ultrasonic generator such that the atomizer discharge tube vibrated at a selected frequency to control the average aerosol droplet size. A flange was welded on the atomizer unit to allow the atomizer to be inserted into a flanged pipe, which serves as the pyrolysis reactor chamber.

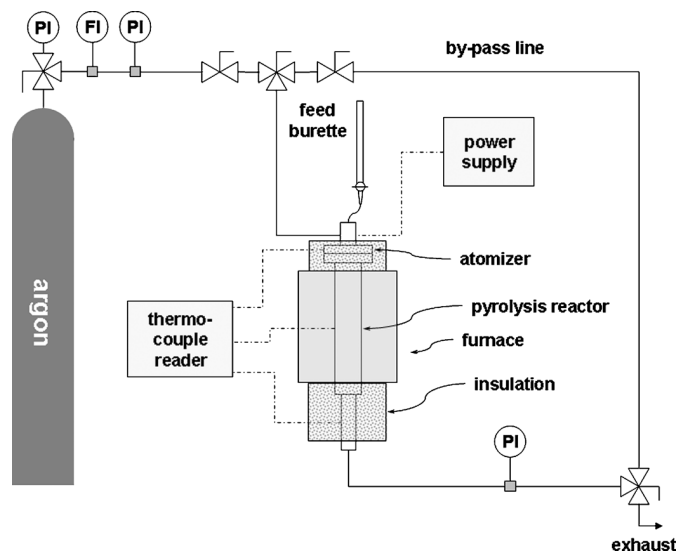


FIG. 1. Schematic diagram of the spray pyrolysis reactor system with support equipment.

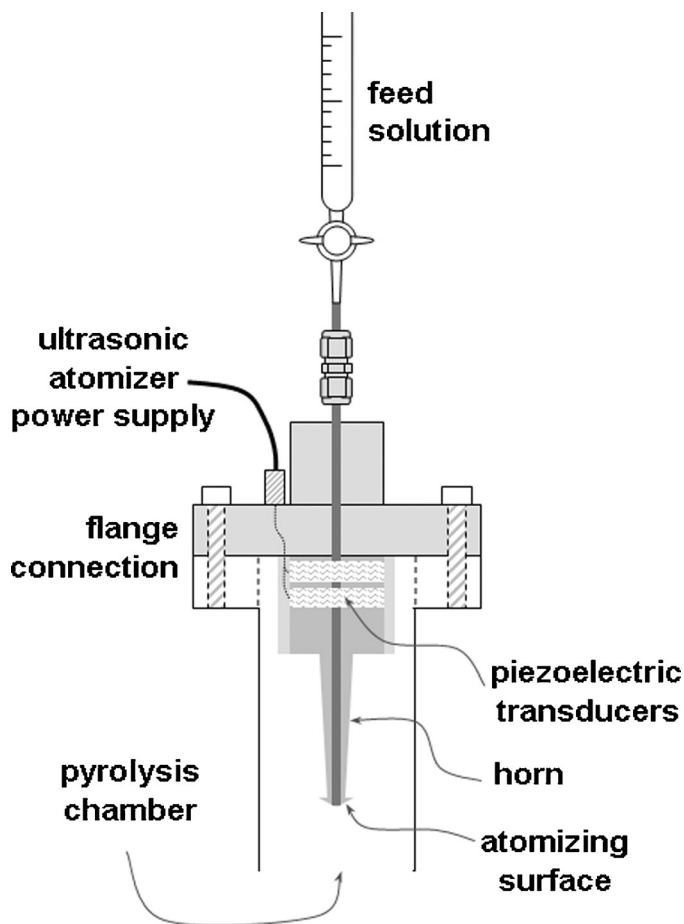


FIG. 2. Schematic diagram of spray pyrolysis reactor system, including details of feed system and ultrasonic atomizer location in pyrolysis chamber.

Particles samples were fit to a normal distribution, and thus characterized by the mean particle size and standard deviation. Individual particle sizes of a sample were manually counted and measured from images obtained by transmission electron microscopy (TEM) with a JEOL 200CX, or scanning electron microscopy (SEM) using a Hitachi S-3200N. Formvar-coated 200-mesh nickel grids were used as substrates. Samples composed of particles greater than  $100 \text{ nm}$  were imaged with the SEM, while those of particles less than  $100 \text{ nm}$  were imaged with the TEM.

