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Perspective

# Aerosol-based Technologies in Nanoscale Manufacturing: from Functional Materials to Devices through Core Chemical Engineering

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## Introduction

Manufacturing of nanoscale materials and devices offers a number of exciting opportunities for chemical engineers to contribute substantially in product development, process scale-up, and environmental compliance. Current research in nanoscale science and engineering has been directed primarily toward the design and synthesis of (a) *materials with passive nanostructures* (e.g., nanostructured coatings, dispersion of nanoparticles, as well as bulk nanostructured metals, polymers and ceramics), and (b) *active devices with nanostructured materials* (e.g., transistors, amplifiers, targeted drugs and delivery systems, sensors, actuators and adaptive structures).[1] Such materials are usually produced through self-assembly of nanoparticles in gas- or liquid-phase processes or through compaction of nanopowders. Even though nanoparticles have been in use for a long time (e.g., carbon black, photographic films, fumed silica), the knowledge base for their synthesis and characterization has increased dramatically in the last 30 years with the development of a number of sophisticated scientific instruments, new synthetic processes at the nanoscale, and computational advances. This progress has contributed decisively to the development of effective and quantitative understanding of (a) nanomaterial properties and their dependence on their constituent parts, and (b) synthesis methods on which their fabrication is based, resulting in the discovery of new materials with an array of new functionalities and potential applications with promises of more to come in the future.

To date, however, rather little of the aforementioned has been translated into actual industrial products. Most of these exciting discoveries have been made in basic science laboratories with little motivation or capacity to investigate and invent *processes* for the economic manufacturing of these nanotechnology products; the ''bread and butter'' of chemical engineers. In fact, little is known about how well these new properties are reproduced during large-scale manufacturing of such nanomaterials. More importantly, there is little understanding on how such manufacturing processes can be designed and operated, while issues arise regarding the controllability of such process operations and sustainability of the product quality, safety and potential hazards for personnel, environment and consumers. The associated risks constitute key issues in developing manufacturing technologies by major industries, a drive that has been part of what is recently referred to as ''green'' manufacturing.

Two of the major challenges are: first, low-cost manufacturing of sophisticated nanostructured materials, and second, the economical and reliable assembly of such materials into functional devices. To meet these challenges a quantitative advancement of the current understanding of the corresponding manufacturing technologies is needed for the synthesis of mixed, functionalized and/or layered nanomaterials, significantly beyond the simple ones in the market today, with close attention to product handling, safety and health effects. Furthermore, assembling of devices with such materials (e.g., synthesis, deposition and processing of multilayers of functional nanoparticles) is needed to meet today's engineering challenges in energy, mobility, health and life sciences (e.g., nonintrusive medical diagnostics and even cures for chronic and serious illnesses).

While most of the current research in nanotechnology is driven by the imperative of scientific questions on the synthesis and characterization of passive nanoscale materials and/or active devices, with minimal attention paid to the

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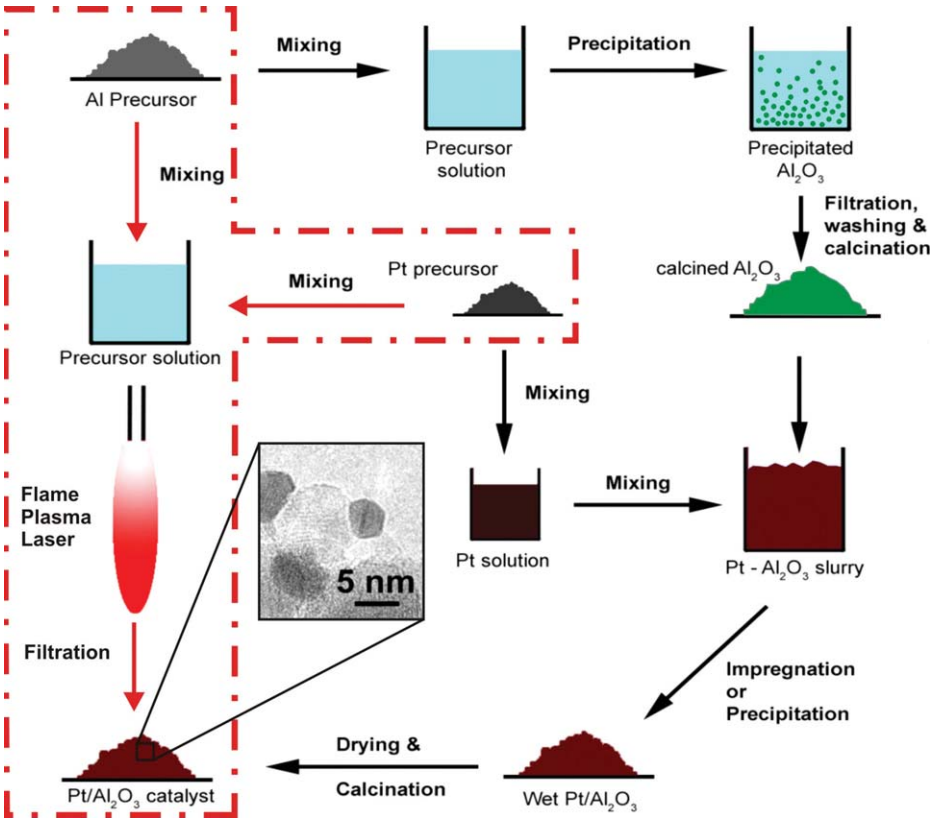


