Generation and Sizing of Particles for Aerosol-Based Nanotechnology

George Biskos 1,2*,
Faculty of Applied Sciences, Delft University of Technology 1
Department of Environmental Studies, University of the Aegean 2

Vincent Vons, Caner U. Yurteri and Andreas Schmidt-Ott
Faculty of Applied Sciences, Delft University of Technology 1

Abstract

Traditionally, the generation of nanoparticles for technological applications has been mostly performed by classical wet chemistry or lithographic methods, and their size has been commonly determined in situ by electron microscopy techniques. Advances in aerosol technology over the past 30 years have provided methods that enable the generation and measurement of nanoscale building blocks, and have opened up new opportunities in the assembly of nanostructured materials and nanodevices. This article provides a brief review on state-of-the-art techniques for generating nanoparticles of well-defined size and chemical composition in view of applications in nanotechnology. Covering atomization techniques from the liquid phase and nanoparticle synthesis from the gas phase, we discuss the advantages and limitations of each method. Considering the advantages of on-line methods that aerosols instruments offer, we describe the most efficient techniques for measuring the size distributions of airborne nanosize particles. Finally, we provide a brief discussion on existing and emerging applications of aerosol-based nanotechnology.

Keywords: gas phase, nanoparticle synthesis, nanostructure, nanomaterials

1. Introduction

Developing methods to manipulate matter and to assemble structures on the nanometer scale is of great interest in many technological applications. Nanostructured materials exhibit novel and enhanced properties compared to their bulk counterparts. Having characteristic scales below 100 nm, the behavior of these materials is primarily determined by the physical and chemical properties of their building blocks, i.e. the nanoparticles, which in turn depend on their chemical composition and size. By controlling the size and composition of these building-block nanoparticles, one can tailor nanostructured materials for specific applications in a relatively simple manner.

Traditionally, the term nanoparticle is used for solid or liquid particles of sizes below 100 nm (cf. Hinds 1999; Baron and Willeke 2001). For particles containing 2 and up to approx. $10^3$ atoms or molecules, the term cluster is often used. In most of the synthesis methods discussed in this paper, the sizes of the particles range from a few nm up to 50 nm.

Nanoparticles can be synthesized in the liquid or the gas phase. Liquid routes such as incipient wetness impregnation, coprecipitation and grafting, and sol-gel, are batch processes that often involve large amounts of solvents. A great drawback of these methods is the introduction of impurities. These are always more abundant in liquids than in gases, and even the most advanced methods apply surfactants that contaminate the particles produced. Nanoparticle formation in the gas phase (i.e. aerosol formation) on the other hand, offers high purity and the ability to synthesize nanostructures in a continuous process (Pratsinis and Mastrangelo 1989; Mädler et al. 2002). In addition, aerosol techniques reduce waste formation thereby making them more attractive for large-
Aerosol-based nanotechnology includes the mechanisms for generating nanoparticles, the techniques for measuring their physical and chemical properties, as well as the processes used for their deposition to form films or specific structures. Aerosol nanoparticles can be generated by a range of methods depending on the desired composition and size. Advances in the field of aerosol instrumentation over the past decades have allowed for high accuracy and precision measurements of the physical and chemical properties of suspended nanoparticles. In addition, the simplicity of the methods for manipulating and depositing gas-suspended nanoparticles to form specific structures makes aerosol science and technology one of the enabling disciplines in the broader field of nanotechnology.

As a result of the growing advances in aerosol technology, nanostructured materials with unique properties are already being fabricated via synthesis in the gas phase. For example, aerosol-based methods are being used in the fabrication of opto- and nano-electronic devices. In addition, nanoparticles synthesized in the gas phase have been shown to have enhanced catalytic (e.g., Stark et al. 2002) and gas sensing properties (e.g., Kennedy et al. 2000). Finally, aerosol techniques are believed to have great potential for medical applications (e.g., Tartaj et al. 2003).

Early reviews on aerosol nanoparticle synthesis have been given by Gurav et al. (1993) and by Kruis et al. (1998), whereas Heidenreich et al. (2003) provided a broader overview on the technical aspects of aerosol science and technology. Other reviews have focused on specific particle generation methods and their applications. For example, Grace and Marijnisen (1994) and recently Jaworek (2008) have provided overviews of particle generation from electrospray atomization. Gutsch et al. (2002) and Swihart (2003) have described the available methods for synthesizing particles from the gas phase, whereas Strobel et al. (2006) and Strobel and Pratsinis (2007) have reviewed particle synthesis techniques using flame reactors for specific applications. A comprehensive description on the available aerosol instruments with emphasis on the measurements of atmospheric particles is given by McMurry (2000). In this paper, we review various methods for generating and sizing aerosol nanoparticles, and highlight some technological applications where aerosol techniques are employed.

2. Aerosol Nanoparticle Generation

Nanoparticle generation via the aerosol route provides a powerful way of manufacturing nanostructured materials of well-defined morphology and chemical composition. Aerosol nanoparticles can be produced by either atomizing a solution of specific composition to form droplets that crystallize to solid particles upon subsequent evaporation of the solvent, or from gas-to-particle conversion via nucleation and growth by condensation and coagulation. Atomization of solutions can be achieved by mechanical methods (i.e., nebulization) or by applying an electrostatic potential between the solution and a counter electrode (i.e., electrophoresis). Gas-to-particle synthesis can be achieved by using furnace, flame, plasma, or laser reactors, glowing wires and spark discharges. In the following paragraphs, we provide a brief overview of the techniques for generating aerosol nanosized particles as well as those that in our opinion have the largest potential for applications in nanotechnology.

2.1 Atomization of liquid solutions

One way of generating aerosol particles is by atomizing liquid solutions of a specified chemical composition. Atomizers can be categorized depending on the forces applied to break up the liquid into small airborne droplets (Hinds 1999). For aerosol-based applications in nanotechnology, the most appropriate methods are pneumatic, ultrasonic, and electrospray atomization because they produce relatively small primary droplets (1-10 μm in diameter). Other methods, e.g., spinning-disk atomizers, produce much larger primary droplets (> 100 μm) and in much lower concentrations, making them inappropriate for use in aerosol-based applications in nanotechnology.

Upon evaporation of the solvent of the atomized droplet, the solute crystallizes to form solid particles. Depending on the solute concentration of the primary droplets, solid nanoparticles of different diameters can be generated. Nanosize solid particles of well-defined composition can be generated by the atomization of solutions of less than 0.1 wt% and subsequent evaporation of the solvent. Fracturing and chemical treatment of the particles can be applied by pyrolysis of the atomized droplets. This technique is in many cases much more favorable because it leads to higher particle number concentrations. Compared to synthesis methods from the gas phase, one limitation of all atomization techniques is the presence of impurities in the solvent. Unless these impurities...
are volatile, they remain on the crystallized solid particles thereby affecting their physical and chemical properties in an uncontrollable manner. The relatively low particle concentration of the generated aerosols restricts these methods for applications that require only small amounts of particles.

### 2.1.1 Pneumatic atomization (nebulization)

In pneumatic atomizers, pressurized air is introduced via an orifice in such a way that the expanding air stream moves perpendicularly to the end of a tube connected to the liquid reservoir. Due to the Bernoulli effect, the low pressure created at the tube end draws the liquid from the reservoir into the air stream. The high forces occurring at the air-liquid interface cause the solution to break up into small liquid droplets which become airborne and are carried away by the air flow. The spray stream is then directed onto an impactor plate where the larger droplets are deposited and are either directed back to the liquid reservoir or break up into smaller droplets and exit the atomizer in the outlet stream.

Depending on the geometric characteristics and the operating conditions, pneumatic atomizers produce primary droplets in the size range of 1-10 μm and concentrations from 5 to 50 gm⁻³. The particles generated by pneumatic atomization are polydisperse (σₚ of 1.4 or greater) with a moderate charging level that depends on particle diameter and solute concentration (Forsyth et al. 1998; Tsai et al. 2006). If their size has to be controlled within a narrower range, a classifier (commonly a differential mobility analyzer, cf. § 3.1) has to be employed downstream of the particle generator.

