Two-component metal-metal and ceramic-metal nanoparticle synthesis by Liquid Flame Spray

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Multicomponent nanoparticles have a great importance in modern material research. Over several decades, flame based aerosol methods have been studied for production of nanoparticles (1). Here we have used Liquid Flame Spray method which was first utilized for glass coloring (2) and has been recently used for single-component particle synthesis (3, 4). The present study takes a look at two comparable systems for two-component nanoparticle synthesis, metal-metal (Ag/Pd) (6) and ceramic-metal (TiO_2/Ag) (7). Ag/Pd-nanoparticles have applications especially in the field of electronics and TiO2/Ag-nanoparticles have unique properties for e.g. photo catalytic applications.

In the Liquid Flame Spray, the liquid solution of precursor is injected as droplets into the high temperature H_2-O_2 flame (T_{max}~3000 ^oC) (2). In the figure 1 is shown the flame axial temperature (4). In the flame, the droplets will evaporate. The new nanoparticles are synthesized by nucleation of the gas phase reaction products of the precursor. Mostly particles are generated by gas-to-particle synthesis but there is still a probability for a minority of the droplets to undergo liquid-to-solid conversion (3). The latter is not a desired route here. Therefore, one aim is to use process parameters which provide full evaporation of the precursor. Important parameters include physical and chemical properties of the precursor which have a strong effect on evaporation and also particle growth mechanism (5, 6, and 7).

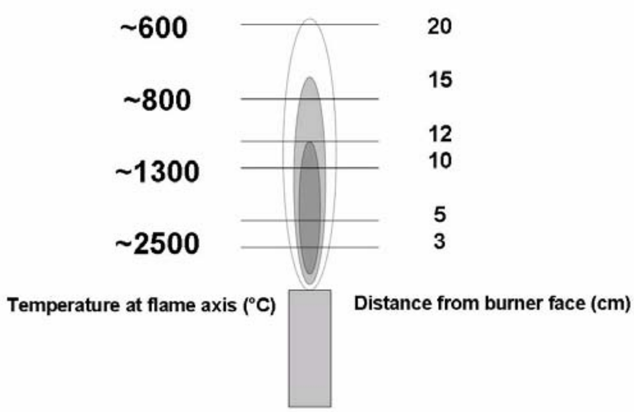

Figure 1. The estimated axial flame temperatures for the sample collecting distances.(4)