**Figure 1. Comparison of aerosol (flame, plasma, hot-wall or laser) and wet-chemistry methods for the synthesis of $Pt/Al_2O_3$ heterogeneous catalysts (inset).**

Aerosol synthesis allows catalyst preparation in one step (within the red line), whereas conventional precipitation or impregnation are multi-step processes (adapted from [6]). Also, the aerosol route affords easy addition of multiple noble metal components for synthesis of bi- or multimetallic catalysts in one step while conventional routes require repetition of the cycle of mixing-impregnation-filtration-drying-calcination (righthand-side) for every additional noble metal component.

development of effective industrial-scale manufacturing processes, there are a few notable exceptions: Simple nanostructured materials (e.g., carbon black, fumed silica, titania, alumina) are manufactured today at tons per hour in aerosol reactors worldwide.[2] Deposition of ceramic films for manufacture of light guide preforms and to protect surfaces (e.g., turbine blades), by the so-called thermal spraying using flame or plasma torches, are fairly advanced technologies. However, despite the size and age of these aerosol-based industrial manufacturing activities, the core technology is poorly understood, especially outside the narrow specifications of its industrial operating implementations and product specifications.

The aerosol-based technological foundation for the manufacturing of nanoscale materials has been built amazingly well mostly by valiant, market-driven[3] needs (market-pull) rather than systematic, engineering science-pushed research efforts. As a result, the quantitative understanding of the fundamental physicochemical processes in aerosol-based manufacturing has been limited.[4]

However, the history of manufacturing nanoscale materials through aerosol processes offers two important observations: First, aerosol-based processes are favored, in many cases, over wet-chemistry based processes such as with dry vs. wet scrubbing for gas cleaning in classic chemical engineering and especially for production of materials; e.g., white $TiO_2$ pigment was made solely by a wet "sulfate" process before the advent of the "chloride" aerosol process, which has captured the 60% of the worldwide production with the expectation that it will eclipse the "sulfate" process in 20 years. Second, industrial experience has demonstrated that the following seven key reasons make aerosol processes very attractive for the manufacturing of nanoscale materials[5]:

(a) Aerosol processes do not generate liquid byproducts that are costly and difficult to clean and dispose. This is a clear advantage for sites with limited water supplies.

(b) Collection of particles is easier and cheaper from gases than from liquids.

(c) Highly pure materials can be formed in the gas phase (e.g., optical fibers).

(d) Products with unique morphology can be made (e.g., filamentary Ni, carbon black and $SiO_2$).

(e) Aerosol-based manufacturing processes are simpler and require fewer unit operations, when compared with wet processes; e.g., Figure 1 compares the complexity of aerosol-based and wet synthesis processes for the manufacturing of $Pt/Al_2O_3$ catalysts.

(f) Metastable phases can be captured by the rapid cooling of aerosol-made products resulting in truly new materials (e.g., low-temperature $BaCO_3$, $\varepsilon$-$WO_3$, amorphous composite $Ta_2O_5/SiO_2$).

(g) Transport phenomena (e.g., diffusion) in gases afford more rigorous treatment than in liquids or solids, facilitating process design from first principles.

These advantages have motivated research that has led to significant advances in the knowledge base of aerosol synthesis of materials in the last 30 years. This perspective considers how core principles from chemical engineering science and methodological approaches have shaped the past and will shape the future of aerosol-based manufacturing processes in nanotechnology. Specifically, it will discuss how new diagnostic tools, detailed chemical reactor models and their integration with sophisticated computational fluid dynamics environments, and novel aerosol reactor configurations offer the potential for the development of effective manufacturing processes, which not only provide at low-cost simple nanoscale materials, but also allow the deployment of new manufacturing prototypes for sophisticated functional materials and devices at the nanoscale. Finally, we will discuss the central challenges to be overcome before aerosol processes can be made the preferred path to manufacturing nanoscale materials and devices of multiple functionalities and varying complexities.