Many designs of pneumatic aerosol atomizers are described in the literature and are commercially available (e.g. May 1973; Liu and Lee 1975). Most of them have been developed for producing particles for inhalation therapy or for calibrating aerosol instruments. Despite this, pneumatic atomization has been successfully used for synthesizing aerosol nanoparticles from colloid solutions for technological applications (e.g. Hampsey et al. 2005).

### 2.1.2 Ultrasonic atomization

Another way of breaking up a solution to micron-sized droplets is by ultrasonically vibrating its air-liquid interface (Wood and Loomis 1927). The mechanical energy applied from a piezoelectric crystal to the system agitates the surface of the solution, thereby creating capillary waves that break up into micron-sized droplets (Faraday 1831; Kelvin 1871; Rayleigh 1883; Lang 1962). A particle-free air stream is passed over the solution to take away the generated airborne particles. The diameter of the primary droplets produced is a function of the frequency of vibration and the physical properties of the solution, i.e. surface tension and density.

Two mechanisms are responsible for the formation of droplets from ultrasonic atomization: the formation of capillary waves and the break-up of cavitation bubbles. Boguslavskii and Eknadiosyants (1969) combined both mechanisms theoretically and suggested that drop formation is initiated by capillary waves initiated and driven by cavitation bubbles. Cavitation is obviously accountable for at least a large proportion of the disintegration from thick and viscous films, in particular at high ultrasonic intensities, but atomization cannot be explained by cavitation effects alone. As the power supplied to the atomizer and the throughput of the atomizer is increased, cavitation effects become more predominant. However, the interaction between them and the limits to which one mechanism could predominate over the other are still under debate and require both experimental and theoretical investigation. The most recent reviews of mechanisms related to ultrasonic droplet formation as well as alternative mechanisms for droplet ejection are provided by Barreras et al. (2002) and Yule and Al-Suleimani (2000).

Due to resonance modes and the limitations of the piezoelectric material, ultrasonic atomizers are limited by a maximum frequency of around 3 MHz. Frequencies greater than that are required to generate droplets of less than 2 μm in diameter. Although frequencies up to the GHz range can be applied using surface acoustic wave devices, the performance of ultrasonic atomizers mainly depends on selection of the driving method and vibration mode (Kurosawa et al. 1995; Ju et al. 2008). As one might expect, the dimensions of transducers for operation at high frequencies are small to limit the possibility of multimode operation. This makes it necessary for throughputs to be particularly low.

A form of ultrasonic nozzle used for generating standard size droplets is the Vibrating Orifice Aerosol Generator (VOAG) (Berglund and Liu 1973). The principle of the VOAG is based on the instability and break-up of a cylindrical liquid jet and dispersion in a proper manner; the size range of droplets can be controlled between 0.25 and 50 μm.

Compared to pneumatic atomizers, ultrasonic atomizers can generate highly monodisperse particles (σₚ of less than 1.02). Although the performance of
ultrasonic atomizers remains inherently stable, their greatest drawback is that the particle number concentrations are significantly lower compared to other techniques.

2.1.3 Electrohydrodynamic atomization

Electrohydrodynamic atomization (EHDA), or electrospraying, is a method for producing very fine monodisperse droplets from a liquid under the influence of electrical forces. By controlling the liquid flow rate and the electrostatic potential between the liquid and the counter electrode, droplets within a narrow size range with mean diameters from nanometers up to several micrometers can be generated. Besides generating monodisperse droplets, electrosprays are also distinguished by their self-dispersing nature due to columbic repulsion, the possibility of trajectory control of the produced charged droplets, and the reduced risk of nozzle clogging due to large size of the orifice compared to the size of the droplets.

Different spraying modes can be obtained depending on the strength of the electric stresses relative to the surface tension stress on the liquid surface and on the inertia of the liquid leaving the nozzle (Zeleny 1914; Zeleny 1917; Cloupeau and Prunetfoch 1994; Grace and Marijnissen 1994). For the production of monodisperse nanoparticles, the so-called cone-jet mode is desirable. In this mode, the liquid is typically pumped through a nozzle at a flow rate of the order of $\mu l \, hr^{-1}$ to $ml \, hr^{-1}$, and an electric field is applied between the nozzle and a counter electrode. This electric field induces a surface charge in the growing meniscus created at the nozzle. Due to this surface charge and the electric field, an electric stress is created on the liquid-air interface. Depending on the electric field strength and the liquid flow rate, the electric stress can overcome the surface tension stress and transform the shape of the liquid surface from a dome to a cone, i.e. the Taylor cone (Taylor 1964). The tangential component of the electric field accelerates the charge carriers at the liquid surface toward the cone apex. These ions collide with liquid molecules, thereby accelerating the surrounding liquid. As a result, a thin liquid jet emerges at the cone apex (Zeleny 1914; Zeleny 1917). Depending on the ratio of the normal electric stress to the surface tension stress on the jet surface, the jet either breaks up due to axisymmetric instabilities, also called varicose instabilities, or due to varicose and lateral instabilities, called kink instabilities (Fernandez de la Mora and Loscertales 1994; Rosell-Lompart and Fernandez de la Mora 1994; Tang and Gomez 1995; Hartman et al. 2000). Monodisperse droplets are produced at a low stress ratio in the varicose break-up mode.

The droplets produced by EHDA carry a high electric charge in the range of the Rayleigh charge limit (Hartman et al. 2000). Upon evaporation, the droplets exceed the Rayleigh charge limit, resulting in their shattering into smaller droplets. To avoid Rayleigh disintegration and to control particle size distribution, the droplets have to be completely or partially neutralized (Davis and Bridges 1994; Smith et al. 2002).

Scaling laws can be used to estimate the operational conditions for producing nanodroplets of a certain size. Fernandez de la Mora and Loscertales (1994), and Gañán-Calvo et al. (1997) have provided scaling laws for estimating the size of the droplets produced (or jet diameter) and the electric current required for a given liquid to be sprayed in the cone-jet mode as a function of liquid properties and flow rate. Hartman and co-workers refined the scaling laws for EHDA in the cone-jet mode using theoretically derived models for the cone, jet and droplet size (Hartman et al. 1999; Hartman et al. 2000). Recent studies on EHDA have focused on the quantitative understanding of the transport and evaporation of the droplets as they leave the nozzle (cf. Wilhelm et al. 2003) in order to provide controlled film morphology in applications such as electroceramics (Wilhelm et al. 2005) and bone prosthetics (Leeuwenburgh et al. 2006).

Several authors have already reported on the production of nanoparticles using the EHDA route (Fernandez de la Mora et al. 1990; Rulison and Flagan 1994; Hull et al. 1997; Lenggoro et al. 2000; Ciach et al. 2002; van Erven et al. 2005). A recent review on the subject is provided by Jaworek and Sobczyk (2008). If the right solvent properties are achieved, EHDA can be seen as a generic way to produce well-defined nanoparticles of various compositions on demand (Marijnissen et al. 2008).

Industrial implementation of EHDA, however, is limited by the low production rates. In order to generate fairly small-sized particles, extremely low flow rates are required. For example, flow rates of less than 0.1 ml h$^{-1}$ for a single nozzle are needed to obtain droplets in a micrometer diameter range. It is impossible to increase the throughput of material production from a single nozzle by simply increasing the flow rate. Thus an out-scaling rather than up-scaling is needed for boosting the number of injection ports.

There have been many efforts reported on the out-scaling of EHDA including the use of an array of capillaries, an array of holes in combination with non-wetting material, serrations, grooves, multijet mode
operation, and MEMS-based manufacturing as summarized by Deng and Gomez (2007). Increasing the number of capillary nozzles seems to be a simple and effective way of increasing the number of droplets. However, out-scaling mainly suffers from electric field intensity variations and thus droplet size changes from nozzle to nozzle.

