Aerosol synthesis of nanomaterials

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Aerosol synthesis of nanoparticles

An aerosol is liquid and/or solid particles dispersed in a gas. The upper size limit (<10-100 µm) of these particles is determined by gravity as big particles are pulled down immediately. The lower limit is about 1 nm because when they hit the surface they have to stick to it, which means these particles are larger than gas molecules that would bounce from the surface. Nanoparticles are particles smaller than 100 nm and they have numerous applications such as catalysts due to their high surface to volume ratio, active parts in semiconductor devices and pigments. Aerosol methods are bottom-up methods, where particles form from precursors in aerosol. Some of most important applications for aerosol methods are carbon nanotube production, pharmaceutical powders, and carbon black for industrial usage. Some other methods for nanoparticle synthesis are solution-based methods where particles form in solution and milling where big particles are broken to smaller until one gets nanoparticle powder. As demand for nanoparticles increases the need for low cost methods to produce them that are scalable to industrial usage increases as well. Aerosol method is one such technique that meets these criteria. Therefore, one can claim that it is often considered as the most useful method for the synthesis of clean nanoparticles.[1, 2]

To prove the statement in following paragraphs I will introduce some advantages of aerosol methods. I will also present some disadvantages and problems regarding aerosol methods.

In liquid phase synthesis, which is one of the main competitors of the aerosol method, solutions containing precursors are mixed together and often heated. During this process, usually many different reactions happen forming not only nanoparticles but also byproducts. Therefore, it is considered a dirty process. To get clean nanoparticles requires multiple post processing steps, which can even damage nanoparticles and result high water usage. Some of these problems are also present in milling, which is considered as an important method for the production of nanoparticles. In aerosol methods, all these problems are avoided as synthesis happens in gas phase and precursors can be chosen so that most of possible byproduct forming reactions cannot happen. These factors mean that aerosol methods allow the production of clean nanoparticles usually without significant post processing thus making the overall process simple, which can be considered as criteria for usefulness. Advantages of aerosol method are clearly visible in Figure1, where process flows for aerosol and liquid phase synthesis are visualized. [3,4]

(Figure removed due copyright, originally Figure 1 at [4])

*Figure **1**. Process flow for aerosol method shown by red arrows and flow for liquid phase synthesis is shown with black arrows. [4]*

Aerosol reactors usually operate in continuous mode meaning that as long precursors are fed to it and conditions within the reactor are favorable synthesis continues. Liquid phase synthesis and milling are on other hand batch processes meaning that only certain amount of material can be produced at a time and then process starts again from beginning. In addition, material characteristics in batch processes can vary from one batch to another. Continuous operation is especially important for industrial production but has also some significance for film deposition applications. [3]

One of the most important properties of aerosol methods is the possibility of online characterization, which is done by diverging part of flow in the reactor to analysis equipment. By taking samples from output and possibly some other parts of the reactor it is possible collect real time information about the process conditions and properties of the end product. This information can then be used to optimize the process parameters while the reactor is running. Size distribution, concentration, and charge distribution of particles are some of the properties usually followed as from them one can determine if the reactor is producing wanted material. Otherwise might happen so that one collects many samples from output and then uses even up to day at a microscope checking the samples only to find that no wanted material was produced. [1]

By controlling process conditions one can control the synthesis thus controlling properties of produced such as material composition, size distribution, and crystal structure. In aerosol methods, this is possible by controlling flow rates, precursor concentration, and temperature distribution. This kind of control can be quite simple in some aerosol methods but especially controlling temperature distribution might be difficult in some other aerosol methods. This kind of control over process conditions is not possible in liquid phase or milling processes. However, it is possible in some methods used by semiconductor Industry but they are more complex than aerosol methods. [1]

Simple sample and end product collection is one of the criteria that characterize simple synthesis methods, aerosol methods meet these criteria because in them collection is performed directly from reactor output from aerosol form. Multiple collection methods exist and in all of them, the device for collection is placed to line leading from reactor output to vacuum pumps. With some collection devices, it is possible to deposit films with thickness up to several micrometers either directly to substrate or by transferring the collected film to substrate. In some cases, reactor output is used as input for another system for deposition or further processing. [1,5]

Compared with many other synthesis methods aerosol reactors are quite simple systems. This due to the fact that they do not usually need vacuum or high pressure to operate and nonvolatile precursors are often used. The simplicity of these systems makes them attractive partly because they are usually cheaper to operate and acquire than equipment to produce the same quality products in similar amounts. When one adds easy collection, characterization, and controlling of process conditions the simplicity of these systems compared with others just increases. These factors are also important when scaling systems from research use to production equipment. [6]

As many other methods aerosol methods also allow the synthesis of many different materials, which is one of criteria for evaluating usefulness. Figure 2 contains electron micrographs of two different nanoparticles produced with aerosol method and gives some idea about their size distributions. One of the factors behind the wide material range is that all precursor chemistries developed for chemical vapor deposition (CVD) that can be used in aerosol reactors, also almost any kind of precursor can be used. [2]

(Figure removed due copyright, originally Figure 3 at [8] and Figure 1 at [2])

*Figure **2**. On left scanning electron microscope picture of ZrO_2 particles. [8] On right transmission electron microscope picture of silicon nanoparticles produced with vapor phase synthesis. [2]*

Many different aerosol methods exist but few of them allow nanoparticle production. However, they can be divided to two main categories according to in what form precursors are fed to the reactor: gas-to-particle and droplet-to-particle conversion. As seen from Figure 1, where process flows for these two approaches are shown, in gas-to-particle route vapor or gas either reacts or condensates forming particles. Next, these particles grow by surface reactions and fusing together or just fuse together when they collide with final product as powder. In droplet-to-particle approach, droplets are generated from solution and end as powder by either surface reaction and drying or evaporation and reaction. The foregoing information is shown in more detail in Figure 3. As process conditions can be quite different in different methods there are some materials for each method whose production is best done with that particular method. Not all materials can be synthesized with all methods although some overlap exists. Available precursor types and chemistries along the properties of synthesized material depend on method used. Complexity of systems used in different methods varies greatly as lasers or plasma equipment are needed for some and in some others, gas phase precursors are fed through a tube with certain temperature distribution where they react eventually forming particles. Also only some of these methods can be used to industrial scale production. [1,6]

(Figure removed due copyright, originally Figures 32-1 and 32-2 at [1])

*Figure **3**. Process flow diagrams depicting two main categories of aerosol synthesis methods. [1]*

One of the main problems in aerosol methods is it that processes are not yet well understood, which makes the scaling of reactors and optimizing process conditions difficult. When the process is well understood predictions about the properties of the end product can be done based on temperature distribution, flow rates, precursor size distribution and concentration, and type of precursor. Lack of understanding also means that one cannot know what happens if a process that works in a research reactor is scaled to commercial use. However, with the ever-increasing speed of computers and better models about process dynamics in aerosol reactors understanding has started to increase significantly. [6,7]

In previous paragraphs, I have presented evidence why the thesis statement is correct but also some counterarguments regarding the matter. Next, I will summarize the content of previous paragraphs to reinforce the argument before the conclusion.

The aerosol method is capable producing wide variety of different materials and the clean end product can be acquired directly from the reactor with no need for post processing associated with some other methods. The whole system used in aerosol synthesis is quite simple and easy product/sample collection makes it even more attractive and enables online characterization. With real-time information about process conditions, process optimazation becomes quite easy. Although limited understanding about process dynamics of the aerosol method causes some problems for the usefulness of aerosol methods, its signify-cance has started to decrease. From these factors, it can be concluded that aerosol method is the most useful method for the synthesis of clean nanoparticles.

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