Mustansiriyah University
College of Science
Chemistry Department

**Post-Graduate(M.Sc.)**

# *Nanomaterials characterization*

## Lecture Title : Two Approach Synthesis and Sol-Gel methods

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# *Synthesis and Patterning Methods for Nanostructures*

## Introduction

The nanofabrication processes can be divided into the two well- known approaches; Top-down and Bottom –up approach.

1- **Top-down approach**

**Definition:** uses traditional methods to guide the synthesis of nanoscale materials, i.e. the top-down approach it all begins from a bulk piece of material, which is then gradually or step by step removed to form object in the nanometer size (~1 billionth of a meter or $10^{-9}$ m) .

**Properties:**

1- These methods are generally not suitable for production on a very large scale because they presently encounter technological limitation
2- Require extremely long and costly processes.
3- They represent some of the most common approaches now used to pat- tern surfaces and create three-dimensional (3-D) features on substrates

**Techniques:**

The most common techniques used for nano applications:
1-Photolithography.
2-Anodization.
3-Ion- plasma etching.
4-Laser machining.
5-Plasma etching and powder blasting.

## 2-Bottom-up approach

**Definition:** It is the new paradigm for synthesis in the nanotechnology, begins from atoms and molecules that get rearranged and assembled to larger nanostructures. This approach allows a creation of diverse types of nanomaterial.

**Properties:**

1-the difficulty in the ability to control the distribution of particle size and shape. In order to overcome this problem can used two techniques:

A-Arrested precipitatio n method: relies on the exhaustion of one of the reactants or on the introduction of chemicals that would block the reaction.

B-Physical restriction method: relies on the confinement of the volume available during growth of the individual nanoparticles. Example of physical restriction includes using the micelle-reverse-micelle reactions or using templates.

2-limits the use of the produced nanomaterial's in applications where a random particle distribution is undesired.

3- Simple and non cost.

4- Nanoscale precipitates can be obtained with various techniques, for example by a controlled phase transformation guided by the free energy diagrams or by controlling the solid-state diffusion.

**Techniques:** There are numerous bottom-up methods used to produce nanomaterial:

1-Sol–gel processing.

2- CVD.

3- Self- assembly and bio-assisted synthesis.

4- Laser pyrolysis, electroplating.

5- Plasma or flame spraying synthesis.

6- Atomic or molecular condensation.

7- Supercritical fluid synthesis.

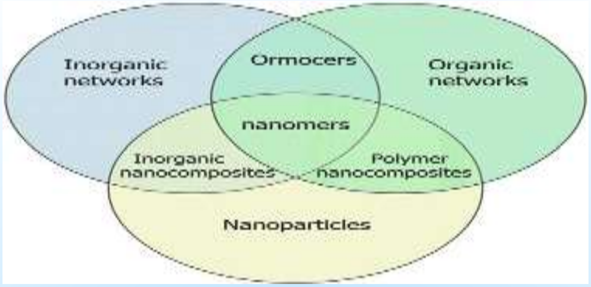
## 1.2 *Nanofabrication by Bottom-Up Methods*

With the first decades of the new millennium, standard top-down techniques for nanomanufacturing have approached a critical limit in the ability to miniaturize components. Further size reduction has required innovative chemical routes. Eric Drexler, a pioneer in nanotechnology, in 1986 said, “our ability to arrange atoms lies at the foundation of technology.” From this point on, several bottom-up approaches have blossomed, trying to build nanostructures one atom at a time, in the most efficient and precise way possible. On this aspect, nature is well-ahead of human engineering: proteins build structures quickly and effectively mastering the self-assembly of molecules as the basic building blocks of life. Nanoengineering is today putting a lot of effort in combining old, well-known chemical methods with new systems, even looking for inspiration from nature in bio-inspired structures and bio-assisted synthesis of nanodevices (Madou 2002).

### 1.2.1 Sol–Gel Processing

The sol–gel process in general is based on the transition of a system from a liquid “sol” (mostly a colloidal suspension of particles) into a gelatinous network “gel” phase. With this, it is possible to create at low temperature ceramic or glass mate- rials in a wide variety of forms. It is a long-established industrial process that is

Fig. 1 System model for nanocomposites produced by sol–gel (modified from Luther 2004)



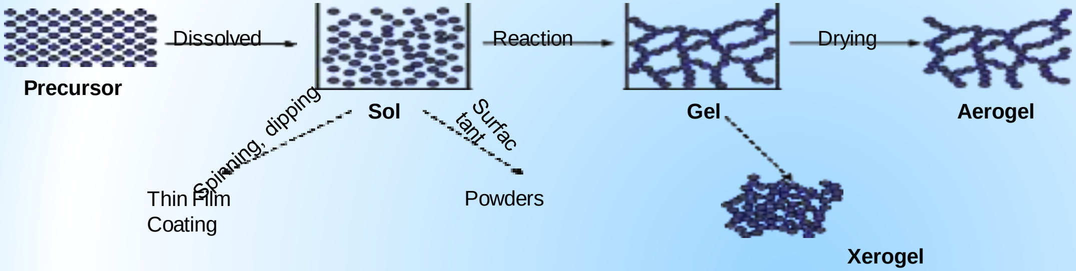




**Fig. 2** Basic flow of a sol–gel process (modified from Madou 2002)

very cost-effective and versatile. It has been further developed in last year for the production of advanced nanomaterials and coatings but also in bio-MEMS appli- cation for the production of piezoelectrics, such as lead–zirconium–titanate (PZT) (Madou 2002) or membranes (Guizard et al. 1992). Sol–gel processes are well- adapted for oxide nanoparticles (Lakshmi et al. 1997) and composite nanopowder synthesis as well as for access to organic–inorganic materials. A summary of all the possible interlinked combination of organic and inorganic nanocomposites that are produced by the sol–gel method is provided in Fig. 1.

The basic flow of the sol–gel process is described in Fig. 2. The “sol” is prepared by mechanically mixing a liquid alkoxide precursor (such as tetramethoxysilane, TMOS, or tetraethoxysilane, TEOS), water, a cosolvent, and an acid or base catalyst at room temperature. During this step, the alkoxide groups are removed by the acid- or base-catalyzed hydrolysis reactions, and networks of O–Si–O linkages are formed in subsequent condensation reactions. After this step, the treatment of the sol is varied depending on the final products desired. For example, spinning or dipping techniques can create thin film coating, and the exposure of the sol to a surfactant can lead to powders. Depending on the water–alkoxide molar ratio *R*, the pH, the temperature, and the type of solvent chosen, additional condensation steps can lead to different polymeric structures, such as linear, entangled chains, clusters, and col- loidal particles. In some cases, the resulting sol is cast into a mold and dried to remove the solvent. This leads to the formation of a solid structure in the shape of the mold (e.g., aerogels and xerogels) with large surface-to-volume ratios, high pore connectivity, and narrow pore size distribution. They can be doped with a variety of organic/inorganic materials during the mixing stage to target specific applications.