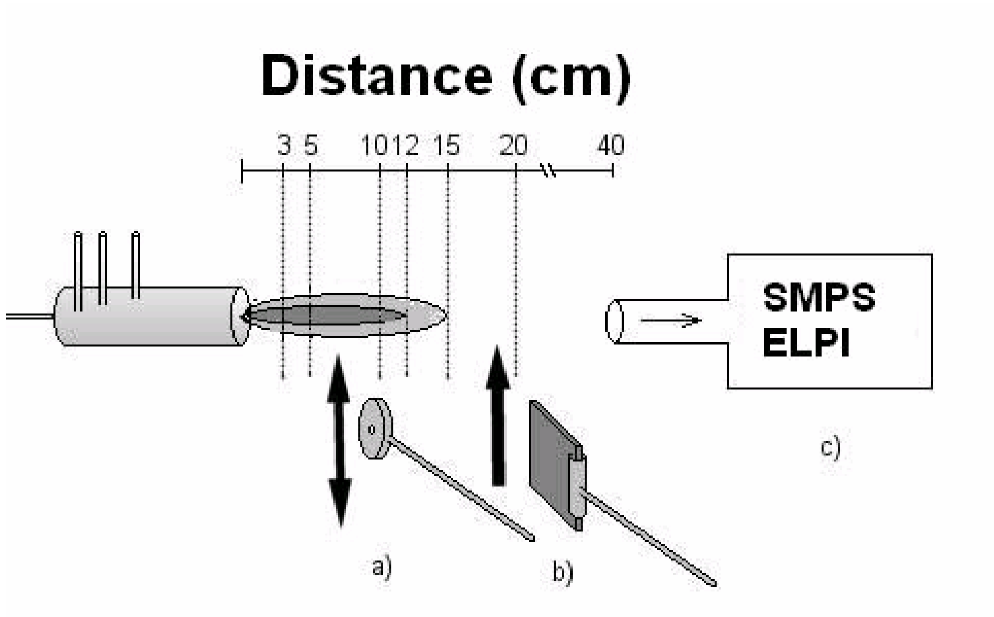

Figure 2. The illustration of LFS spray gun and flame. a) TEM sampling b) steel surface coating for XRD c) aerosol measurement (SMPS, ELPI).(4)

The experimental equipment for both metal-metal and ceramic-metal nanoparticles synthesis were: Transmission Electron Microscopy (with elemental mapping), Energy Dispersive Spectroscopy (EDS), Selected Area Diffraction (SAED), X-Ray Diffraction, Scanning Mobility Particle Sizer (SMPS) and Electrical Low Pressure Impactor (ELPI). In the figure 2 is shown the illustration of spray gun and flame and different analysis methods.

For silver-palladium particle synthesis the used precursors were metal nitrates (AgNO3, Pd(NH3)4NO3) in a water solution. The three Ag/Pd-metal mole ratios: 10-90, 50-50 and 90-10 were used. In the experiments, metal mass flow rates of 0.01-0.8 g/min were covered. The metals were almost completely vaporized in the flame and the generated nanoparticles (10-50 nm) had a quite narrow size distribution (GSD 1.35-1.5). The particle growth for the silver/palladium nanoparticles was collision limited. The mass flow rate e.g. metal vapors concentration in the flame determines the final particle size (Figure 3). The mole ratio of Ag/Pd in the precursor determines the final nanoparticle mole ratio and the mole ratio has no effect on the particle size. The particles were spherical and slightly agglomerated (Figure 4). The synthesized nanoparticles were observed to consist of Ag/Pd-alloy. (6)

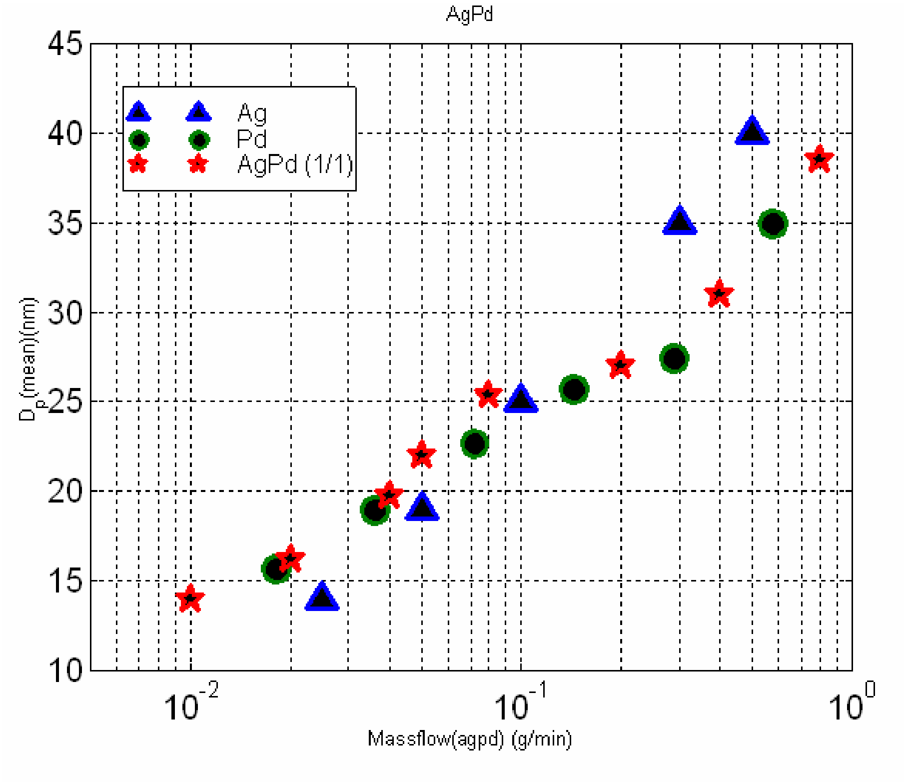

Figure 3. Geometric (number) mean diameters of the generated particles for silver, palladium and silver-palladium compound as a function of metal mass flow rate (6).