2.1.4 Spray pyrolysis

Suspended solution droplets produced by atomization need drying in order to produce solid particles upon crystallization of the solute in most applications. Depending on the temperature used for conditioning the droplets, the processes can be classified as freeze drying, spray drying and spray pyrolysis. Although all three processes are very similar, the lower temperature associated with the freeze and spray drying prevent any reactions from taking place within the particles (cf. Baron and Willeke 2001). In spray pyrolysis on the other hand, the high temperatures not only rapidly evaporate the solvent and initiate reactions within the solution droplets, but can also cause fragmentation of the particles. As a result, solid particles smaller than 100 nm can be easily produced by spray pyrolysis, making the process very favorable for applications in nanotechnology. Solid particles produced by the low-temperature drying of atomized solution droplets (i.e. freeze and spray drying) are typically larger.

In spray pyrolysis, the atomized particles are heated in a furnace (e.g. Messing et al. 1993), a flame (e.g. Mädler et al. 2002), or a laser beam (e.g. Cauchetier et al. 1994). The high temperatures cause rapid evaporation of the solvent of the droplets and the initiation of inter-particle reactions that lead to the final product. The physical (size, morphology, and density) and chemical properties of the particles generated by spray pyrolysis depend on the composition of the liquid precursors, the atomization method, and the operating conditions of the apparatus. Solid particles are formed with proper choice of the precursor solution and careful control of the temperature history of the particles, but morphology control is still largely an empirical process (Sproson et al. 1986; Lenggoro et al. 2000). Often, hollow or fragmented particles are obtained when the solvent evaporation rate is too high compared to the rate of crystallization.

Particles of a uniform composition and size can be produced via spray pyrolysis. A great advantage compared to particle synthesis from the gas phase (cf. § 2.2) is that multicomponent materials can be easily produced by controlling the stoichiometry of the precursor solution. Particle synthesis techniques from the gas phase introduce a higher difficulty in manufacturing multicomponent particles because of the differences in the pressures and the nucleation/condensation rates of the involved vapors (Gurav et al. 1993). In addition, the capability of producing unagglomerated and high-purity particles makes spray pyrolysis a favorable process for many applications.

Spray pyrolysis at low pressures has been shown to produce particles of a much smaller diameter compared to higher pressure systems (e.g. Kang and Park 1996). In low-pressure spray pyrolysis, the solvent evaporation rate is much higher than the solute crystallization rate. As a result, larger particles are fragmented into smaller pieces that undergo simultaneous solvent evaporation to produce nanoparticles or weakly agglomerated particles, thereby avoiding the formation of hollow particles. In the case of low-pressure spray pyrolysis, particle morphology is highly dependent on the temperature of the heating section, whereas the solubility of the precursor solutions can greatly influence the degree of agglomeration of the particles (Lenggoro et al. 2003).

Apart from reaction furnaces, lasers (e.g. Cauchetier et al. 1994) and flames (e.g. Mädler et al. 2002) have also been used to pyrolyse atomized aerosol droplets. In laser spray pyrolysis systems, the droplets generated by atomization are passed through a laser beam allowing highly localized heating and subsequent rapid cooling. Heating is generally done using lasers whose energy is either absorbed by one of the precursors or by an inert photosensitizer such as sulfur hexafluoride. In flame spray pyrolysis, atomized particles are directed into a flame. Two types of flame spray pyrolysis are identified: in the first case the atomized droplets sustain the flame that is made by evaporating and burning droplets, and in the second case a supporting fuel is supplied separately from the precursor-atomized droplets. Particles with sizes from 1 to 200 nm at production rates that reach up to 250 g h⁻¹ have been produced using flame spray pyrolysis (e.g. Laine et al. 1999).

2.2 Particle synthesis from the gas phase

Material evaporation followed by subsequent nucleation and condensation in an inert gas is a widely used approach for generating aerosol particles of uniform chemical composition. The great advantage of particle synthesis from the gas phase is the high purity and the high production rates (Pratsinis and Mastrangelo 1989). In addition, when the cooling of the
gas-vapor system is well controlled, the morphology and size of the particles can be precisely adjusted.

Various energy sources can be used to evaporate materials for particle synthesis in the gas phase. Furnace reactors, glowing wires, and spark discharges use electrical energy to heat and vaporize the desired materials. Flame reactors utilize the heat from combustion to oxidize the vapors which then form clusters and nanoparticles in the cooler regions of the reactor. Plasma and laser reactors utilize the high energy of an ionized gas (plasma), whereas laser reactors employ the high energy and precision of a laser beam.

Particle synthesis from the gas phase is most appropriate for generating single-component particles. One of the great advantages of gas-phase routes for particle synthesis is that small high-purity particles within a very narrow size range can be generated in great quantities. Although several studies have shown that synthesis of binary and ternary mixed particles can be achieved via the gas-phase route, these methods are not as convenient for producing multicomponent particles because differences in the vapor pressures and subsequently in the nucleation and growth rates of the various species can easily lead to internally and externally mixed aerosols. Other drawbacks include the formation of agglomerates and problems in handling hazardous gases.

The following paragraphs outline some of the most commonly used methods for evaporating bulk materials for aerosol nanoparticle synthesis in the gas phase.

2.2.1 Furnace generators

Applying heat to evaporate materials is the most straightforward technique for synthesizing high-purity nanoparticles in the gas phase. In practice, the materials of interest are evaporated by heating in a tubular flow reactor, typically at atmospheric pressure. A gas stream is passed over the evaporating material to carry the vapors away from the heating section of the generator. As the vapors cool downstream of the heating section, they nucleate into clusters containing a few thousands of atoms or molecules which subsequently grow to nanoparticles by coagulation and condensation. The residence times and cooling rates can be adjusted to allow good control over particle size and morphology.

Furnace generators have been successfully used to generate nanoparticles of a range of compositions (Scheibel and Porstendörfer 1983; Gurav et al. 1994). Employing a differential mobility analyzer (cf. § 3.1) downstream of the generator, many research groups have produced monodisperse nanometer-sized particles made of noble metals (e.g. Magnusson et al. 1999; Lehtinen et al. 2004) and semiconductors (e.g. Kruis et al. 2000). One drawback of this technique is that for sizes larger than a few tens of nanometers, the particle morphology becomes irregular since agglomeration occurs as a result of the high particle concentrations. Although for some applications the agglomerated shape of the particles may not be a great problem, generation of uniformly shaped particles is desired in many cases.

Restructuring of the particles can be accomplished by after-treating the agglomerated particles. Depending on the chemical composition, different treatment techniques can be used for particle restructuring. Metal particles for example, can be sintered by heating them up to moderate temperatures (e.g. Schmidt-Ott 1988; Shimada et al. 1994; Ku and Maynard 2006). Salt particles, on the other hand, can restructure upon interaction with water vapor (cf. Mikhailov et al. 2004; Biskos et al. 2006).

Another limitation of the furnace generators is that the material to be evaporated needs to have a much lower melting point than that of the material used for the inner walls of the furnace. If this is not the case, then vapors emanating from the inner walls of the furnace can contaminate the particles. As a result, the production of particles from metals with a high melting point is difficult using furnace reactors. In an attempt to minimize particle impurities from the heated walls and the required heating energy of furnace reactors, Jung et al. (2006) proposed the use of a small ceramic heater for the evaporation of various metals to form aerosol particles, and demonstrated that high-purity silver particles can be generated in this way.

2.2.2 Glowing-wire aerosol generator

There is a need for clean particle production for all applications where surface contamination has an impact on basic properties. This is generally the case for particles smaller than some tens of nanometers and to a larger extent in the range of atomic clusters, where every single atom matters. The glowing wire method fulfills the condition of extreme purity, and very recently it has been demonstrated that atomic cluster production with this method is feasible (Peineke et al. 2008). Material is evaporated from a resistively heated wire and subsequently quenched by a gas stream. The high purity achieved by the glowing wire method arises from the fact that only
the particle-forming material is heated, which avoids hot surfaces as sources of contaminants. The amount of material produced hardly reaches 1 µg hr⁻¹, so that possible applications are restricted to those that require only small amounts such as gas sensors (e.g. Favier et al. 2001).