## Aerosol Reactors

New diagnostic tools and detailed reactor models have shown how process variables affect product particle characteristics. For example, the introduction of thermophoretic sampling of particles from flames essentially opened the "black box" of aerosol reactors unraveling how fractal-like nanostructured particles were formed.[7] Furthermore, quantification of such phenomena as coagulation and sintering,[8] motivated the development of the so-called two-dimensional (2-D) in size (volume and surface area) population balances, describing the evolution of such nanostructures and explaining the difference in morphology (e.g., fractal-like vs. compact) between materials (e.g., $SiO_2$ vs. $TiO_2$) made at identical conditions.[9] This understanding emboldened creation of amazingly simple models for aerosol formation and growth, taking advantage of the rapid attainment (within microseconds) of the so-called self-preserving particle-size distribution (SPSD)[10] in such concentrated aerosol systems. Once a SPSD is attained its shape is time-invariant, so two of its moments (e.g., number and mass) suffice to describe the complete particle dynamics. That way measurable product properties, primary particle or grain size (specific surface area) obtained by microscopy or $N_2$ adsorption, can be readily connected to process variables, dramatically simplifying process design and operation and explaining quantitatively the characteristics of a number of product particles.[4] Furthermore, this understanding pointed out the most important process variable: temperature and the need to monitor and control it.

This success of chemical engineering in explaining product particle characteristics in aerosol reactors had three effects: First, such models were integrated with fluid dynamic simulators to describe an entire aerosol reactor[11] and unravel areas of fluid recirculation, motivating redesign of such processes, especially in industrial facilities. This guided also the construction of rather large facilities even at academic laboratories making nanomaterials like carbon-coated $SiO_2$ or $TiO_2$ at respectable rates, e.g., up to 700 g/h.

Second, the understanding of the elementary physicochemical steps of this technology motivated further development of diagnostics for such processes: Small and ultra-small angle X-ray scattering covers today an unprecedented four-order size spectrum from nano- to micrometer particle sizes, essentially from primary to agglomerate diameter.[12] Such capability allowed nonintrusive monitoring of the formation of perfectly spherical or fractal-like nanoparticles along with their temperature history in robust and flexible diffusion flames.[13] Interfacing particle mass and mobility measurements[14] led also to extraction of particle structure (fractal-like dimension $D_f$), showing that aerosol particles hardly attain the asymptotic $D_f$ predicted by the well-known fractal simulations of Meakin, Mandelbrot and others.[15]

Third, and most important for the synthesis of nanostructured materials, the understanding of how process variables affect product particle characteristics has enabled research for the synthesis of better performing materials than those available by other techniques. For example, air-fed flames result in low-temperatures forming aggregated (chemically- or sinter-bonded) particles, while pure $O_2$-fed flames create high-temperatures and steep cooling rates resulting in nonaggregated, beautifully-looking, colloidal-like, spherical titania particles,[16] by limiting their sintering upon collision and the ensuing neck growth between them.[17] As a result, photocatalytically better $TiO_2$ particles[18] could be made than the "gold standard", Degussa or Evonik's (now) P25 $TiO_2$, and more efficient $V_2O_5/TiO_2$ catalysts than wet-made ones for the selective catalytic reduction of $NO_x$ with ammonia[19] to harmless $N_2$, a development that essentially opened up the potential of flame aerosol reactors in catalysis,[6] a field dominated by wet chemistry since medieval times, so-to-speak!

## Nanostructured Materials with Engineered Structure, Composition and Surface

Classic vapor-fed flame aerosol reactors, similar to those employed by the "chloride" or oxyhydrogen industrial processes for the synthesis of $TiO_2$ and $SiO_2$, may be thought of as being of limited value in the synthesis of more complex functional nanostructured materials; the reason being the lack of inexpensive gaseous metal precursors. In contrast, spraying in a flame[20] or plasma,[21] or combusting liquid precursor sprays[22] can be used to make an array of functional particles and films.[23] Combustion of sprays is the oldest and largest industrial process for synthesis of the cheapest nanostructured particles, carbon black, by the so-called "furnace" process.[24] As with flame synthesis of silica and titania, there is a strong technology base here as it is evidenced by patents and world-wide distribution of carbon black plants. To this day, however, the knowledge base of this process (fuel-rich combustion) is quite limited, again, to the process conditions of a given process/product combination; carbon black in this case. As a result, rather little of that technology can be readily used for synthesis of other materials although certain aspects pertaining to product handling, process safety and health, especially at high-production rates, are invaluable and important in aerosol manufacturing of every product.