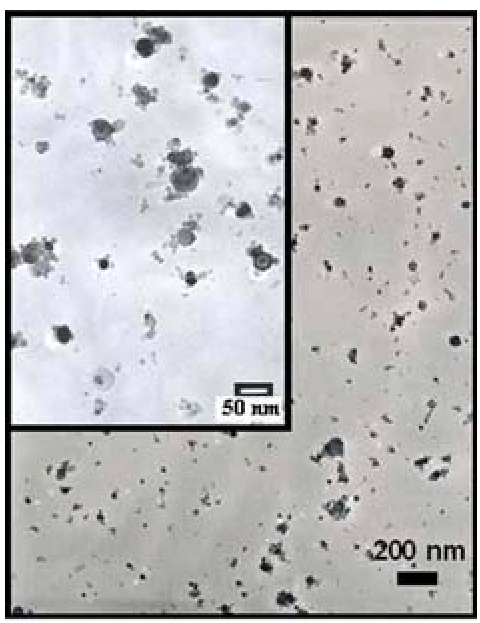

Figure 4. TEM micrograph of Silver-Palladium particles at ratio 50-50 and 0.2 g/min. (6)

The precursors for titania-silver nanoparticle synthesis were titanium(IV)ethoxide (TEOT) and silver nitrate in ethanol solution. The mole fractions in solutions for Ti/Ag were: 99-1, 98-2 and 97-3. The mass flow rates (rate for sum of Ti and Ag mass into the flame) of 6 and ~23 mg/min were covered. In this study, the particle formation process in the flame was also considered. TEM samples were taken at six axial distances from the flame torch: 3, 5, 10, 12, 15 and 20 cm. The precursor of titania (TEOT) is rather volatile (b.p. = 110 -115 oC). Therefore, the droplets are expected to evaporate right after they get into the flame. The synthesized particles were seen to consist of agglomerates. The particle size increases with the axial distance from the flame torch (Figure 5).

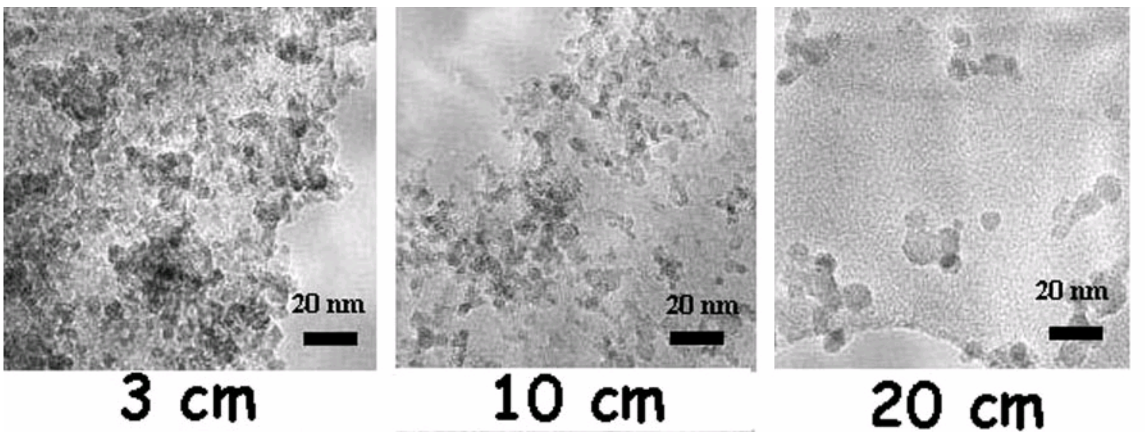

Figure 5. TEM figures from different sampling distances at mass flow rate of 23 mg/min (4).

