

**MUSTANSIRIYAH UNIVERSITY
COLLEGE OF SCIENCE
CHEMISTRY DEPARTMENT**



Post-Graduate(M.Sc.)

Nanomaterials characterization

**Lecture Title : Chemical Vapor Deposition (CVD)
methods**

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1.2.2 Chemical Vapor Deposition

The CVD process is now probably the most common of all bottom-up approaches. It is used today to grow structures, like nanotubes, nanowires, and nanoparticles aided by several different types of chambers and growth-enhancing methods. The process consists of decomposing a gaseous precursor that adheres and accumulates onto a substrate (i.e., a silicon wafer or a quartz slide) (Jensen 1989). The presence of a catalyst, either predeposited on the substrate or provided in the gas feedstock, activates the chemical reaction between the substrate surface and the gaseous precursor. The CVD reaction can be achieved either with temperature (thermal CVD) or with plasma (PECVD). Plasmas can be obtained with DC electric fields, RF fields, or microwave fields, and their presence allows decreasing significantly the process temperature compared to the thermal CVD process. The presence of plasma also enables a more aligned or directional growth of the desired nanomaterials. A number of forms of CVD systems are in wide use and are frequently referenced in the literature. Some examples include atomic-layer CVD (ALCVD) in which two complementary precursors [e.g., $\text{Al}(\text{CH}_3)_3$ and H_2O] are alternatively introduced into the reaction chamber; metal-organic CVD (MOCVD) in which metal-organic precursors are used to obtain specific crystalline structures [e.g., tantalum ethoxide, $\text{Ta}(\text{OC}_2\text{H}_5)_5$, to create TaO nanostructures, and tetra dimethyl amino titanium (TDMAT) to create TiN]; laser-assisted CVD (LCVD); rapid thermal CVD (RTCVD) that uses heating lamps or other methods to rapidly heat the wafer substrate; ultrahigh vacuum CVD (UHVCVD); and more (Adams 1988; Jensen 1989).

The CVD process is widely used to produce CNTs and semiconductor nanowires, such as Si, GaN, and ZnO. CNTs have received much attention in the recent years for their potential application in several fields of bioengineering, from enhanced cell growth to biosensing, biomanipulation, and drug delivery. The most common synthesis routes for CNTs are CVD processes because they allow large-scale production of CNTs with high purity and good yield. To clarify how the CVD process works, we show a schematic diagram of a thermal CVD growth system used for the synthesis of CNTs (Fig. 7). In this example, a carbon-containing precursor is



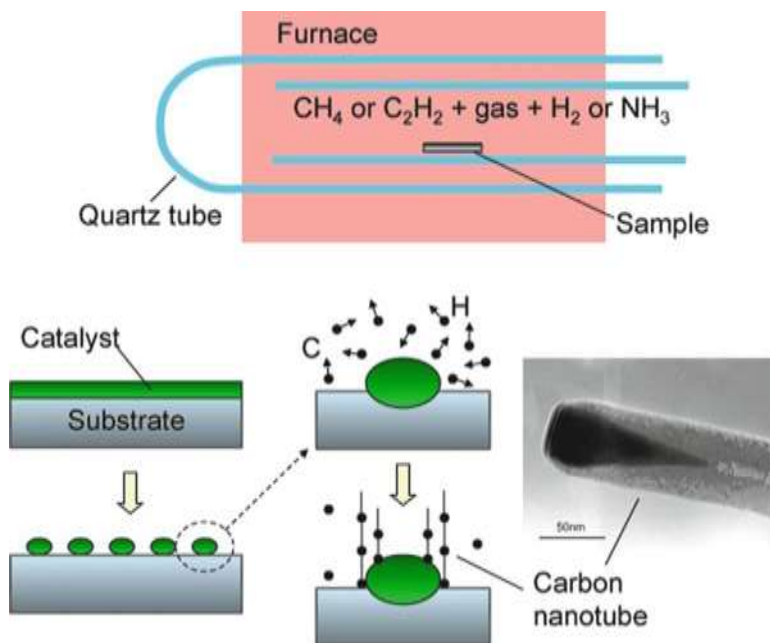


Fig. 7 Schematics of a thermal CVD furnace (*top*) and basic flow of a carbon nanotube growth process (*bottom*)