The method was introduced by Schmidt-Ott et al. (1980) and has been applied for the production of metallic particles for research purposes since then (e.g. Burtscher et al. 1982; Müller et al. 1987; Schmidt-Ott et al. 1997; Fernandez de la Mora et al. 2003; Nasibulin et al. 2005). The fact that a significant fraction of the particles formed is charged is of special interest because the aerosol is directly applicable for mobility classification, avoiding additional charging which usually introduces contaminants, as shown by de la Mora et al. (2003). The self-charging effect has been studied and explained in a recent publication by Peineke and Schmidt-Ott (2008). The extreme purity achieved by this method was demonstrated by the group of Burtscher and Schmidt-Ott (Müller et al. 1987). More recently, Peineke et al. (2006) have examined the glowing wire method more systematically, and in a very recent unpublished study of the group, it was demonstrated that a glowing wire can be applied as a source of atomic clusters. Together with the newest developments in mobility analyzers for the ionic range, this technique introduces aerosol technology into the domain of atomic cluster research.

Nanoparticles are formed by condensation from a supersaturated vapor. The material is evaporated by passing a high current through a conducting wire suspended in a flowing inert gas. By mixing with the gas, the vapor is drastically quenched, reaching supersaturations higher than 10⁶. A minimum evaporation rate is required for particles to be formed by this process. Most metals reach this minimum value below the melting point. A list of metals for which the method is applicable is given by Peineke et al. (2006). Glowing wire generators are usually composed of standard stainless steel UHV parts, making them easy and cost-effective to build. Water cooling may be added to avoid the housing heating up. The wire is resistively heated close to its melting temperature by a DC low-voltage/high-current supply. The output remains most stable when operated under constant voltage U because the heating power P reduces if the resistance R of the wire increases according to, $P = \frac{U^2}{R}$ and wire breakage due to temperature variations and decreasing wire diameter is avoided. The wire diameter changes very slowly, resulting in a change of some 10 mA (<0.1%) during one hour. The constant voltage mode delivers a sufficiently constant aerosol output for most purposes. Electric mobility measurements show that the size distributions of the particles generated by glowing wires are log-normal. The self-charging phenomenon allows the production of high concentrations (10⁵-10⁶ cm⁻³) of monodisperse particles by means of a differential mobility analyzer, if the charged particle concentration is enhanced by biasing the wire potential with respect to the surrounding metal housing (Peineke and Schmidt-Ott 2008).

2.2.3 Spark-discharge generator

Spark discharge is one of the most versatile techniques for generating nanoparticles in the gas phase. The method was introduced by Schwyn et al. (1988) and has been applied by a number of research groups since then (e.g. Evans et al. 2003; Evans et al. 2003; Horvath and Gangl 2003; Roth et al. 2004). The technique has already been used for the production of carbon (Helsper et al. 1993), metals (Schwyn et al. 1988; Tabrizi et al. 2008b), and metal oxide nanoparticles (Kim and Chang 2005; Oh et al. 2007). The particles produced by this method are very similar to those obtained by laser ablation (Ullmann et al. 2002). With respect to this frequently used technique, spark discharge has the advantage of not requiring a laser, applying only inexpensive components and having a potential for scaling-up by operating many sparks in parallel. The method has been characterized in detail in a very recent publication by Tabrizi et al. (2008a). The method has the same advantage of extremely high purity as the glowing wire method, since only the material that forms the nanoparticles is heated. It can be applied to any conductive material including semiconductors. Due to the extremely fast quenching of the vapor, it is unique for mixing materials (Evans et al. 2003). Substantial progress in mixing on an atomic scale as well as a nanoscale on metals that are miscible (Tabrizi et al. 2008b) and immiscible (Tabrizi et al. 2008c) has recently been made and will be published shortly. These new possibilities of mixing on a nanoscale are of great interest, for example in preparing advanced catalysts.

The process of spark discharge is initiated by gas breakdown and formation of a conducting plasma channel. The rapid discharge consists of a current associated with a high temperature (typically 20000 K). As a result, electrode material is evaporated in the vicinity of the spark. This is followed by rapid cooling, initially governed by adiabatic expansion and radia-
tion. Below the evaporation temperature, cooling is dominated by thermal conduction. Because the vapor cloud is small compared to other evaporation-condensation processes, the cooling period at temperatures below the boiling point is relatively small, thereby leading to the formation of high concentrations of very small particles. Spark generators typically consist of a chamber of the order of a few hundred cm$^3$ in volume, in which two opposing cylindrical electrodes are mounted at an adjustable distance. The electrodes which are several mm in diameter and up to a few millimeters apart are connected to a high-voltage power supply, and in parallel to a capacitor with a capacitance of some tens of nF. The power supply delivers a constant current, periodically recharging the capacitor after discharge has occurred at the breakdown voltage. The electric circuit including the spark contains an inductive component, which leads to a damped oscillatory discharge process of a few microseconds in duration (Tabrizi et al. 2008a). Because the current is temporarily reversed during this oscillation, both electrodes are ablated. This would not be the case in a unipolar discharge, because the positive ions in the plasma ablate the cathode more strongly than the electrons ablate the anode. The spark frequency can typically be adjusted up to 1 kHz. Above this frequency a continuous discharge tends to occur. Such a process produces much larger particles (tens of nm in diameter), while fast sparks lead to nanoparticles smaller than 10 nm in diameter.

The mean particle size can be controlled via the energy per spark, which is in turn determined by the capacitance and the distance between the electrodes. The particle mass produced per unit time is proportional to the spark frequency. Separated, unagglomerated particles a few nanometers in size can be obtained if the inert gas flow through the generator is high enough with respect to the spark repetition frequency. In principle, this enables the coating of individual particles when a vapor deposition step is added. The nanoparticulate mass produced is typically a few g kWh$^{-1}$. Using the example of gold it was shown that with gases purified at the spot, the method produces particles which are so clean that sintering of the particles occurs at room temperature, leading to branched solid structures (Tabrizi et al. 2008b). Different electrode materials lead to different mean primary particle sizes and mass production rates, where thermal conductivity, evaporation enthalpy and the boiling point have a major influence. Knowing these properties, an estimate for the mass production rate can be obtained (Tabrizi et al. 2008b).

In the latter publication, it is also shown that if the spark generation of nanoparticles is performed in a standing or almost standing gas in the presence of an electric field, an aerogel is formed. It has a web-like structure that bridges the space between surfaces of different electric potential.

### 2.2.4 Flame synthesis

Using flames has been another popular way of generating particles in the gas phase. Due to the high production rates, flames have been widely employed in industry to produce carbon black and ceramic particles (e.g. titanium dioxide, silica, etc.) for use as material reinforcing agents, and for the manufacture of catalysts and optical fibers (Ulrich 1984; Pratsinis 1998).

Flame reactors for aerosol generation can be classified as vapor- or liquid-fed depending on the state of the reactants used to form the desired particles. Particle formation is initiated by the combustion of vapor- or liquid-phase precursors during the fast temperature increase in the flames, which can reach up to approx. 2500 K. Initially, oxidized vapors form clusters that grow to nanoparticles through further vapor condensation and coagulation with other particles. Depending on the target application, a range of particle compositions can be manufactured by carefully selecting the gas or liquid precursors. The physical properties of the produced particles (i.e. size and morphology) can be tailored by empirically controlling the operating parameters of the flame (i.e. flow rates and temperature gradients). The crystalline structure of the particles can be also adjusted by adding dopants to the feed stream (Vemury and Pratsinis 1995) and by controlling the temperature history of the particles, as has been demonstrated by Jiang et al. (2007) and shown computationally by Johannesssen et al. (2000; 2001) and Tsantilis et al. (2002). The application of external electric fields has also been shown to provide good control of the physical and chemical characteristics of the produced particles (Vemury and Pratsinis 1995; Kammler and Pratsinis 2000; Kammler et al. 2003).