What is new, however, with combustion of sprays by the so-called flame spray pyrolysis (FSP)[25] for synthesis of nanostructured materials, is the systematic assembly of such reactors capitalizing on the knowledge[16,17] of particle formation in vapor-fed flames. So materials with sophisticated composition and structure like spinels, mixed ceramic, metal/ceramic, *Janus-like* or layered-like[23] particles can be made by aerosol technology well beyond the simple ones of the past. Such particles have unique and quite novel properties finding diverse applications such as heterogeneous catalysts, with well over 100 articles published in the last few years,[6] gas sensors, fuel-cell electrodes, phosphors, battery materials, bone and dental prosthetics, nutritional supplements,[23] as well as pure metals[26] for ferromagnetic fluids, sensors and alloys.[27] Furthermore, thin carbon films on these metals are made of graphene[28] adding further to the potential of aerosol-made particles.

Going one step further beyond particle composition[23] and structure,[12–14] there is a need for synthesis of nanostructured materials with engineered surfaces to take advantage of functional core properties (e.g., optic, magnetic, plasmonic, thermal or support) and avoid adverse ones (e.g., catalytic, toxic or flocculating). That way, *surface-engineered* nanoparticles can be readily incorporated in host matrices and devices. During co-synthesis of such multicomponent materials, their composition alone dictates which component resides on the particle surface, depending on process temperature history and material properties (e.g., free energy). For example, in the synthesis of noble metal clusters on ceramic supports that are essential in heterogeneous catalysis and sensors, the ceramic support precipitates first out. Then, the noble metal clusters form heterogeneously on it, stochastically. A similar picture emerges when two ceramic oxides of vastly different boiling points are made simultaneously like $V_2O_5/SiO_2$ or $V_2O_5/TiO_2$ catalysts. There silica or titania particles precipitate out first and then $V_2O_5$ condenses on them forming core–shell structures with amorphous shells at low $V_2O_5$ concentrations that are catalytically active. In contrast, at higher $V_2O_5$ concentrations polymeric and crystalline vanadia-based shells and separate $V_2O_5$ particles are formed that are typically undesirable.

When component properties are similar, mixed and segregated regions or domains are formed; the so-called *Janus-like* particles. For example, in aerosol synthesis of mixed silica-titania, such segregated silica and titania phases are typically formed (Figure 2g, h). Silica-coated titania (shell-core) particles can be obtained either by reducing the Ti- or Si-precursor concentrations and controlling process temperature, or by nozzle quenching in processes, albeit with limited scalability. Today even for simple oxides, surface functionalization during their aerosol synthesis is difficult. In fact, titania particles made in the flame aerosol reactors up to 25 t/h are dispersed in solutions to be surface-engineered. This undercuts the process advantages of aerosol technology. So, one step aerosol synthesis and functionalization of $TiO_2$ has been the *holy grail* in the manufacture of white pigments.

Such challenges can be addressed by decoupling the gas-to-particle conversion of the core and shell components.[29] For instance, a mostly rutile $TiO_2$-producing flame reactor (Figure 2a) is enclosed, to better control the process temperature and enable judicious injection of hexamethyldisiloxane (HMDSO, precursor of the $SiO_2$ shell) vapor in $N_2$, after $TiO_2$ formation. The HMDSO vapor is delivered through multiple jets in swirl cross-flow to the freshly-formed $TiO_2$ aerosol to prevent formation of ''dead volume'' upstream, using computational fluid dynamic (CFD) simulations and systematically designed experiments. Figure 2 shows how this is carried out by CFD monitoring of the aerosol gas composition along (Figure 2b) and across (Figure 2c–f) the reactor axis at various heights (0–3 cm) above the jet level. There, rather small or large (but fluffy agglomerate) core particles are coated. So the aerosol gas composition corresponds well to its particle composition (in contrast to conventional fluidized bed reactors involving much larger particles) during mixing of the core aerosol with the shell aerosol (carrier gas and precursor vapor and its product silica particles). So within 3 cm (Figure 2f), the core aerosol and shell precursor vapor streams have been mixed well (light green) resulting in rather minimal gas and particle concentration variation across the reactor radius. As a result, uniformly and hermetically coated core–shell particles are produced[29] (Figure 2i, k). The actual coating quality is assessed visually by microscopy and most importantly by the performance (photocatalytic, catalytic or antibacterial) of such core–shell particles.

Hermetically-coated particles are sought in bioapplications where any adverse properties (e.g., toxicity or disintegration) from or to the functional (e.g., magnetic, plasmonic) core particles need to be fully shielded by the shell. On the other hand, rough coatings could be acceptable if the residence time of core–shell particles in subsequent processes is rather short so diffusion of ions or molecules from/to the core through the rough porous shell is slow enough not to harm the performance of such particles.