decomposed in the furnace at high temperature. The growth reaction is activated by the presence of a catalyst that can be deposited on the sample's surface (as in the figure) or in the gas mixture fed to the reactor (e.g., injecting ferrocene $\text{C}_{10}\text{H}_{10}\text{Fe}$). The most common carbon sources used in thermal CVD growth of CNTs are mixtures of ammonia (NH_3) and acetylene (C_2H_2) while the catalyst metal can be cobalt, iron, or nickel. The growth proceeds through several steps: first, the catalyst metal breaks up into islands at high temperatures and forms metal seeds for the reaction; then, the hydrocarbon gas supplied in the quartz tube decomposes creating floating C and H atoms; the floating atoms are then attracted by the catalyst seeds that become supersaturated and condensate forming ordered tube-shaped graphene sheets. The catalyst particle can then either stay attached to the substrate (base growth) or get pushed to the tip of the formed nanotube (tip growth) conferring different properties to the final structure. This type of growth process, although being relatively inexpensive, forms a randomly distributed array of CNTs with a complex hierarchical microstructure. Bundles of tubes grow vertically, but the tubes are intertwined and partially curled at small scales. This lack of complete alignment is normally overcome by the use of PECVD systems, which are a bit more complex and expensive, since they need additional constituents like electrodes, pumps, voltage supplies, etc.

1.2.3 Self-Assembly and Bio-Assisted Synthesis

As mentioned in the earlier section for the case of CNT growth, the assembly of nanostructures or nanoparticles in a periodically aligned fashion or in a functionally engineered geometry is often desired over random or disordered structures. Approaches for ordering or assembling nanostructures in a desired geometry have been widely investigated in the past and are still pursued in many different laboratories. Self-assembly provides the most convenient way for alignment, especially considering that at such small scales, single-structure manipulation and postgrowth rearrangement appear to be very expensive if not at all impractical. Chemistry and molecular biomimetics are the dominant fields leading the design of hybrid technologies combining the tools of molecular biology and nanotechnology. Molecular biomimetics combines the physical and biological fields to assemble nanomaterials using the recognition properties of proteins.

Researchers have found ways to process nanoparticles of a wide range of materials – including organic and biological compounds, inorganic oxides, metals, and semiconductors – using chemical self-assembly techniques. In these cases, molecules are attached, patterned, or clustered on specific substrates or to themselves using chemical and biomolecular recognition (e.g., the preferential docking of DNA strands with complementary base pairs). Other techniques, like micelle, reverse micelle, and photochemical and sonochemical synthesis, are also employed to realize one-, two-, and three-dimensional self-assembled nanostructures. Lately, viruses have also been used to assemble specific nanostructures (Mao et al. 2004). A review of the path to nanotechnology through biology is provided in (Sarıkaya et al. 2003). It was shown that proteins, through their specific interactions with inorganic and other macromolecules, could be used in nanotechnology to control structures and functions just like they do biological tissues in organisms. Taking lessons from nature, polypeptides can be genetically engineered to specifically bind to selected inorganic compounds for specific applications, as outlined in Fig. 8 (Sarıkaya et al. 2003).

The use of organic molecules is also a powerful technique in the synthesis and arrangement of semiconducting nanoparticles, for example quantum dots, used in biological labeling and tagging. One of the major issues in the synthesis of these isolated islands of materials is to prevent particles' agglomeration and coarsening. Micelle processes and organic ligands capping (TOPO) are synthesis methods based on the simple mixing of surfactant with desired materials' sources. With these methods, it is possible to synthesize and/or align a wide range of nanomaterials spanning from magnetic nanoparticles (i.e., Fe_3O_4 particles found in magnetotactic bacteria) to the bright CdS quantum dots used for bioimaging. Micelles are employed as small chemical-reacting chambers in which nanomaterials are synthesized in fixed-sized cells (Fig. 9). One of the first examples of nanoparticle synthesis using a reverse-micelle process was for fabrication of FePt nanoparticles (Sun et al. 2000) using a combination of oleic acids and oleyl amine to stabilize the monodisperse FePt colloids and to prevent oxidation. With this method, the authors showed that it is also possible to control the size of the synthesized nanoparticles and their composition,