Although the most common application of particle flame synthesis has been the manufacturing of carbon blacks in fuel-rich flames using aromatic hydrocarbons as precursors (cf. Donnet et al. 1993), recent efforts have focused on the oxidation of the metal halide vapors in hydrocarbon-supported flames for generating metal oxide (e.g. Jensen et al. 2000; Arabi-Katbi et al. 2002; Jensen et al. 2003), and alloy nanoparticles (e.g. Stark et al. 2001; Keskinen et al.)
2004; Chakraborty et al. 2005) for a range of applications. The most characteristic example of nanoparticle generation by flame reactors is titanium dioxide, which as a rutile is commonly used in pigments, and as an anatase is preferred in photocatalysis and as an effective UV absorber (Strobel and Pratsinis 2007).

Aggregate formation has been a disadvantage associated with flame particle synthesis as it can lead to problems in consolidation and sintering during the fabrication of large ceramic parts. Recent studies, however, have shown that non-agglomerated (Mueller et al. 2004) or weakly agglomerated particles (Mueller et al. 2004) can be generated in diffusion flames depending on the operating conditions. Another disadvantage is that flames may present difficulties in synthesizing multicomponent particles due to differences in nucleation and growth rates of the various species involved. Despite this difficulty, however, multicomponent particles have been successfully manufactured using aerosol flame reactors (cf. Strobel et al. 2006; Strobel and Pratsinis 2007 and references therein).

The great advantage of flame synthesis is that high particle production rates (up to a few hundreds of g h⁻¹) can be easily achieved at a very low cost. Considering also the flexibility of these methods to control the physical and chemical properties of the particles, flame synthesis is one of the most prominent methods for fabricating particles for applications in nanotechnology.

2.2.5 Plasma synthesis

The number of different types of plasma is very large, and quite a few have been explored for nanoparticle production. Plasmas can be broadly divided into two types: thermal or hot and cold. Hot plasmas are in or close to the local thermodynamic equilibrium, the gas molecules and the free electrons have approximately the same temperature (several thousand K). In cold, non-thermal plasmas, the free electrons have temperatures of several eV, whereas the overall gas temperature is close to ambient.

Particle production with cold plasmas usually starts with a volatile precursor which is introduced into the plasma as a vapor in a carrier gas. The precursor can be hydrocarbons, metal halides, metal organics or volatile silicon compounds. Once introduced into the plasma, the molecules of the precursor are dissociated by the energetic species in the plasma, resulting in a cloud of metal or silicon atoms. Due to the low overall gas temperature, these atoms rapidly nucleate to clusters which then grow to nanoparticles through further condensation of the vapors. Hydrocarbons tend to polymerize under the influence of the active species, eventually they form particles. Vollath and Sickafus (1992) used a cold microwave plasma at reduced pressure to produce metal-oxide nanoparticles. The process takes place between 400 and 750 K, and particles leave the reaction zone carrying charges of the same (positive) sign. This greatly reduces agglomeration, as identically charged particles will repel each other (Vollath and Szabo 2005). This process therefore results in very monodisperse particles. Vollath and co-workers also investigated the subsequent in-situ coating of the nanoparticles using monomethylmetacrylate (MMA) vapor (Vollath and Szabo 1999), which in a second microwave plasma results in polymerization to form a coating of PMMA (Perspex). The only disadvantage of the process is that it requires a vacuum system, as it takes place between 5-100 mbar, also limiting the production rate. The vacuum is required to prevent the plasma from turning into a hot plasma.

At atmospheric pressure, cold plasmas can be generated by using a dielectric barrier discharge (DBD). A non-conductive material such as alumina or borosilicate glass (the dielectric barrier) is placed between two electrodes, between which an oscillating electric field is applied. The dielectric barrier prevents the transition into a hot arc plasma since the charges produced by the discharge are deposited on it (Kunhardt 2000). Using such configurations, simple atmospheric plasma systems using nitrogen, argon or helium as a carrier gas can produce high particle concentrations without requiring a complicated vacuum system.

Particles have been successfully produced from ferrocene, acetylene and hexamethyldisiloxane (Vons et al. 2006), and from titaniumisopropoxide for the production of titania particles (Bai et al. 2004; Chen et al. 2007). Furthermore, this type of plasma can also be used for gas-phase particle coating, both for particles from another DBD plasma or particles produced using other methods (e.g. Lei et al. 2006; Marino et al. 2007). Under certain conditions, particles can be generated by sputtering of the dielectric barrier (Jidenko and Borra 2004). DBD plasmas are used on a large scale for the generation of ozone from air and for water purification, which proves that up-scaling of the process is possible.

Other cold plasma systems have been used for the production of iron and carbon nanoparticle production (Barankin et al. 2006). These systems use a commercial atmospheric pressure plasma jet system described by Nowling et al. in 2002. In these systems,
Particle synthesis in hot plasmas is performed by dissociation of volatile precursors. However, the highly reactive and extremely hot environment of thermal plasmas allows the use of many other feedstocks in the gas, liquid or solid phase. The extreme heat of a thermal plasma can be used to evaporate micron-sized solid particles of nearly any material introduced as an aerosol into the plasma, which can subsequently recondense to nanoparticles under the right conditions. This has been done mostly in inductively coupled (ICP) radiofrequency (RF) plasma torches (Gutsch et al. 2002; Goortani et al. 2006; Ye et al. 2007), and also in thermal microwave plasmas (Weigle et al. 2004). ICP plasmas are generated by applying RF power to a coil wrapped around a quartz tube through which the plasma flows. The coil induces currents on the boundaries of the plasma, thus transferring the energy to sustain it. A separate electrode and ignition system are required to initiate the plasma. The advantage of the ICP is that no electrodes are in contact with the plasma, thereby reducing contamination from electrode wear. To obtain the high cooling rates required to reach the supersaturations sufficient for nanoparticle formation, quench gas is often injected behind the plasma. Liquid-fed ICP processes have been developed with both solutions containing the desired element (Suzuki et al. 1992), or pure liquids (Ishigaki et al. 2005). Using normal spray techniques, the liquid is atomized and the resultant spray is fed to the plasma.

In a direct current (DC) arc, a discharge between two electrodes draws high currents (1-250 A), while the voltage drop over the plasma is rather low, i.e. in the order of a few tens of volts. The high current densities cause the extremely high temperatures. Two different arc configurations have been applied for nanoparticle production: normal arcs and arc jets or plasma torches. Normal DC arcs are used to evaporate the electrode or material contained in a basket or boat-shaped electrode (Mahoney and Andres 1995; Chen et al. 2007), and the vapors are subsequently condensed to form nanoparticles using a high quench gas flow. DC arc jets operate in a similar way to the ICP torches, but the plasma is made by striking a DC arc between an axial cathode and a coaxial anode with a conical gap. A high gas flow between the cathode and the anode forms a high-temperature arc jet downstream of the gap. Nanoparticles are generated by introducing gaseous precursors such as SiCl₄ and CH₄ into the plasma (Rao et al. 1995; Hafiz et al. 2006). Although the electrical circuitry for DC arc jet plasmas is simpler than for ICP plasmas, the fact that the cathode and anode are in contact with the plasma increases the chance of wear of the electrodes and contamination of the product.

Both hot and cold plasmas have their advantages. The hot plasmas all have high production rates, and can operate with many different materials, especially the ICP plasmas. This makes them very interesting for industrial application. They do, however, require very high gas flows and have high power consumption (in the case of ICPs, only 20-40% of the input power actually goes to the plasma, the remainder is lost in associated circuitry; cf. Reece Roth (1995)). High-temperature plasmas usually result in larger particles compared to cold plasmas, mainly due to sintering.

Cold plasmas require the right vapor precursors, which can be quite expensive for some elements, and usually have lower production rates. However, the cold gas temperature is beneficial for energy consumption and getting energy exactly where it is needed (i.e. into the dissociation of the precursor and not the heating of the plasma gas). Furthermore, the low temperature reduces sintering, which is reflected by the fact that the primary particle size for cold plasmas is usually smaller. Cold plasmas are also suitable for the coating of already formed particles in the aerosol phase, as the low temperatures prevent further sintering of the particles.