Scalable synthesis of coated multifunctional or hybrid nanoparticles by smooth or rough shells are a challenge, where ever such processes can be used, provided of course, that is better understood. For example, *Janus-like* particles with a plasmonic (Ag), and a magnetic ($Fe_2O_3$ or Fe) component are sought for monitoring and even curing serious illnesses like cancer, given their thermal capacity. Making and coating such particles with a nanothin silica film, as earlier, could ''cure'' the toxicity that could arise from leaching of Ag ions in solutions.[30] Furthermore, such particles can be functionalized ''on the fly'' by mixing them with appropriate organic precursors further downstream with a process similar to the coating one described earlier. Through this mechanism the surface of particles can be modified with organic functional groups to stabilize their suspension in final product formulations or nanocomposites, drastically simplifying the manufacture and processing of such products.

## Devices

The incorporation of compatible and inexpensive nanoparticles in the construction of nanostructured devices is a major scientific and technological frontier in nanotechnology. Nanoparticles are the building blocks of such devices, as bricks are for houses. Today, most of industrial applications involve passive nanoparticles; since there are only simple oxides in the market. There are a few exceptions although,

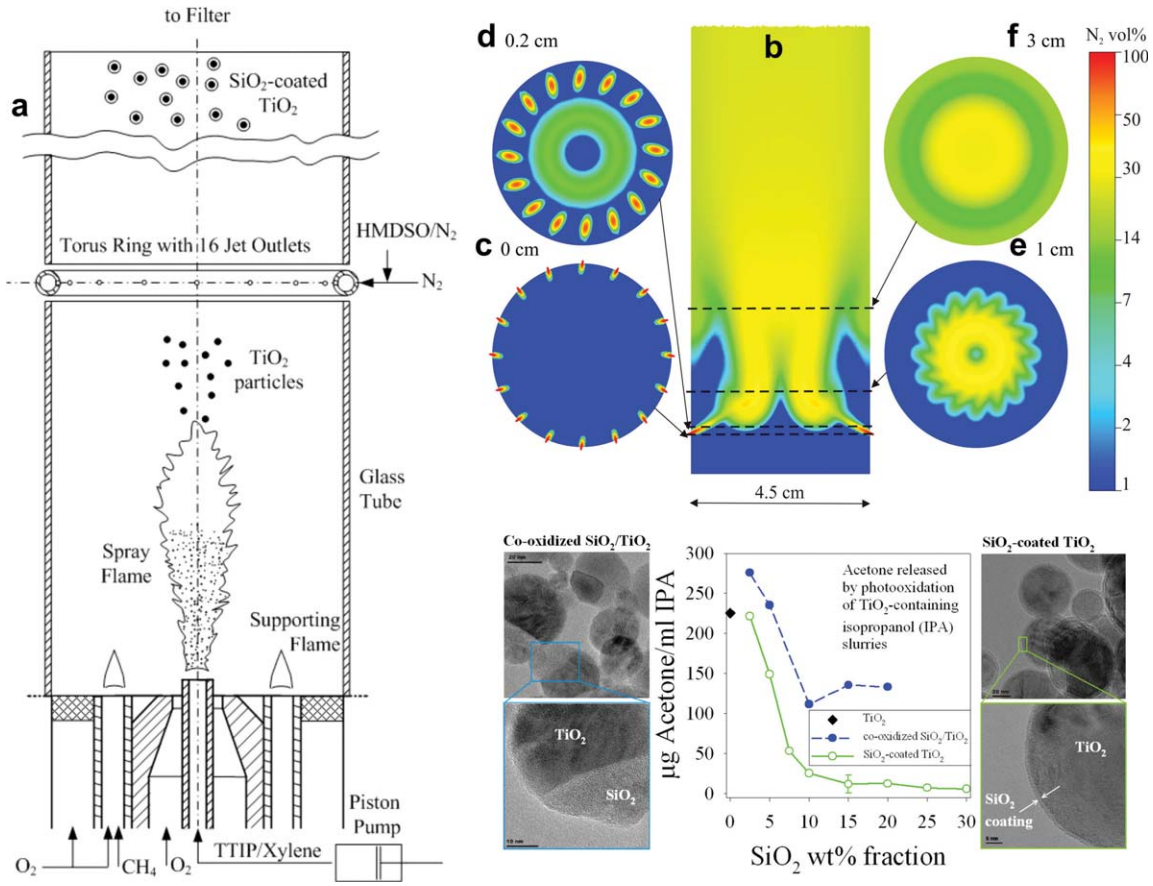


**Figure 2. (a) Experimental setup for in situ $SiO_2$-coating of $TiO_2$ made in an enclosed FSP reactor and a torus pipe ring with 16 outlets for injection of a silica precursor (HMDSO) vapor in $N_2$, (b) contours of the shell precursor carrier gas ($N_2$) volume fraction along the reactor axis with a total flow of 15.8 L/min $N_2$. The gas composition across the reactor radius is shown also at 0 (c), 0.2 (d), 1 (e), and 3 cm (f) above the outlets (adapted from [29]). Co-oxidizing Si/Ti precursors instead of the aforementioned sequential oxidation results in particles with segregated (Janus-like) amorphous and crystalline domains (g, h). Such particles exhibit a high-photocatalytic activity when suspended in isopropyl alcohol solutions under UV light as indicated by the released acetone (i, blue broken line) as a function of their silica content. In contrast, particles that were in-situ coated with a uniform silica thickness (j,k) by injection of a silica precursor vapor downstream of $TiO_2$ formation (a-f) exhibited very little photoactivity (i, green solid line) above 10–15 wt % silica content.