Nanomaterials from Aerosols

Aerosols are suspensions of liquid or solid particles in a gas. Aerosol particles can range in size from molecular-scale to hundreds of microns with a typical example being clouds with water droplet sizes on the order of 5 to 50 micron suspended in air.

Nanomaterials can be synthesized by aerosol routes where precursor species are dispersed either in a vapor or in micron-scale liquid droplets. Synthesis of nanoparticles in aerosols can proceed at ambient conditions (ASG process developed at UC), through heating of the stream in a tubular oven, or, most commonly, by pyrolysis of the aerosol in a free flame (fig. 1). Aerosol synthesis is the most promising route for large scale production of nanomaterials since most aerosol synthetic approaches are amenable to continuous production and since aerosols offer high dispersablity, easy separation of nanoproducts from byproducts and much more rapid reaction rates when compared to solution chemistry due to high transport rates and large surface areas. Nanomaterials such as pyrolytic titania are already produced at the industrial scale (hundred of tons per hour) in continuous reactors by companies such as Dupont and Degussa with particle sizes on the order of 5 to 10 nm. In research labs, aerosols have been used to produce quantum dots and single walled carbon nano-tubes in continuous processes amenable to large scale production. The future of nanomaterials, especially in the chemical process industry, depends to some extent on understanding the details of nucleation and growth of nanomaterials in aerosol streams.

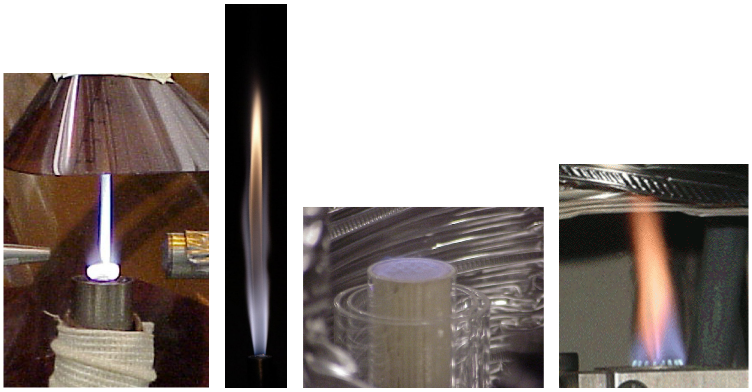

Figure 1. In situ SAXS and XRD from pyrolytic synthesis. a) diffusion titania flame (DND APS, submitted *Journal American Chemical Society*). b) diffusion silica flame (ID02 ESRF, *Nature Materials*. c) premixed silica flame (UNICAT APS, accepted *Journal of Applied Physics*. d) spray flame (ID02 ESRF, in preparation).

In addition to nanomaterials, aerosols are of vital importance to the environment. Anthroprogenic and natural aerosols are believed to significantly contribute to global climate changes which are evidenced by changes in the temperature of the oceans and rapid melting of the polar and glacial ice packs. Of pollution sources, aerosols represent the least understood and could potentially offset climate changes caused by ozone depletion in the upper atmosphere. Environmental aerosols include anthropogenic carbon soot, sulfate particles, as well as natural aerosols of silica and alumina from expanding arid regions in China and Africa. Such aerosol streams have been shown to travel around the globe with silica aerosols from China impacting air quality in the continental US and alumina and titania deposits in Jamaica having been derived form the Sahara desert in North Africa via the trade winds.

Finally, particulate aerosols are seen both as a nemesis as well as a God send in the medical field where human exposure to aerosol streams containing silica, diesel soot and asbestos are gaining attention as sources for recent increases in allergies and asthma among children. Aerosols have also been recognized as effective delivery mechanisms for a variety of drugs as an alternative to injections. As delivery devices, nanomaterials are advantageous due to their extremely high surface area and the related increase in physiological activity.

Despite the importance of aerosol processes, the understanding of aerosol synthetic mechanisms is at an early stage, particularly, nucleation of nanomaterials in aerosol streams both pyrogenic (flames) as well as environmental aerosols. For example, Gibbs-Thompson theory is commonly used to predict the size of nanomaterials from the supersaturation (vapor pressure) of a precursor species and the surface energy and bulk enthalpy of formation of the solid nano-particles (see for instance web notes on this page for nano-powders class). For silica, for instance, Gibbs-Thompson theory predicts nascent particle sizes on the order of 0.05 nm due to the low vapor pressure of solid silica. However, pyrolytic (flame) synthesis can produce, under the best conditions, 4 nm particles as supported by recent in situ measurements from the University of Cincinnati done at ESRF in France in collaboration with ETHZ. Current theory has resolved this discrepancy by proposing "*chemical*" nucleation where conversion to solid products in an aerosol stream leads to molecular-scale nuclei (rather than the Gibbs-Thompson sub-atomic size) on the order of 1 nm with no traditional number density burst and a continuous production of nascent molecular-scale nuclei. The chemical nucleation theory has been the basis of most simulations of nanomaterials growth in aerosols, however, recent measurements by Cincinnati researchers using small-angle x-ray scattering (SAXS), have completely disproven chemical nucleation and demonstrated a traditional nucleation burst of 4 nm nuclei in silica synthesis, among many other systems. Cincinnati workers are now focusing on developing a new theory for nanomaterial nucleation consistent with these seminal in situ observations.

Current work is aimed at understanding the fundamentals of nanomaterial nucleation in aerosol streams through in situ observation of particle nucleation under variable conditions. Nucleation occurs on time scales of 50 milliseconds to 50 microseconds under conditions of supersaturation and rapidly changing composition and phase. Such observations can only be made through the use of synchrotron radiation and modern instrumentation available at international user facilities such as ESRF in Grenoble France. A collaborative team, lead by UC and composed of partners at ETHZ, Zurich Switzerland and ESRF, has addressed this problem and are making significant headway towards understanding nanomaterial growth in aerosols. One paper has been published in *Nature Materials* and a number of other papers are in preparation associated with the sabbatical leave. The experimental work is on going with experiments targeting environmental aerosols and carbon formation planned in October and in the spring of 2005. The work has been featured at several meetings including Nanomaterials Workshop in Nottingham England, ESRF web page highlight, ETHZ research highlights, the AIChE meeting in San Francisco, the American Crystallographic Association and the Denver X-ray Conference. This work has been funded by NSF, the Swiss National

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