2.2.6 Laser ablation

Laser ablation is another way of generating nanoparticles from the gas phase. In this method, solid targets are typically rotated in a cylindrical ablation chamber. The beam from an excimer laser enters the ablation chamber through a quartz window onto the target material. Upon interaction of the laser beam with the target material, the surface is heated beyond its boiling point and forms vapors. By increasing the irradiances even more, the vapor becomes superheated and ionized, forming plasma. Carrier gas flowing over the heated surface takes the vapors out of the ablation chamber. As the vapors move away from the ablation region, they cool down and form clusters, which then grow to nanoparticles by further condensation of the vapors and coagulation with other particles. Particles of a range of compositions can be easily generated by changing the target material. Typical mass production rates are of the order of 100 ng per
pulse. Control over the ablated mass is achieved by varying pulse energy and frequency of the laser.

Laser ablation techniques have been employed to produce a range of metal oxide nanoparticles (cf. Kato 1976). Metal oxide particles can be generated by ablating metal oxide targets in an inert gas or pure metals in an oxidizing gas. For example, ablation of aluminum in the presence of oxygen can produce alumina nanoparticles of very high purity (Johnston et al. 1992). Several studies have focused on the operating parameters that control particle size and morphology in laser ablation systems (Sasaki et al. 1998; Camata et al. 2000; Ogawa et al. 2000). An increase in flow rate produces smaller aggregates and smaller primary particles. Increasing pulse energy and pulse frequency causes an increase in the aggregate size, primary particle size, and number concentration. Nevertheless, the size of the primary particles has been shown to range within a narrow size range up to approx. 15 nm, independent of the materials used (Ullmann et al. 2002).

The purity of the aerosol product depends primarily on the purity of the carrier gas and the target material. Since the laser beam is focused on the target, contamination by materials released from other surfaces in the ablation chamber is less likely.

3. Sizing and Counting Aerosol Nanoparticles

There are numerous methods for sizing aerosol particles in the nanometer range. These methods can be classified depending on whether the particles are deposited on a surface or suspended in a gas. The size and morphology of deposited particles can be estimated by microscopy techniques. Scanning and transmission electron microscopes (SEM and TEM, respectively) can be applied for direct size and morphology measurements of deposited nanoparticles. Advanced image analysis software has been developed and used for the rapid estimation of particle size and morphology distributions.

The great advantage of electron microscopy techniques is that they can be applied for a relatively wide range of particle sizes. TEMs for example, allow sizing of particles from the nanometer up to the micrometer range. SEMs typically have a lower size resolution but are also suitable for a similarly wide range of particle sizes. SEM and TEM imaging requires the collection of particles on substrates before examination. One drawback of the microscopic techniques is that particle deposition has to be carefully planned so that the substrates have a good coverage of sample particles. Depending on the composition and size of the particles, evaporation by the high energy beams can also affect the measurements. In this case, special coatings can be applied to the particles prior to imaging in order to overcome this limitation.

Sizing nanoparticles on-line when they are suspended in the gas is in many cases much more favorable due to the ability of probing their dynamic behavior. Although a wide range of techniques is commercially available (e.g. aerodynamic particle sizing, optical particle sizing, etc.), their application depends on the particle size range to be measured. By far the most efficient and widely used method for sizing particles in the nanometer range is by measuring their electrical mobility. Electrical mobility techniques were initially developed to measure ions in gases (Zeleny 1900; Erikson 1921; Zeleny 1929). Around the 1920s and 30s when the technique was widely accepted, researchers started realizing that heavier ions (what we now call nanoparticles) exist in the atmosphere (Erikson 1922; Chapman 1937). Rohmann (1923) was one of the first investigators to employ the method for measuring airborne particles. However, it was not until the 1960s that the technique was seen to be useful for measuring aerosol size distributions and the first mobility analyzers, i.e. the Whitby Aerosol Analyser (Whitby and Clark 1966), became commercially available. A thorough review of the available designs at that time is given by Tammet (1970). A historical retrospect of the developments in electrical mobility measurements is provided by Flagan (1998).

Available instruments for electrical mobility particle measurements are the Scanning Mobility Particle Sizer (SMPS) (Wang and Flagan 1990), the Electrical Aerosol Analyser (EAA) (Whitby and Clark 1966), the Electrical Aerosol Spectrometer of Tartu University (Tammet et al. 1998; Tammet et al. 2002) and the recently announced Differential Mobility Spectrometer (DMS) (Biskos et al. 2002; Biskos et al. 2005) and Engine Exhaust Particle Sizer (EEPS) (Johnson et al. 2004). Although these instruments are all designed to measure aerosol size distributions using the same principles, one might prove better than the others for special applications depending on the concentration of particles, the response, and the spectral resolution required.

The most commonly used electrical mobility spectrometer for measuring nanoparticles is by far the SMPS. Compared to the other instruments that use the same operating principles, the SMPS exhibits very high size resolution, enabling detection of par-
ticle size differences of the order of less than one nanometer. SMPS systems consist of two main parts: the electrostatic classifier and the particle counter. Charged aerosol particles are classified according to their electrical mobility by the classifier (typically a differential mobility analyzer; cf. § 3.1) and their concentration is subsequently measured by the particle counter (a Faraday cup electrometer or a condensation particle counter; cf. § 3.2 and 3.3, respectively). By varying the operating conditions of the classifier, particles having a range of electrical mobilities can be classified in different size bins. The entire particle size distribution can be estimated by measuring the particle number concentrations that correspond to the different size bins. Finally, the measured electrical mobility distributions are converted to particle size distributions using inversion algorithms.

The classifier-counter arrangements can be operated in a scanning (SMPS) or a stepping (DMPS: Differential Mobility Particle Sizer) mode. The next paragraphs give a description of the most widely used electrical mobility classifier (i.e. the Differential Mobility Analyzer, DMA) and particle counters (i.e. the Faraday cup electrometer, and the Condensation Particle Counter, CPC) used in SMPS and DMPS systems.

3.1 The differential mobility analyzer

The DMA consists of two concentric electrodes with the inner rod maintained at a controlled potential and the outer tube electrically grounded. The polydisperse aerosol enters the DMA in a perimetric flow close to the outer electrode surrounding a particle-free sheath flow. The sheath flow is introduced into the DMA from the same end of the column around the central rod and both streams flow in the same direction. A narrow aerosol inlet annulus is designed to uniformly distribute the particles in the main flow of the instrument, which, maintained laminar, facilitates high-resolution classification.

Depending on their polarity, charged particles move towards or away from the high-voltage central rod, whereas uncharged particles are unaffected by the electric field in the column. Most commonly, a negative voltage is applied to the central rod so that positively charged particles are drawn towards it. The landing location of the particles on the central rod is a function of their electrical mobility and the operating conditions of the DMA (flow rate and central rod voltage). Particles of high electrical mobility precipitate close to the aerosol inlet, whereas particles of lower mobility precipitate further down the column. Particles within a narrow range of mobilities exit the DMA through the monodisperse sample flow, i.e. a circumferential slit on the central rod located downstream of the aerosol inlet. The monodisperse flow is then transferred to the detector where particle number concentrations are measured. All the remaining particles exit the DMA via the excess flow.

Most DMAs are based on the improved version of the Hewitt mobility analyzer proposed by Knutson and Whitby (1975). This original design is associated with high diffusional losses in the aerosol inlet and outlet thereby restricting the performance of the DMA for particles smaller than approx. 10 nm. Many research groups have focused on improving the penetration efficiency of sub-10 nm particles through the DMA by proposing different designs. Winklmayr et al. (1991) developed a cylindrical DMA (the Vienna DMA) with a novel tangential flow aerosol inlet that minimizes diffusional losses. Reducing the residence time of the particles in the DMA by shortening the total length and increasing the flow, they achieved higher transmission efficiencies and managed to classify particles with diameters as small as 1 nm. In the same direction, Chen et al. (1998) developed and tested a new cylindrical DMA (the Nano DMA) that uses a modified aerosol inlet and a much shorter column compared to the original design. A more innovative design was proposed by Zhang et al. (1995) and later by Mesbah et al. (1997), who independently developed the Radial DMA (R-DMA). The R-DMA classifies particles in a radial flow towards the center of two parallel disk electrodes. Although the high transmission efficiencies of ultrafine particles through the R-DMA made it more favorable compared to the cylindrical DMA, its low resolution for the larger range of particle sizes limited its wide use in SMPS and DMPS systems. More recent developments have led to high-flow DMAs capable of size-separating small ions and molecules. It has been applied to protein and polymer molecules, and recent work to be published soon involving one of the authors (A.S.), showed that it is a useful instrument for atomic cluster separation down to 2 atoms.