**

that point to the emerging opportunities. For example, sensors assembled with aerosol-made $SnO_2$ or $TiO_2$ nanoparticles are, at least, as good as ones made conventionally by wet chemistry processes for detection of various gases including, NO, CO and organic vapors.[31]

Most remarkably, new simpler aerosol processes have been developed for building such sensors.[32] Through this approach, cumbersome processes involving doctor-blading, drying and sintering of pastes or slurries of nanoparticles on electrodes are totally bypassed.[23] Figure 3 shows freshly-made $SnO_2$ nanoparticles (a) directly depositing to a cooled, (b) Si-wafer, (c) through a shadow steel mask, (d) for micropatterning and forming lace-like, (e) semiconducting films. For subsequent processing (e.g., cutting, washing, polishing, etc.), the adhesion and cohesion of such films is drastically enhanced by *in situ* annealing with a hot particle-free flame, (f) converting them to cauliflower-like films, and (g) having identical crystallinity and gas sensing performance as the initially deposited ones.[33] That way, transparent $SnO_2$ gas sensors are deposited onto complementary metal oxide semiconductor (CMOS) integrated circuitry, containing temperature sensors and Pt-heaters.[34]

Doping such $SnO_2$ particles with $SiO_2$ revealed the existence of an optimal composition at about 2-3 wt % $SiO_2$, at which composition both thermal stability and sensitivity of these nanostructured sensors is enhanced by forming aggregates of nanoparticles with neck sizes in the order of twice the Debye length of $SnO_2$. These developments make it possible to actually build such devices directly from the gas phase, especially when combined with standard microengineering (e.g., MEMS) processes.

Very recently, this process has been used successfully also in the synthesis, stabilization with silica doping and direct deposition of metastable $\varepsilon$-$WO_3$ nanoparticles between a set of Au electrodes, developing a highly selective sensor for acetone, a tracer for diabetes type-1 in the human breath, at realistic (90%) relative humidities.[35] This sensor could be used, for example, by emergency room doctors to determine whether a patient has developed diabetic ketoacidosis, a potentially serious complication that happens when diabetics do not take enough insulin. Someday it may also be used by