The effects of feed solution concentration and atomizer power on particle characteristics were studied. The concentration of the aqueous feed solution dictates the number of moles of silver that will be contained in an aerosol droplet of a given volume. As the feed concentration is increased, the number of moles of silver in each drop of aerosol also increases for a fixed droplet size. Concentration was studied across several orders of magnitude, from  $10^{-1} \text{ kmol/m}^3$  to  $10^{-7} \text{ kmol/m}^3$ , to determine the effect of concentration on particle size. Aerosol size is inversely proportional to the ultrasonic frequency applied to the atomizer ( $0.79$  power as mentioned previously). Power was varied between

4 W and 11 W (or a frequency range of approximately 50 to 100 kHz).

### 3. RESULTS AND DISCUSSION

Evaporation of solvent occurs rapidly in the reaction chamber due to the exposure of the high surface area aerosol to temperatures above the pyrolysis temperature and below the melting temperature of silver, resulting in the formation of a particle composed of the silver solute from each aerosol droplet. Samples of nanoparticles accumulated on substrates were characterized by fitting particle size data obtained manually from SEM and TEM images to a standard normal distribution. Figure 3 presents TEM images of silver nanoparticles of average particle size 27.6 nm in diameter. TEM images of the particle distributions were taken at various locations of the sample. Figure 4 presents an SEM image of a sample with an average particle size of 176.8 nm, prepared with a feed concentration of  $10^{-4}$  kmol/m<sup>3</sup>, ultrasound power of 4 W, at 800°C. In this image, 51 particles were considered and counted.

The effect of solution concentration on the particle size was studied by varying the solution concentration while maintaining the furnace temperature at 800°C and the ultrasound power to the atomizer at 8 W. The results of this study in Figure 5 show the expected trend, as feed solution concentration is decreased, there is a corresponding decrease in the resultant particle size. The trend was linear on a semilog scale over the six orders of magnitude change in concentration that was studied.

The effect of the ultrasound power applied to the atomizer was studied at a pair of fixed conditions: (i) solution concentration of  $10^{-5}$  kmol/m<sup>3</sup> and a reactor temperature of 900°C while

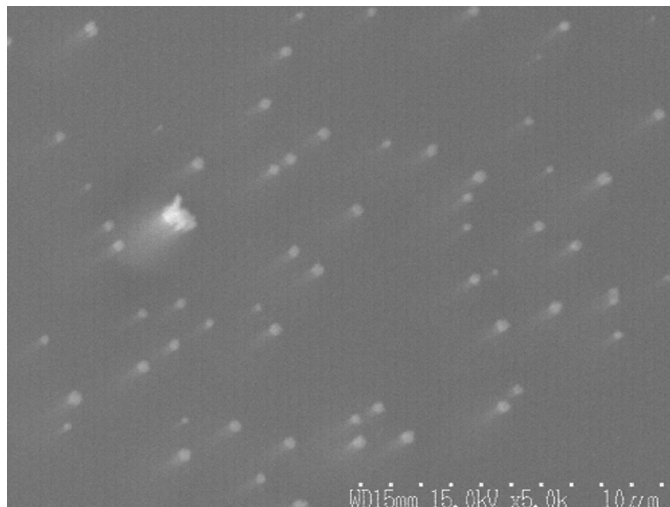


FIG. 4. SEM image of silver nanoparticles at 5,000 $\times$ . The sample was created using a solution concentration of  $10^{-4}$  kmol/m<sup>3</sup>, atomizer ultrasound power of 4 W, and a reactor temperature of 800°C. The average particle diameter is 176 nm.

ultrasonic power was varied from 4 W to 14 W, and (ii) solution concentration of 0.1 kmol/m<sup>3</sup> and temperature of 800°C, with ultrasonic power ranging from 4 W to 8 W. As power to the atomizer was increased, particle size decreased accordingly as seen in Figure 6.

Precursor concentration has no impact on aerosol droplet diameter, as the droplet size was dependent on the power supplied to the atomizer (though there may be a slight effect of concentration on physical properties that influence droplet size, such as surface tension and viscosity, the ultrasonic vibration of

