

## Materials Synthesis: Contributions and Challenges to Aerosol Science

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Keywords: agglomerates, coagulation, fractals, particle concentration.

Aerosol routes are very attractive for materials manufacture as they offer unique advantages over classic wet chemistry: fewer process steps resulting in high purity products (e.g. optical fibers), easier particle collection from gas rather than from liquid streams and no liquid by-products that require costly effluent cleaning (Pratsinis and Mastrangelo, 1989). Today a number of particulate and film commodities are made with flame (carbon blacks, fumed silica and titania) and hot-wall (zinc oxide, filamentary nickel and tungsten carbide) aerosol processes to name few.

Most of these products were developed with little, if any, formal aerosol science. As a result, early practitioners developed ingenious ways to characterize, control and handle industrial aerosol products. Some of the first attempts to characterize agglomerates were made by carbon black engineers in their effort to connect reinforcing performance to carbon black characteristics and eventually to their reactor operation. Medalia and Heckman (1969) found that the number of primary particles in agglomerates was related to agglomerate size by a power law, the so-called fractal dimension, that was introduced years later by Mandelbrot (1982). In fact, carbon blacks were frequently cited as applications of fractals by Mandelbrot and others. Ulrich (1971) at Cabot predicted that fumed silica attains a self-preserving size distribution and calculated it first in the free-molecular regime, a year ahead of Lai et al. (1972) who have been largely credited for it. Also, the self-preserving theory explained measured size distributions of flame-made titania at Tioxide in 1973 where thermophoretic sampling was used to explore the contribution of surface growth on TiO<sub>2</sub> formation, a technique systematically introduced by Dobbins and his colleagues in 1987, to effectively “open up the black box” of combustion aerosol synthesis of materials. Today aerosol science is used routinely in characterization and processing of aerosol-made materials in chemical, microelectronic and pharmaceutical industries.

The quest of synthesis of functional materials brings new challenges as their performance relies on particle composition and morphology. As with bulk commodities today, there is also keen interest to make nanorods and nanotubes in the gas-phase to facilitate and scale-up their manufacturing so the potential of nanoscale is realized economically. Characterizing such particles create new challenges to aerosol science. Making multicomponent particles

with spatially controlled component distribution is essential for developing the required functionalities of such materials. For example, particles with uniform Pt/Ba/alumina composition perform worst catalytic NO<sub>x</sub> storage-reduction than particles with segregated components (Strobel et al., 2006).

Aggregates or agglomerates of nanostructured particles occupy far more volume than their equivalent solid mass (Matsoukas and Friedlander, 1991). Though these particles may grow initially by surface growth and/or Brownian coagulation, very quickly grow to a state that is no longer covered by the Smoluchowski theory. This indicates that a transition from dilute to concentrated aerosol dynamics takes place (Heine and Pratsinis, 2006). As a result, there is less “free gas” volume per agglomerate, so the steady-state concentration profile away from the receiving particle surface during coagulation does not form showing the need for extending coagulation theory to high aerosol concentrations. At these conditions such particles are likely to restructure and eventually break-up.

Distinguishing between aggregates and agglomerates brings another challenge to aerosols. Even though conditions leading to synthesis of either state are known in case of coagulation and sintering (Tsantilis and Pratsinis, 2004), there is a need for their undisputable characterization. Aggregates are needed for catalysts and gas sensors to facilitate easy access to their surface while agglomerates are needed for nanocomposites to facilitate mix in polymer matrices for dental, optic, biomaterial and other applications.

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