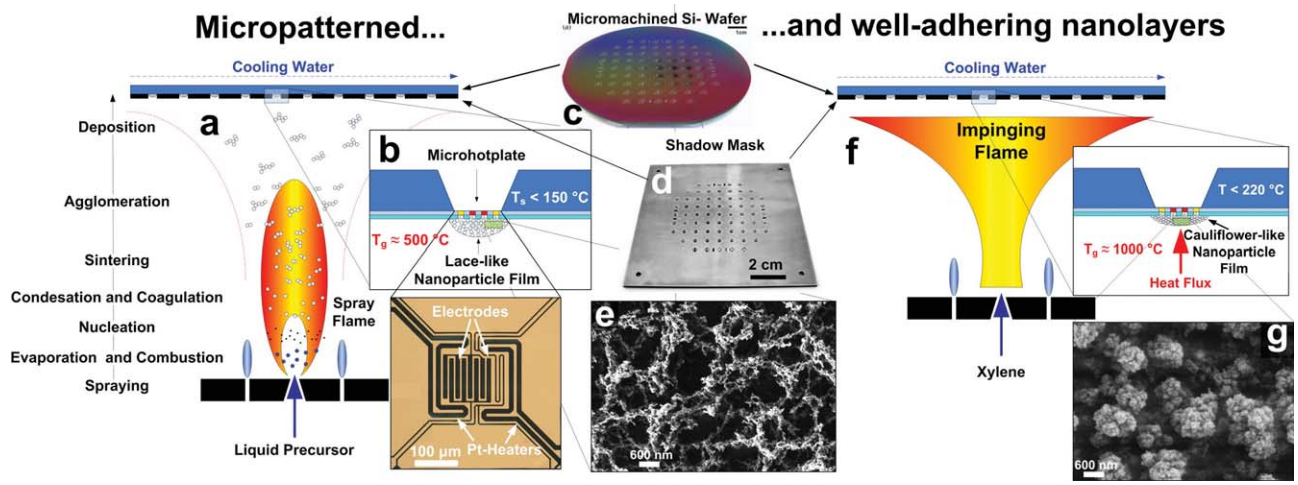


**Figure 3. Highly porous (98%) layers of $SnO_2$ nanoparticles (a) are deposited on a back-cooled (b) silicon wafer (c) through a shadow metal mask (d) from a flame aerosol reactor (adapted from [33]). These lace-like layers (e) are in situ mechanically stabilized by an impinging, particle-free xylene flame (f), resulting in well-adhering cauliflower-like films (g) that are superior CO, ethanol[33] and acetone[35] sensors.**

diabetics, in their own homes, to determine whether they need more insulin. In another field, nanostructured $LiMn_2O_4$ films have been directly deposited from particle producing flames on aluminum and stainless steel supports, to serve as battery cathodes. Furthermore, Eu-doped $Y_2O_3$ nanophospor screens were made that way. Their light scattering in the visible range showed a Rayleigh-like dependence on wavelength and was two-orders of magnitude lower than that of screens made with the commercial micrometer-sized phosphor powder.[36] As a result; the nanophosphor coatings maintained nearly constant brightness in a very wide range of film densities promising a substantially improved screen resolution. These developments underline the potential of aerosol synthesis and direct deposition of nanostructured functional layers at ambient pressure for other devices and the imperative need to solve the scaling-up problem.

## Challenges in Designing the Manufacture of Nanoscale Materials

The nanoscale is a new frontier in engineering disciplines. The Newton, Fourier and Fick's laws along with Navier-Stokes equation are used in every engineering course to describe, momentum, energy and mass transfer. Such laws and equations make the educational backbone for the quantitative description of transport phenomena from industrial processes to natural systems (weather, climate, air pollution, sea currents, etc.). At the nanoscale level, the very effective concept of continuum is no longer applicable. For example, collisions between gas molecules leave empty distances of 65 nm even at room-temperature and pressure. To make materials with characteristic sizes below 20 nm, where all bulk material properties start to differ, one needs to search for alternative concepts to support quantitative product and process design.

Clearly, one may start with the kinetic theory of gases and molecular dynamics to properly describe such systems. However, the kinetic theory of gases, cannot be used alone, since its fundamental hypothesis of elastic collisions between molecules, giving rise to macroscopic phenomena (e.g., temperature), collapses during the growth of clusters by completely inelastic collisions (e.g., during sintering or coalescence); leading to cluster growth rather than bouncing as with gas molecules, the so-called "granular cooling". Such concepts and tools are commonly used in physics or chemistry, but in a rather elaborate form making their application by engineers to process design rather cumbersome and unattractive for creative and imaginative engineering solutions. For example, detailed dynamic simulations shed ample light to the exact motion of the tiniest form of nature. Is it possible to simplify these for a certain material and process window and reduce them to a tractable form to be imported in a CFD simulator to optimally design a process for scaling-up the manufacture of nanoscale materials? Something like this was done in replacing multidimensional population balance simulations[9] with monodisperse ones in CFD design of aerosol reactors,[11] by taking advantage of the self-preserving size distribution[10] principle, as discussed earlier.

Clearly there is a need to advance the wealth of knowledge, generated by molecular dynamics, density functional theory and other simulations, to an elegant and simple quantitative framework that field engineers in industry can readily deploy and implement in practical systems. To accomplish this, engineers need to appreciate the details of matter in a more substantive manner than simply requiring multiscale modeling. Even the aforementioned described success with particle dynamics in seemingly simple practical systems (e.g., silica, titania, etc.) was only attained *after* detailed simulations and experiments[4] had unraveled the dynamics of particle coagulation and coalescence (sintering).[8] This may appear as an arduous task. It might be, however, a tractable one since a lot is already known[37] and can be used to describe fairly accurately the early stages of aerosol manufacturing. For example, primary particle ($d_p$), and aggregate or hard-agglomerate ($d_{cH}$) diameters can be predicted from first principles when all material properties and particle-temperature history are known.[17] Inversely, such (e.g., effective) properties or process variables can be estimated or back-tracked (e.g., chemical reaction pathways) from the evolution of particle properties

without any adjustable parameters in simple (premixed flame) reactors and simple products,[38] e.g., pure $TiO_2$; a practice well-known to chemical engineers.