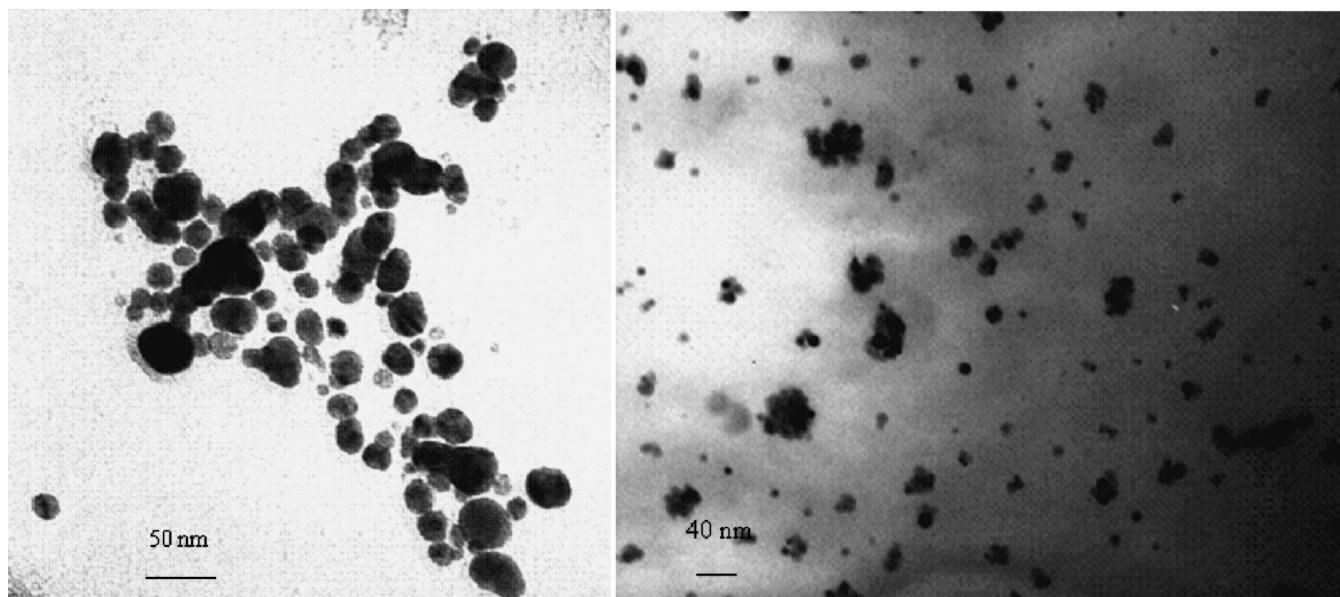


FIG. 3. TEM images of a sample of silver nanoparticles at 150,000 $\times$  (left) and 80,000 $\times$  (right) magnification at of an average diameter of 27.6 nm. The sample was created using a solution concentration of  $10^{-7}$  kmol/m<sup>3</sup>, atomizer power of 8 W, and a reactor temperature of 800°C.

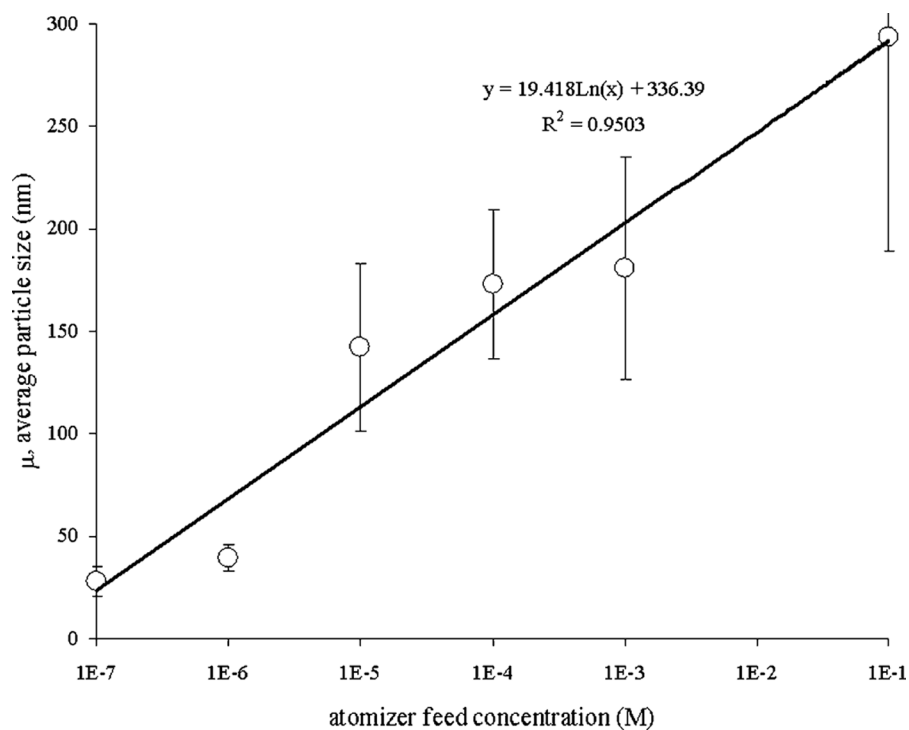


FIG. 5. Effect of solute feed concentration (silver nitrate) to the atomizer on the average particle size ( $\mu$ ) at a fixed reactor temperature of 800°C and an atomizer power of 8 W. Error bars display one standard deviation ( $\sigma$ ) about the mean.

