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Seeded growth of monodisperse and spherical silver nanoparticles

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ABSTRACT

Aiming at spherical and monodisperse silver nanoparticles with diameters up to 100 nm, the potential of heterogeneous nucleation of silver particles was explored. Gold seed particles, mainly produced with a spark discharge generator, were carried by nitrogen through a three-zone tube furnace. Silver was evaporated at 1210 °C in the first zone of the furnace and particle growth and shaping took place in the subsequent zones, heated to 730 °C and 390 °C, respectively. The generated aerosol was monitored by a scanning mobility particle sizer (SMPS), while parameters, such as furnace temperature, seed particle size and concentration and nitrogen carrier gas flow, were investigated. Off-line atomic force microscopy (AFM) and transmission electron microscopy (TEM) were used to characterize the morphology of the silver nanoparticles in addition to the SMPS scans. Spherical silver nanoparticles with a mobility diameter of more than 115 nm and a geometric standard deviation of typically 1.09 or lower at concentrations as large as $5 \times 10^5\ \mathrm{cm}^{-3}$ could be produced. The mobility diameter of the monodisperse aerosol could be varied in the range of 50 nm to 115 nm by changing the furnace temperature or the gold seed particle size. Elemental analysis revealed that the gold from the seed particles formed a homogeneous alloy with the silver (≤ 3.5 at.% of gold). The growth mechanism could not be identified unambiguously since the obtained silver particles could both originate from heterogeneous nucleation of silver vapour on the seed particles or from coagulation and coalescence of the seed particles with smaller, homogeneously nucleated silver particles. Moreover, the narrow size distribution opens the opportunity to obtain an exclusively singly charged, monodisperse calibration aerosol at sufficient concentrations after an additional mobility selection process.

1. Introduction

Metallic nanoparticles are one of the most studied subject within the area of nanoscience. Furthermore, there are already numerous applications in nanotechnology employing metallic nanoparticles, especially silver nanoparticles. Silver nanoparticles are used in many different areas, including metrology (calibration of condensation particle counters (CPCs), CEN TC 264 WG 32), antimicrobial applications (Tran, Nguyen, & Le, 2013), plasmonic applications (Harra et al., 2012) and thermal anchors inside ^{3}He/^{4}He dilution fridges (Clark, Schwarzwälder, Bandi, Maradan, & Zumbühl, 2010), just to mention a few. Full control over particle size and shape is often demanded by technological applications since the optical, electronic,

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magnetic and catalytic properties of nanoparticles crucially depend on their size and shape (Byeon & Kim, 2012). A large surface-to-volume ratio, quantum confinement effects and curvature-induced surface effects are responsible for many novel properties. For example, the size and shape, as well as the dielectric environment of metallic nanoparticles essentially determine the localized surface plasmon resonances of silver nanoparticles (Harra et al., 2012). In metrology, a monodisperse aerosol of known size consisting of spherical particles is required to calibrate differential mobility analyzers (DMAs). Additionally, full traceability in calibration of CPC detection efficiencies requires the use of a monodisperse and singly charged calibration aerosol. Since the particles are classified according to their mobility diameter in aerosol science, spherical particles are a further advantage as it allows to connect the mobility diameter to the real geometric diameter of the particle.