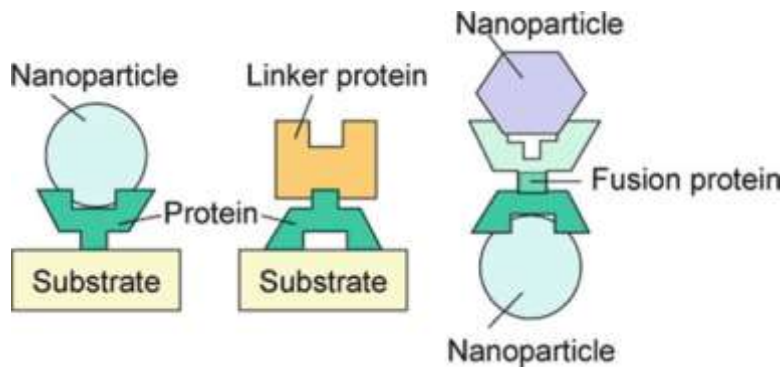


Fig. 8 Examples of molecular biomimetics (adapted from Sarikaya et al. 2003). Proteins can be used, for example, to bind nanoparticles to a functionalized substrate, to create linkers onto a specific substrate, or to connect different nanoparticles with each other

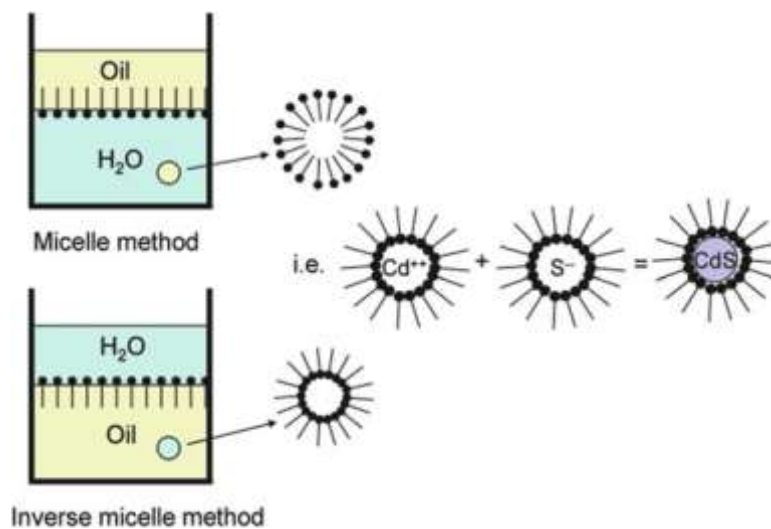


Fig. 9 Micelle and reverse micelle processing for synthesis of nanoparticles. On the *right*, it is shown the schematic for the synthesis of CdS quantum dots via reverse (inverse) micelle method

simply tuning the molar ratio of the solvents. Upon drying, the particles could self-assemble into three-dimensional superlattices that are chemically and mechanically robust and can, for example, support high-density magnetization reversal transitions.

The micelle process is also commonly used in the synthesis of semiconducting quantum dots. For example, CdSe nanoparticles capped with ZnS coating offer significant advantages as bioimaging agents as compared to the commonly used organic

fluorescent dye materials. Quantum dots are ~20 times brighter than the typical organic dye molecules, and their emission is ~100 times more stable to photobleaching than conventional fluorescent dyes (e.g., rhodamine). They can be made water soluble by chemical functionalization and can also be made specific cell- or organ-targetable via chemical or biological conjugation (Chan and Nie 1998; Akerman 2002). They can be imaged with a conventional fluorescence microscope. Besides the visible-emitting quantum dots, both near-IR and UV-emitting dots can also be synthesized.

The essence of bottom-up processing of nanotechnologies is mastered by nature in biological systems. For example, cells function on similar length scales to those of synthetic nanosystems. The molecules that operate and react in living cells are similar to the devices imagined for building nanosystems. Rather than using biological elements for the assembling of inorganic nanostructures, another way proposed for the synthesis of nanomaterials relies on incorporating the biological components themselves into artificial nanoscale structures and devices. Biological molecular motors, for example, have been incorporated into artificial structures, and the light harvesting complexes of plants or photosynthetic bacteria have been incorporated into synthetic membranes. From this point on, a vast array of applications that combine artificial structures with biological components can be envisioned and investigated, defining the future of nanobiotechnology.

4. Laser Pyrolysis

Laser pyrolysis is a technique that uses IR laser energy to decompose materials by heating gas-phase reactants in an oxygen-deprived environment. This method is used to produce extremely pure spherical nanoparticles with small-diameter, small-size distribution and with a low agglomeration level (Herlin-Boime et al. 2004). Such particles are used, for example, as precursors for surface treatments of ceramics. A similar technique, called laser ablation, is also used for the production of CNTs and nanowires.

