Introduction to Nanoscience

Study Guide

Chapter 4 - Fabrication Methods

Nanotools, in the context of this text, include the categories of characterization and fabrications. Synonyms for fabrication include synthesis (on the small scale) and manufacturing (on the larger scale). We focus mostly on small-scale fabrication (since we are mostly science and not technology), but many of the methods we discuss in this chapter can most certainly be applied to large operations.

More prevalent than ever, the terms top-down and bottom-up have gained significant meaning via nanaotechnology. The terms are self-explanatory and understanding that, we could technically be done with this study guide and stop here. ***Top-down*** fabrication is a subtractive process from bulk starting materials to make nanomaterials and ***bottom-up*** fabrication is an additive process that starts with precursor atoms or molecules to make nanomaterials.

Chapter Objectives:

- Understand the distinction between top-down and bottom-up fabrication as it relates to nanomaterials
- Try to probe into the details of fabrication methods and in mixed methods, try to isolate the top-down from the bottom-up
- Familiarize yourself with the different types of top-down methods: mechanical, thermal, high energy, chemical and lithographic
- Familiarize yourself with the different types of bottom-up methods: gas-phase, liquid phase, lithographic and biological
- Fabrication methods are rich in chemistry, engineering, physics and biology. Try to discern among them if possible. Take some fab methods and dissect them according to discipline of origin
- In all fabrication methods, there are advantages and disadvantages. Please keep a tally as you read through the chapter with regard to each one
- Each method has its limitations and expectations with regard to quality, dispersion and throughput (and energy input). Throughput, quality, energy investment, equipment cost and long-range order are sometimes at odds with each other
- Mechanical methods are the usually lowest in cost– an advantage

- Boundaries are blurred continually. For example, many mechanical methods involve heating or they produce heat upon activation– are they then a thermal method as well? Please do not let such distinctions get in the way.

Top-Down Methods

Mechanicanosynthetic Methods Mechanical methods offer the least expensive ways to produce nanomaterials in bulk. Ball milling is perhaps the simplest of them all. Ball milling produces nanomaterials by mechanical attrition in which kinetic energy from a grinding medium is transferred to a material undergoing reduction. ***Compaction and consolidation*** is an industrial scale process wherein nanomaterials are "put back together" to form materials with enhanced properties. Metallic alloys can be made this way. Many top-down mechanical methods are utilized by industry.

Thermal methods form a nebulous category and we try and focus on those that provide heat to a fabrication process. Of these, ***electrospinning*** is a means to form nanothread materials.

High energy methods are those that require an excessive input of energy– whether in the form of heat, electricity or solar energy. ***Arc discharge*** was the first controlled means of making carbon nanotubes. ***Laser ablation*** and ***solar flux*** also work well. The problem is control of quality and potential upscale. We include ***plasma methods*** in this category. Plasmas are created in high-energy situations (high potential bias, etc.). The problem with this and other high-energy methods is upscale potential– with the possible exception of solar flux methods as sunlight is easily available.

Top-down ***chemical fabrication*** methods are always easy to upscale and many, such as ***anodizing***, are widespread industrial processes.

Lithographic methods, as we all know quite well, although energy intensive and requiring expensive equipment and facilities, are top-down methods capable of producing for the most part micron-sized features. Lithography is the means of making printed circuits and computer boards for several decades now. The push to miniaturize in the future is a costly venture as more powerful sources (high energy electron beams and shorter wavelength sources), support equipment and facilities are required.

Some nano techniques are top-down / bottom-up, depending on your point of view. ***Nanoimprint lithography*** (NIL) is lithography but not according to typical standards. It is more like ***template synthesis***. A template material is made first and then stamped into a soft polymeric material to form a pattern. The template stamp is formed by top-down method as is the stamped material. Nanosphere lithography utilizes latex spheres that form a templated matric. Nanomaterials (reduced from by a top-down process from a solid or liquid source) are formed from the bottom-up to thought the interstices of the lattice template. So, we can call these techniques template process as well.

Discussion Topic: Discuss the advantages and disadvantages of top-down lithography methods.

Bottom-Up Methods

Bottom-up methods start with atoms or molecules to form nanomaterials. ***Chemical vapor deposition*** is a gas-phase process by which reactive constituents react over a catalyst or pre-templated surface to form nanostructured materials. The economical synthesis of carbon nanotubes is by CVD. Precursors in the form of methane or acetylene or other carbon source gases are passed over Co, Fe or Ni catalyst. Once decomposed into carbon, nanotubes are formed by the catalyst particle.

Atomic layer deposition is an industrial process that is capable of coating any material, regardless of size, with a monolayer or more of a thin film. A relatively pure bottom-up process starting with gas-phase constituents. ***Molecular beam epitaxy*** and ***MOCVD*** are other industrialized processes that are considered to be bottom-up.

Liquid phase methods are also numerous. It is within the liquid phase that all of biology ***self-assembly*** and synthesis occurs. Molecular self-assembly is covered in more detail in *chapters 11* and *12*. Liquid phase methods are upscalable and low cost.

Electrodeposition and ***electroless deposition*** are very simple ways to make nanomaterials (dots, clusters, colloids, rods, wires, thin films).

Anodizing aluminum to make a porous oxide structure is a simple way to make nanomaterials. The porous structure is a nanomaterial as well as any material synthesized within. Porous membranes are in many ways the ultimate template.

A new generation of nano bottom-up methods have made the scene. Many of the new methods are both inexpensive and offer high throughput. Disadvantages include establishment of long-range order. The new methods include nanolithography (dip pen method), nanosphere lithography

Discussion Topic: Discuss the advantages and disadvantages of bottom-up lithography methods.

Discussion Topic: We also mixed in gas-phase methods with catalysts, a solid phase material. Should we be too worried about these boundaries?

Chapter Summary

- Nanomaterials can be fabricated by numerous procedures: top-down, bottom-up and mixed methods.

- The starting material for a top-down method is a bulk material. Substance is subtracted from the bulk material to form nanomaterials.
- The starting material for a bottom-up method is an atom or a molecule. Bottom-up methods build nanomaterials by addition of substance
- Top-down methods include mechanical, thermal, high-energy, chemical and other techniques
- Bottom-up methods include gas-phase methods like CVD, MOCVD, ALD and others.
- Bottom-up liquid phase methods are the primary vehicle for self-assembled systems
- Template methods are mostly bottom-up methods
- Sol gel synthesis is an age old method to make colloids and now incredible nanostructures
- Molecular modeling and simulation is the wave of the future.... keep it on the frontburner