There exist various techniques to generate metallic nanoparticles in general and silver particles in particular. Whereas wet chemical colloidal chemistry and vacuum technologies are associated with drawbacks (e.g. costly equipment) and are tedious to operate, aerosol techniques offer many advantages, such as production of ultra-pure particles (e.g. for noble metal), scalability and an environment friendly and easy production. Commonly, silver nanoparticle aerosols are produced by either liquid flame spray processes (Mäkelä, Keskinen, Forsblom, & Keskinen, 2004), electrospraying of silver colloidal suspensions (Lenggoro, Widiyandari, Hogan, Biswas, & Okuyama, 2007), glowing wire generators (Peineke, Attoui, & Schmidt-Ott, 2006), spark discharge generators (Byeon, Park, & Hwang, 2008), (Tabrizi, Ullmann, Vons, Lafont, & Schmidt-Ott, 2009) or by the evaporation/condensation method of silver in a tube furnace (Scheibel & Porstendörfer, 1983). The latter is one of the simplest methods to generate silver nanoparticles. Thereby, silver is evaporated in a tube furnace and the hot silver vapour, when leaving the furnace, is immediately cooled down, which forces the silver vapour to condense into small primary nanoparticles (a few nanometres in diameter). Due to a high concentration of the primary silver nanoparticles, coagulation, leading to larger and fractal-like nanoparticles, is mostly unavoidable. Heating the silver aerosol in a second furnace transforms the fractal-like particles into compact spheres (Schmidt-Ott, 1988, Shimada, Seto, & Okuyama, 1994). Larger spherical but polydisperse particles (up to ≈ 200 nm) can be produced by inserting a coagulation volume between the two furnaces (Ku & Maynard, 2006). A monodispere aerosol of spherical silver nanoparticles with a mobility diameter of up to 100 nm was recently produced by Harra et al. (2012) using this technique. In this case however, monodispersity was achieved by the introduction of a DMA in front of the second furnace.

Inspired by the heterogeneous nucleation of water in the atmosphere (Pruppacher & Klett, 1997) and by the SCAR (Yli-Ojanperä, Mäkelä, Marjamäki, Rostedt, & Keskinen, 2010), we investigated the potential of heterogenous nucleation of silver. The main difference between homogeneous and heterogeneous nucleation is the absence, respectively, the presence of a nucleation site (e.g. the surface of a seed particle). The energy barrier for the formation of a stable nucleus of the condensed phase is reduced in the case of heterogeneous nucleation and therefore, the nucleation rate is increased (Hinds, 1982). The reduced energy barrier for heterogeneous nucleation can also be expressed as a reduced supersaturation ratio, which is needed for an appreciable nucleation rate and subsequent growth of particles. In the case of heterogeneous nucleation, the number of nucleation sites is controlled by the number of seed particles. One can expect heterogeneous nucleation to yield larger particles than homogeneous nucleation, since the available vapour evenly distributes over a smaller number of nucleation sites. Moreover, a controlled nucleation and growth, starting from monodisperse seed particles, can be expected to yield a narrow and controllable size distribution of silver nanoparticles.

Coating of nanoparticles or the production of core–shell nanoparticles is closely related to the heterogeneous generation of nanoparticles. Boies, Lei, Calder, and Girshick (2011) and Zdanowicz et al. (2013) reported the successful decoration of silica nanoparticles with gold and silver, respectively. However, in both cases the seed silica nanoparticles are substantially larger than the metallic nanoparticles on its surface. Furthermore, the metal nanoparticles do not converge into a continuous shell. The gas-phase production of binary alloyed nanoparticles consisting of gallium and gold in varying configuration (core–shell or fully alloyed particles) were reported by Karlsson, Deppert, Magnusson, Karlsson, and Malm (2004).

The potential of heterogenous nucleation of silver in that respect was explored with different seed particle materials and generation methods. The resulting silver nanoparticles were first characterized with a scanning mobility particle sizer (SMPS), consisting of a differential mobility analyzer (DMA) and a condensation particle counter (CPC). The morphology of the nanoparticles was further investigated with off-line atomic force microscopy (AFM) and transmission electron microscopy (TEM).

In this study, we present a novel generation method of silver nanoparticles based on heterogeneous nucleation of silver on gold seed particles, aiming to obtain spherical nanoparticles larger than 100 nm. The experimental setup is presented and explained in Section 2, whereas Section 3 contains the results and a discussion.

2. Materials and methods

The following section explains the generation of heterogeneously nucleated silver particles using a single furnace setup. The generation of the silver particles can be divided into two steps: the formation of appropriate seed particles (e.g. gold seed particles suspended in N_2 as a carrier gas) and the subsequent growth of silver particles in a single furnace (see Fig. 1). After the generation of the silver particles, the aerosol was analyzed and monitored using an SMPS, a CPC or particles were deposited onto substrates by means of electrostatic precipitation for further off-line analysis.