The emphasis of this approach is on describing the detailed dynamics of particle growth from molecular clusters of less than 1 nm to fractal-like particles of several micrometers in diameter as they are encountered in large-scale aerosol manufacture[39] of $TiO_2$ and $SiO_2$ in the fluid dynamic environment of flame reactors.[11] Such analysis has to account for the detailed aerosol phenomena of particle formation, growth by surface chemical reactions and coagulation, sintering, transport to reactor walls and particle surfaces (coating or functionalization), restructuring and fragmentation by Brownian, shear and even field forces. Although the basic collision laws might be reasonably well understood, significant and critical challenges remain in describing the fusion or coalescence of such particles from an early amorphous form to a crystalline state, requiring implementation of molecular dynamics to a tractable form again.

Synthesis of multicomponent, functionalized and layered materials offers a number of challenges in product and process design. It offers the very attractive opportunity of drastically mitigating adverse (e.g., toxic) effects of nanoparticles, while maintaining and taking full advantage of their highly desirable properties. To achieve such multilayered materials, the *chemistry* of deposition of shells on cores is essential. As with CVD on microeletronic substrates, that has been proven to be the key technology on building layered structures on substrates, chemical engineers are confronted with a tougher challenge and opportunity here with aerosol particles that are tirelessly moving around. One may imagine a window of "opportunity" for the deposition of such shells on haphazardly moving core nanoparticles similar to the "strike zone" in baseball. Premature conversion of the shell precursor vapor may interfere with formation of the core nanoparticles altering their desired characteristics (e.g., conversion of desirable rutile to undesirable anatase in pigments by Si that instead of coating the titania surface, interstitially enters its lattice promoting anatase formation and *Janus-like* particles). On the other hand, belated conversion may result in nucleation of shell material particles ("snow formation" as is referred in CVD) and rough, granular shells that are nonhermetic and rather undesirable.

The structure of nanoparticles is another design challenge. Understanding the dynamics of soft-agglomerates (restructuring and fragmentation) is an important frontier for academic and industrial research in making new nanocomposites with polymers containing nanoparticles beyond silica. This challenge is significant when addressing the potentially toxic effects that might be caused by nanoparticles that are components of such soft agglomerates and can be easily "broken" away on their deposition on lung airways, if these agglomerates are hydrophilic and penetrate through membranes.[23]

Another challenge is the dynamics of dense suspensions that are important not only to aerosol reactors, but even more in liquid (slurries and pastes) and solid processes (granulation). The aerosol framework may offer a rare opportunity to understand such dynamics from first principles taking advantage of its rigorous description of transport phenomena. For example, when fractal-like agglomerates of very fine nanoparticles ($d_p < 10$ nm) undergo coagulation, their apparent density rapidly decreases and their collision diameter increases, influencing much larger reactor volume than that of equivalent spheres. As a result, even though their solid-volume fraction might be low, say 0.001 and a chemical engineer may consider such processes as equivalent to "transport reactors", following Levenspiel, they are quite dense as their apparent volume fraction could be 0.1 to 0.2, equivalent to fluidized beds. Such aerosols encounter high-concentration particle dynamics that are no longer described by Brownian coagulation.[37] Their coagulation rate is up to 30 times higher than that predicted by classic Smoluchowski coagulation that may lead to agglomerate restructuring and compaction to denser structures and eventual gelation consistent with experimental observations of soot formation.[40]

## Summary

Although a lot needs to be learned in this rather unexplored interface of science and engineering, enough is known to systematically employ chemical engineering principles for its further understanding and development of processes for large-scale manufacturing of promising materials and devices. In fact, even if one cannot predict the future, extrapolating the success of nanostructured products in the market today (optical fibers, carbon blacks, fumed silica and pigmentary titania) he or she can be sure that if the promises of nanotechnology are to be materialized in our everyday life, this will involve sound chemical engineering.

With today's sensitivity to the adverse effects of technology to the environment, workers and consumers, the promising and unknown properties of nanoscale materials might be looked with skepticism before being fully embraced. Again this is a challenge and an opportunity for chemical engineers who are well aware and continuously deal with the adverse effects of poisonous chemicals and anticipate and prevent accidental exposure to hazardous materials and incidents. For example, as cleanrooms for microelectronics had to be kept overpressure to prevent microcontamination, laboratories for manufacture of nanomaterials should be kept under pressure to prevent accidental release of such materials to the environment. Process gases in nanomaterials manufacture have to be totally cleaned before released into the environment capitalizing on baghouse filtration, a technology well developed on sound particle engineering. There is no doubt that the experience of chemical industry will be invaluable in developing safety protocols and measures to responsibly manufacture and use nanoscale materials to build functional materials and devices in the not too distant future.

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