5. Electrochemical Deposition/Electroplating

Electrochemical deposition is a technique used for manufacturing ordered arrays of nanomaterials, like quantum dots on a flat surface, for coating different surfaces or for patterning thin films (Allred et al. 2005). It represents one of the most powerful techniques that allow obtaining high-density and high-aspect ratio designs, with excellent reproducibility of the process and with great precision of the final products. Similarly to lithographic techniques, electrochemical deposition requires a polymer mask through which metal is deposited. Differently from other mask-based techniques like isotropic etching, ion milling, and RIE, electrochemical deposition avoids the problem of shadowing near edges or interfaces and builds structures atom by atom. The techniques rely on the presence of an electric field in a solution, which allows metal ions to discharge and conform to the smallest features of a mold.

Metal deposition can be carried on under two major techniques (Madou 2002): with current (pulsed or DC) or electroless (via catalytic, exchange, or electrophoretic reactions). The first method takes place in an electrolytic cell and involves a reaction under an imposed bias and current flow. In this case, important process parameters to control are pH, current density, temperature, agitation, and solution composition. The second technique, the electroless deposition, is based on a substantial oxidation reaction that replaces the dissolution of a sacrificial substrate.

6. Spraying Synthesis

Spraying processes are a viable technology for coating large area devices, and represent a simple and inexpensive alternative to produce sensing devices and nano-sized coating of surfaces (Mooney and Radding 1982). Spraying processes take place in a chamber containing a high-energy flame produced, for example, using plasma spraying equipment or using a carbon dioxide laser. A flow of reactants (gas or liquid in form of aerosols or a mixture of both) is forced into the flame and decomposes, forming particles by homogeneous nucleation and growth. The subsequent rapid cooling of the material completes the formation of nanoscale particles. In its simplest form, the reagent is simply dissolved in a carrier liquid and sprayed on a hot surface in the form of tiny droplet of ~100-nm diameter. In this case, the spray is formed from a liquid pressurized by compressed air or mechanically compressed through a small nozzle.

7. Atomic or Molecular Condensation

Condensation is a well-known technique used to produce primarily metal-based nanoparticles. The process takes place in a vacuum chamber: first, a bulk piece of metallic material is heated, melted, and vaporized to produce a stream of atomized matter. A gas flow (either inert or reactive) is then introduced into the reaction chamber to rapidly cool the metallic vapor. The cooled metallic atoms form condensed liquid nanoparticles, which then coalesce in a controlled environment, preserving a spherical shape with smooth surfaces. As the liquid particles are further cooled, they solidify and stop growing. The so-formed nanoparticles are very reactive and sensitive to agglomeration, which is prevented by adding coating or surfactants to keep them separated. If oxygen is present in the gaseous stream of the second chamber, the reaction results in the formation of metal oxide nanoparticles.

8. Supercritical Fluid Synthesis

Supercritical fluids are materials forced in a state above their critical point by regulating their pressure and temperature. They are obtained by vaporizing a liquid in a closed chamber, until the vapor phase becomes as dense as the liquid phase.

This supercritical state is very sensitive to the process' parameters and tunable. Methods using fluids in such a unique state are now used for the synthesis of nanoparticles, exploiting the rapid expansion of the supercritical solution, and they are also used for coating and filling nanostructures (Ye et al. 2004). The most common reaction media used in this process are supercritical carbon dioxide (scCO₂) and water (scH₂O) because they are nontoxic, nonflammable, inexpensive, and environmentally benign. In addition, they ensure much higher reaction rates and an increased selectivity. Although it has many advantages, supercritical fluid synthesis remains technically demanding, and it is still being adapted for large-scale production.

2 Conclusions

Top-down and bottom-up approaches are complementary in nanofabrication and comprise a numerous set of techniques. Their use and development have been at the center of material research for the past few decades, promising a wide range of applications in (non)biologically related nanotechnology fields. The use of a particular approach is often dictated by the specific need for a particular characteristic, shape, or composition of the nanomaterials for the different applications. Often, methods are used in combination to complement each other.

This chapter presented a brief overview of the most common techniques used for the fabrication of nanostructured bulk materials and nanomaterials with potential applications in biology and bioengineering fields. Most of the techniques described are continuously evolving even as we write and they represent a wide and active area of research in physics, chemistry, and engineering fields. A deep understanding of the mechanisms behind all the nanofabrication methods requires a broad and profound knowledge of the interdisciplinary aspects that regulate the properties of the materials and of the processes used. The details of the chemistry, physics, and mechanics of these methods go beyond the scope of this chapter and can be found in the related technical literature.