These studies confirmed that the particles grow by surface growth, coagulation and sintering. The silver doping has an effect on the particle size. At larger amounts of Ag-doping, the size of agglomerates were decreased (Figure 6) (7). The titania agglomerates (d ~ 70-100 nm) containing smaller spherical silver nanoparticles (d~ 1- 5 nm) were detected by elemental mapping and TEM figures. The output is similar to study of Backman et al. who used a flow reactor in their work (8). The crystal form of titania particles was detected to be mostly anatase.

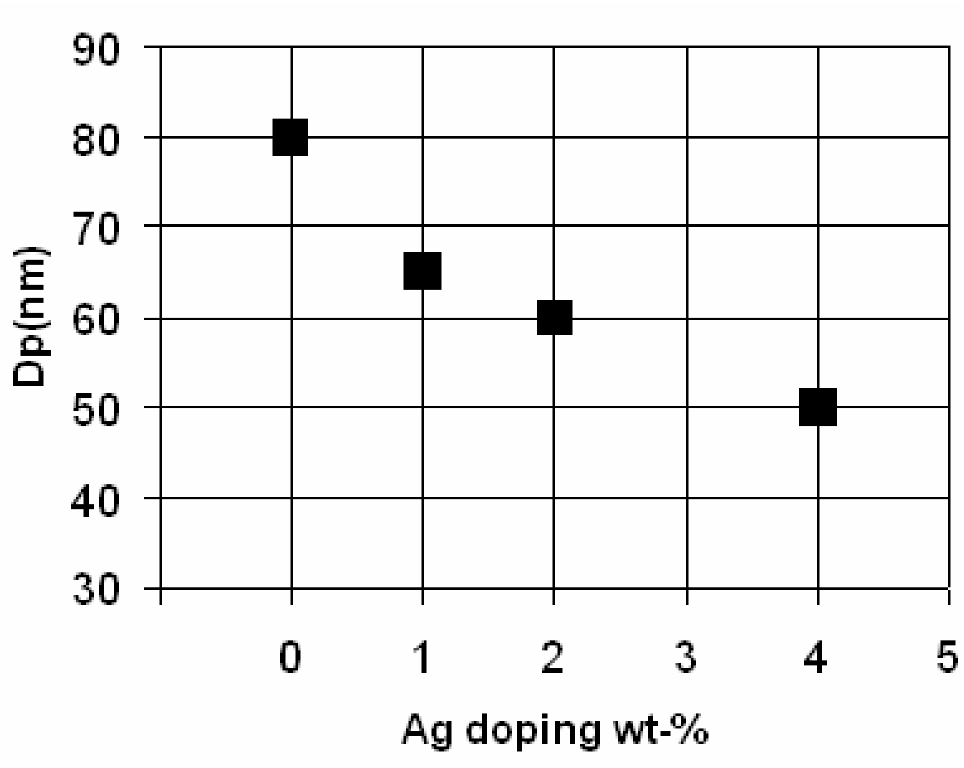

Figure 6. The agglomerate mean diameter as a function of amount of silver doping. (7)

These studies for metal-metal and ceramic-metal nanoparticles synthesis by Liquid Flame Spray highlighted an interesting result. The chemical and physical properties of the precursor seem to have a strong effect on particle growth mechanism in multicomponent particle synthesis. In metal-metal system where silver and palladium have quite similar chemical and physical properties, the growth mechanism is clearly collision limited (6). In the case of synthesis of ceramics for example titania particles the growth mechanism is well known to be coalescence limited (5). In the synthesis of ceramic-metal particles the growth mechanism of ceramic particles is interfered by this metal component in case of titania-silver (7).

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