Originally, the DMA was designed to generate monodisperse particle samples from polydisperse aerosols for calibration purposes (Liu and Pui 1974). A year later, Knutson and Whitby (1975) proposed using the instrument for measuring aerosol size distributions. Further work by Hoppel (1978) and Haaf (1980), who proposed algorithms to determine size distributions from mobility measurements by the DMA, showed that the technique can be very
powerful. Using the DMAs both as a way of generating monodisperse particles and as a classifier for measuring particle size distributions has been very useful in aerosol science and technology. The feature of the DMA for producing monodisperse particles is in many cases important in nanoparticle synthesis via aerosol methods, because most aerosol generation methods produce polydisperse particles from which only a very narrow size range is desired.

Highly concentrated aerosols produced by most generation methods outlined in the previous section require dilution before they can be efficiently classified in a DMA. This can be a serious limitation when DMAs are used in the generation process to select particles of a narrow size range, as it can significantly reduce the production rates. Another limitation of these classifiers is that particles are classified according to their electrical mobility and not directly based on their size. As a result, particles of different size and shape can be included in the monodisperse samples depending on the charge and the morphology distribution of the particles, respectively.

3.2 Faraday cup electrometers

The number concentration of an aerosol flow carrying charged particles can be determined using a Faraday cup electrometer. In this type of detectors, particles from the sample flow are collected in a high-efficiency filter housed in a metal enclosure, i.e. a Faraday cup. This filter is isolated from the metal housing which is connected to the ground through the electrometer. The metal housing shields the electrometer from any external disturbances. Charges that are trapped in the Faraday cup induce a current which is proportional to the amount of charge collection rate on the filter. The particle number concentration can then be estimated from the current if the number of charges on each particle and the aerosol flow rate are known.

Typically, Faraday cup electrometers have sensitivities of the order of a few fA (He et al. 2007). Considering that the sampled particles are moderately charged, the minimum particle number concentration that Faraday cup electrometers can measure is of the order of $10^2$-$10^3$ particles cm$^{-3}$ for typical flow rates.

3.3 The condensation particle counter

Another method of measuring the particle number concentrations of an aerosol sample is by using optical instruments. Because particles smaller than approx. 100 nm are difficult to detect optically since their size is smaller compared to the wavelength of most light sources, growth of the particles to a detectable size is required. Particle growth is achieved by condensation prior to detection in CPCs.

The CPC consists of three main parts: the saturation tube, the condensation tube, and the optical detection system. The incoming sample passes first through the saturator where the aerosol becomes saturated with a working fluid (typically butanol). Upon cooling of the aerosol, the vapors supersaturate and condense on the particles which grow into larger droplets. Finally, the grown droplets pass through the optical detector where their total number in a unit volume is measured. The commercial CPCs are based on the design originally proposed by Agarwal and Sem (1980). Single-particle counters such as the CPC are much more powerful devices than multiple-particle counters that measure extinction of light through the aerosol (Sinclair and Hoopes 1975; Davies and Egilmez 1985). In principle, their ability to detect single particles makes them capable of measuring particle concentrations down to any level. However, for highly concentrated aerosols typically produced by the methods described in the previous section, Faraday cup electrometers may be more appropriate.

4. Applications of Aerosol-Based Nanotechnology

Nanoparticle building blocks of a well-defined size and chemical composition are necessary in many technological applications. Some aerosol techniques for synthesizing such nanoparticles are already being used in industry, whereas recent advances in aerosol science and technology indicate that several other techniques have a great potential for up- and out-scaling. This section gives a brief outline of existing applications of aerosol-based nanotechnology and provides an outlook of the potential that these techniques can have.

Perhaps the most widespread use of aerosol-based methods in industry has been for the synthesis of carbon black nanoparticles. Carbon black nanoparticles have been used as strengthening or reinforcing agents for rubber in automobile tires (Medalia 1978). Other applications of carbon black particles include the manufacture of pigments, coatings, and various polymers with enhanced electrical and mechanical properties (Donnet et al. 1993). Despite the fact that synthesis techniques and applications of carbon black nanoparticles have been well established, recent research has shown that particle mixtures of carbon
black and silica are opening up a new generation of reinforcing agents for rubber (Wang et al. 2000). Internally mixed carbon black/silica particles have also been manufactured in premixed flame aerosol reactors by the combustion of acetylene and SiCl$_4$ (Spicer et al. 1998; Kammler et al. 2001). The combination of carbon black and silica is more effective in reinforcing rubber because compared to carbon black alone, it provides the capability for manufacturing the so-called “green tires”.

The synthesis of ceramic particles has been another widespread application of aerosol methods in the industry. Flame-synthesized fumed silica particles are used as fillers in silicone rubber, as strengthening and reinforcing agents, catalyst carriers, polishing materials in microelectronics, and in the manufacture of optical fibers (cf. Pratsinis 1998). Titanium dioxide nanoparticles also find many applications depending on their crystallinity. For example, rutile titanium dioxide particles with a diameter of approx. 250 nm are commonly used in pigments to provide maximum whiteness and opacity. This is by far the largest application of titanium dioxide particles typically generated by flame synthesis techniques. Titanium dioxide particles can also be used in photocatalysts for water and gas purification, in gas sensors, and as supports in the manufacturing of catalysts (cf. Pratsinis 1998 and references therein). Alumina particles produced via the aerosol route have also been used for the fabrication of integrated circuit substrates, high-pressure sodium-vapor lamps, catalyst supports and high-performance materials (cf. Kaya et al. 2002; Ye et al. 2007).

Nanoparticle building block synthesis methods via the aerosol route exhibit great potential for applications in the fabrication of electronic components (e.g. Prost et al. 1998). Alloy particles synthesized by spray pyrolysis have been used for the formation of conductive films in electronic devices such as hybrid integrated circuits and multilayer ceramic capacitors (e.g. Nagashima et al. 1991). Due to their dielectric and ferroelectric properties, barium titanate nanoparticles have been synthesized via the same technique for the fabrication of multilayer ceramic capacitors, transducers, and thermistors (Lee et al. 2005), whereas $\gamma$-Fe$_2$O$_3$ nanoparticles synthesized in the same way have shown great potential for use in magnetic recording media (Gonzalez-Carreno et al. 1993).

Nanoparticle building blocks with sizes below a few nanometers have various potential applications in electronics where quantum confinement effects may be advantageous (Flagan et al. 1991; Wiedensohler et al. 1992). These nanosized systems, commonly referred to as quantum dots or zero-dimensional structures, have altered electrical properties compared to their large-particle counterparts, because the electronic state space in these structures is discrete as a result of the three-dimensional confinement. Silicon nanocrystals for example, are widely considered a material with great potential for a wide spectrum of applications and novel devices (e.g. single-electron transistors, vertical transistors, and floating gate memory devices), as well as for applications in solid-state lighting (e.g. Kang et al. 2006).

Nanoparticles synthesized via the aerosol route can also have great potential in the manufacture of materials for efficient energy storage. For instance, solid-state batteries that use electrodes made of nanoparticles of transition-metal oxides exhibit higher electrochemical capacities and lifetimes (Poizot et al. 2000). Nanostructured metal hydrate materials can also exhibit higher hydrogen storage capacities and rapid kinetics (Zaluska et al. 2001). Such materials can have a strong impact on energy storage systems in transportation (e.g. Schlapbach and Zuttel 2001).

