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Review

# Advances in scalable gas-phase manufacturing and processing of nanostructured solids: A review

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ABSTRACT

Although the gas-phase production of nanostructured solids has already been carried out in industry for decades, only in recent years has research interest in this topic begun to increase. Nevertheless, despite the remarkable scientific progress made recently, many long-established processes are still used in industry. Scientific advancements can potentially lead to the improvement of existing industrial processes, but also to the development of completely new routes. This paper aims to review state-of-the-art synthesis and processing technologies, as well as the recent developments in academic research. Flame reactors that produce inorganic nanoparticles on industrial- and lab-scales are described, alongside a detailed overview of the different systems used for the production of carbon nanotubes and graphene. We discuss the problems of agglomeration and mixing of nanoparticles, which are strongly related to synthesis and processing. Finally, we focus on two promising processing techniques, namely nanoparticle fluidization and atomic layer deposition.



**Contents**



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## Introduction

In recent years, chemistry has focused much attention on large molecules and supramolecular assemblies thereof, while engineering has become able to create increasingly smaller devices. They meet each other naturally at the nanometre scale, in the field known as nanoscience or nanotechnology. Great advances have been made, yielding all kinds of novel, nanostructured materials such as graphene, nanowires, and quantum dots. Such nanostructured materials are of great importance; they have the potential to significantly contribute to solutions to the great challenges faced by society today, e.g. energy conversion and storage. The building blocks of such materials are often nanostructured solids or particles: solid objects with a size <1 mm, consisting of multiple elements and/or multiple materials, at least one of the elements of which has a nanoscale dimension. These elements can be classified as 0D, 1D or 2D depending on the number of dimensions in which they have a size smaller than a threshold $d^*$. This threshold $d^*$ is defined by a critical characteristic of some physical phenomenon (free path length of electrons, phonons, length of de Broglie wave, length of external electromagnetic or acoustic waves, correlation length, penetration length, diffusion length, etc.) that gives rise to size-effects (Pokropivny & Skorokhod, 2007). However, in this review we will focus on the generic, commonly used value of 100 nm for $d^*$.

Nanostructured solids exhibit extraordinary properties compared with those of their bulk counterparts. To give a few examples, nanoparticles have lower melting points and higher solubilities than bulk materials; quantum dots emit specific photons depending on their size; carbon and inorganic nanotubes exhibit high mechanical strength and controllable electric conductivity; graphene has a very high electrical and thermal conductivity. However, to fully exploit these special properties it is crucial that the material has a high level of quality, reflected by demanding specifications. For example, for quantum dots to emit well-defined photons, it is crucial that the standard deviation in their size is less than 5%. This corresponds to a precision of a single consistent atom layer throughout the 1–15-nm range (Pokropivny & Skorokhod, 2007). Such precision can now only be achieved in small-scale ultra-fast processes, using tricks from colloidal chemistry. This generates samples for R&D, but there is no clear route to a scalable commercial process. In catalyst preparation, synthetic strategies based on molecular principles yield better-defined catalyst structures than traditional and cruder catalyst preparation techniques such as impregnation and deposition/precipitation. This can aid mechanism determination and the development of novel catalytic routes in several classes of reactions (Murray, Kagan, & Bawendi, 2000). Additionally, for consumer products based on nanostructured materials it is of utmost importance that morphology is precisely controlled. For example, the fabrication of transparent electrodes requires high-quality large-area graphene sheets (Wegener, Marks, & Stair, 2012). The strength of ultra-strong nanostructured materials is largely determined by the extent to which the amount of defects present can be minimized (Li et al., 2009a). A high level of control over morphology is thus crucial, both in fundamental studies and in the application of such materials.

Many of the current methods for manufacturing nanostructured materials do not lend themselves to large-scale production, which greatly inhibits innovation and actual use in society instead of in the lab (Roebben et al., 2014; Wegner, Schimmoeller, Thiebaut, Fernandez, & Rao, 2011; Zhu & Li, 2010). Large-scale production with high quality is required to achieve breakthroughs in seemingly unrelated fields, from the nanostructured materials required for personalized medicine without side-effects to those for high-power, fast-charging batteries. The technologies used to manufacture such materials expected to impact global problems related to food, water, energy and the environment must be scalable. "The main reason that these problems are so grand is that they are ubiquitous and therefore the related commercial markets have become commoditized. Very often, a technology that exploits a unique attribute of a nanomaterial can offer improvements in functional or engineering performance, but almost as often, these technologies require scarce materials (and therefore expensive) or slow or complicated manufacturing processes (and also expensive)" (Giges, 2013). The scaling-up of nanotechnology is not just something that remains to be done after all the interesting scientific work has been carried out; it should be an integral part of the scientific process leading to breakthrough solutions. When nanostructured materials are synthesized in such a way that the relevant processes concerning kinetics, thermodynamics and transport phenomena are known and controlled, then the knowledge is intrinsically scale-independent. In other words, rational design facilitates large-scale production. The urgent need to pay more attention to this topic is also reflected by the title of the Kavli Futures Symposium four years ago: "Plenty of Room in the Middle", paraphrasing Feynman's famous quote. With this title the organizers implied the need to master mesoscale structures and to bring nanoscientific discoveries to scale, bringing them to devices that can affect our everyday lives. It was concluded that "great opportunities that lie in scaling up from atomic assembly and individual nanodevices to macroscopic systems and structures with emergent properties and functionality" (Kavli Foundation, 2011).

While the majority of researchers currently working on nanostructured materials focus on liquid-phase synthesis, it is our firm belief that gas-phase routes deserve more attention if scalable processes are to be achieved. Currently, most single-material nanoparticles are commercially produced via gas-phase processes (Teoh, 2013). In this review, we discuss gas-phase approaches used to produce, transport and functionalize nanostructured solids, focusing on methods that have good prospects for scale-up. First, we discuss the gas-phase synthesis of nanoparticles (0D materials), with a strong emphasis on the use of flame reactors because this is the most widely used technique at the industrial scale. We then address the synthesis of carbon nanotubes and graphene as examples of 1D and 2D materials that can already be produced at a relatively large scale. This is followed by a section on the subsequent physical processing of nanoparticles, discussing agglomeration, fluidization and mixing. Finally, we look into structuring at the nanoscale involving multiple materials (e.g., a host nanoparticle with a film or nanoclusters on its surface) using atomic layer deposition. It is certainly not our ambition to discuss all the developments in the field. We rather focus on a number of developments that we see as promising ways to produce nanostructured solids at the industrial scale that are already in use or are expected to find their way to industry in the short term.