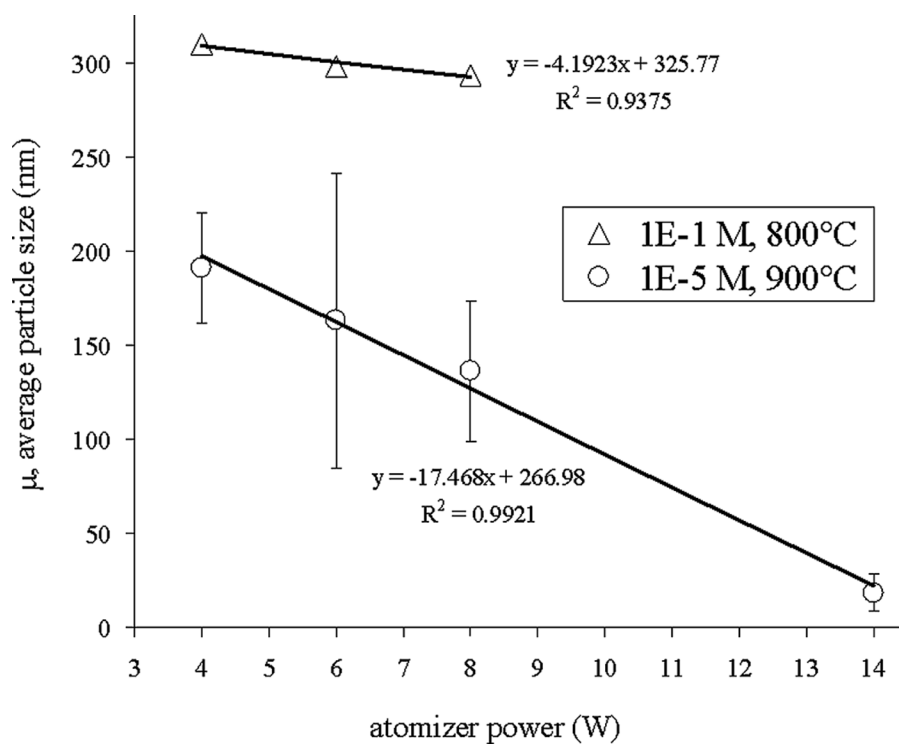


FIG. 6. Effect of power input to the ultrasonic horn of the atomizer on the average particle size ( $\mu$ ) at a reactor temperature of 800°C for a silver nitrate feed concentration of 10<sup>-5</sup> kmol/m<sup>3</sup>, and for a reactor temperature of 900°C for a silver nitrate feed concentration of 10<sup>-1</sup> kmol/m<sup>3</sup>. Error bars on the 10<sup>-5</sup> kmol/m<sup>3</sup> data display one standard deviation ( $\sigma$ ) about the mean.

the nozzle remains the dominant factor affecting droplet size). The ultrasonic power to the atomizer was adjusted to generate aerosols of various size range as is suggested by the operating instructions provided with the unit. If the aerosol diameter is controlled through ultrasonic frequency, the number of atoms within each droplet is managed by selection of the feed concentration, and the degree to which droplet coalesce occurs is limited by controlling total throughput, the particle size of the product can be established within a relatively monodisperse range.

#### 4. CONCLUSIONS

The independent variables of solution concentration and atomizer ultrasound power were observed to have a significant impact on the size of particles produced by spray pyrolysis in producing silver nanoparticles down to 20 nm in diameter. The following conclusions can be established based on the results of this work: (1) one-step spray pyrolysis of ultrasonically-atomized dilute solutions of metal solutes represents a potentially viable means of generating relatively monodisperse particles, with the capability of obtaining a mean particle size less than 20 nm; and (2) feed concentration and ultrasound frequency applied to the atomizer can be adjusted to affect the average particle size and size distribution.

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