Nanoparticle building blocks can also be used in the fabrication of simple and cost-effective gas sensors (e.g. Favier et al. 2001). The underlying operating principle of these sensors is that the electrical properties of films or wires made of metallic or semiconducting particles can change as a result of adsorption of gaseous species onto their surfaces. The high specific surface of these nanostructures significantly enhances gas transfer rates to the structure and thus the sensing capabilities of the sensors.

Thin films made of tin oxide particles were shown to have gas sensing properties almost three decades ago (Ogawa et al. 1981; Ogawa et al. 1981). Adachi et al. (1988) showed that such films can selectively detect hydrogen, nitrogen, and oxygen gases. Doping the tin oxide films with metal particles was shown to enhance the gas selectivity of the sensors (Gautheron et al. 1993; Labeau et al. 1993; Labeau et al. 1994; Tadeev et al. 1998; Renault et al. 1999). The conductivity of nanostructured films and wires made of palladium nanoparticles have been shown to be very sensitive on the concentration of hydrogen in the overlying gas (Volkening et al. 1995; Kovacik et al. 2008). Recently, Teleki et al. (2008) showed that Nb- and Cu-doped TiO$_2$ structures can also be used for sensing carbon monoxide and ethanol.

Nanoparticle building blocks produced by aerosol
methods have been also used in catalysis. Flame synthesis has been extensively used to produce nanoparticles for catalysts. For example, Stark et al. (2001) demonstrated that flame-synthesized vanadia–titania nanoparticles exhibit high activity for the selective catalytic reduction of nitrogen monoxide by ammonia. Chakraborty et al. (2005) produced mixed platinum-ruthenium nanoparticles by flame aerosol synthesis to catalyse the methanol oxidation reaction in direct methanol fuel cells. A thorough review on nanoparticle formation using flame synthesis techniques for fabricating catalytic materials is given by Strobel et al. (2006). Using spray pyrolysis, Backman et al. (2004) demonstrated the enhanced photocatalytic activity of silver-doped titanium dioxide particles. Finally, the catalytic activity of airborne versus deposited Ni nanoparticles has been suggested as a way to increase the transport rate of the gaseous species to the surface of the particles (Weber et al. 2006).

Nanoparticles synthesized via the aerosol route can also have therapeutic or diagnostic applications in medicine. Drugs in the form of aerosol nanoparticles can be delivered efficiently to certain parts of the human body (Dames et al. 2007). Magnetic nanoparticles (commonly referred to as magnetopharmaceuticals) can also be administered to the human body to aid nuclear magnetic resonance imaging for diagnostic reasons (Tartaj et al. 2003). Other medical applications of nanoparticles include the biodetection of pathogens, tumor destruction via heating, tissue engineering, and localized treatment such as hyperthermia (Salata 2004). Considering the great advantages of aerosol synthesis techniques for high purity and great control over the size of the nanoparticle, one can envisage their potential future applications for advanced diagnostics and treatment methods.

5. Conclusions

In this paper we provide a brief review on state-of-the-art techniques for generating and sizing aerosol nanoparticles of well-defined size and chemical composition for applications in nanotechnology. Compared to nanoparticle synthesis via the liquid route, aerosol processes are attractive for their high purity and simplicity as they do not involve large volumes of liquid by-products. In addition, their ability to operate in a continuous rather than in a batch mode makes them favorable in many industrial and technological applications.

Aerosol particles can be synthesized from the liquid or the gas phase. Techniques that fall into these two categories have been described, and their advantages and drawbacks in view of the different application are discussed. The most efficient technique for sizing nanoparticles suspended in a gas is by measuring their electrical mobility. The operating principles of the individual components (i.e., the classifier and detectors) of the most widely used electrical mobility spectrometer are briefly described. This paper closes with a discussion on the existing applications of aerosol-based nanotechnology and an outlook of their potentials.

References


sol Science, S67-S68.


KONA Powder and Particle Journal No.26 (2008)


Platinum nanoparticle production by EHDA, Aerosol Science and Technology, 39, pp.941-946.


Electric aerosol particle counting and size distribution measuring system for the 0.015 to 1 µ size range, Tellus, 18, pp.573-586.


The physical and biological effects of high frequency sound waves of great intensity, Philos. Mag., 4, pp.417-436.

Controlled synthesis of alumina nanoparticles using inductively coupled thermal plasma with enhanced quenching, Thin Solid Films, 515, pp.4251-4257.


The velocity of the ions produced in gases by Röntgen rays, Philosophical Transactions, 195, pp.193-234.

The electrical discharge from liquid points, and a hydrostatic method of measuring the electric intensity at their surfaces, Physical Review, 3, pp.69-91.


Author’s short biography

George Biskos

George Biskos is an Assistant Professor at the Department of Environmental Studies at the University of the Aegean, and a Visiting Assistant Professor at the Department of Chemical Technology at Delft University of Technology. Previously he was a Research Associate at the School of Engineering and Applied Sciences at Harvard University. He holds a Ph.D. (2004) in Engineering from Cambridge University, and an M.Sc. (2000) in Environmental Engineering from Imperial College, UK. His research interests are in the broader area of aerosol science and technology, ranging from development of instrumentation for measuring airborne particles, to atmospheric aerosol chemistry and aerosol based nanotechnology.

Vincent Vons

Vincent Vons is a Ph.D. student at the Department of Chemical Technology at Delft University of Technology. He holds a Bachelor’s degree in Chemical Technology and Bioprocesstechnology, and a Master’s degree (with honours) in Chemical Technology, also from Delft University of Technology. He has worked on atmospheric pressure cold plasma nanoparticle formation, using a dielectric barrier discharge. Currently he is in the final year of his Ph.D. degree on nanoparticulate metal hydride hydrogen storage using (amongst other techniques) spark discharge nanoparticle formation.

Caner U Yurteri

Caner U. Yurteri is a visiting Assistant Professor at Delft University of Technology. He received a B.S. (1987) in Mechanical Engineering from Istanbul Technical University, Istanbul, Turkey and an M.S. (1992) and PhD (1997) degrees in Mechanical Engineering from Case Western Reserve University, Cleveland, Ohio. He then joined the Chemical Engineering Department of Purdue University as a post-doctoral researcher, the Applied Science Department of the University of Arkansas at Little Rock as a research associate, Terronics Development Corporation as a research scientist, and Particle Engineering Research Center as an assistant scientist, respectively. His work extensively involved Laser Doppler and Phase Doppler Anemometry and their applications to particle-laden flows. His research interests include particle and powder technology, medical aerosols, electrostatic coating, electrospraying and out scaling of electrospraying process.
Author's short biography

Andreas Schmidt-Ott

Andreas Schmidt-Ott, born in 1952, completed his Ph.D. thesis at the Faculty of Mathematics and Physics of the Swiss Federal Institute of Technology (ETH) in Zurich, Switzerland in 1979. He was then Research Fellow at the Atmospheric Physics Department and later Senior Research Scientist at the Solid State Physics Laboratory of the same institute. In 1988 he spent a term at the Chemical Engineering Department of the University of California, Los Angeles (S.K. Friedlander) as a Visiting Assistant Professor before joining Duisburg University (Germany). Here he was first Assistant Professor at the Faculty of Electrical Engineering and then became professor in the Mechanical Engineering Dept. of the same University. Between 1996 and 1997 he spent a 5-month sabbatical with K. Sattler at the Physics Dept. (Nanophysics Group) of the University of Hawaii at Manoa. He was Deputy Chair of the Mechanical Engineering Faculty at Duisburg University 1998 - 2001. Since March 2001 he is a Professor of Particle Technology in the Nanostructured Materials Section at Delft University of Technology, Netherlands. He served as Secretary General of the German Aerosol Association (GAeF) and Board Member of the American Association for Aerosol Research (AAAR). He is or was a member of several Editorial Boards of journals. His most prestigious award was the Smoluchowski Award, which he obtained in 1989.