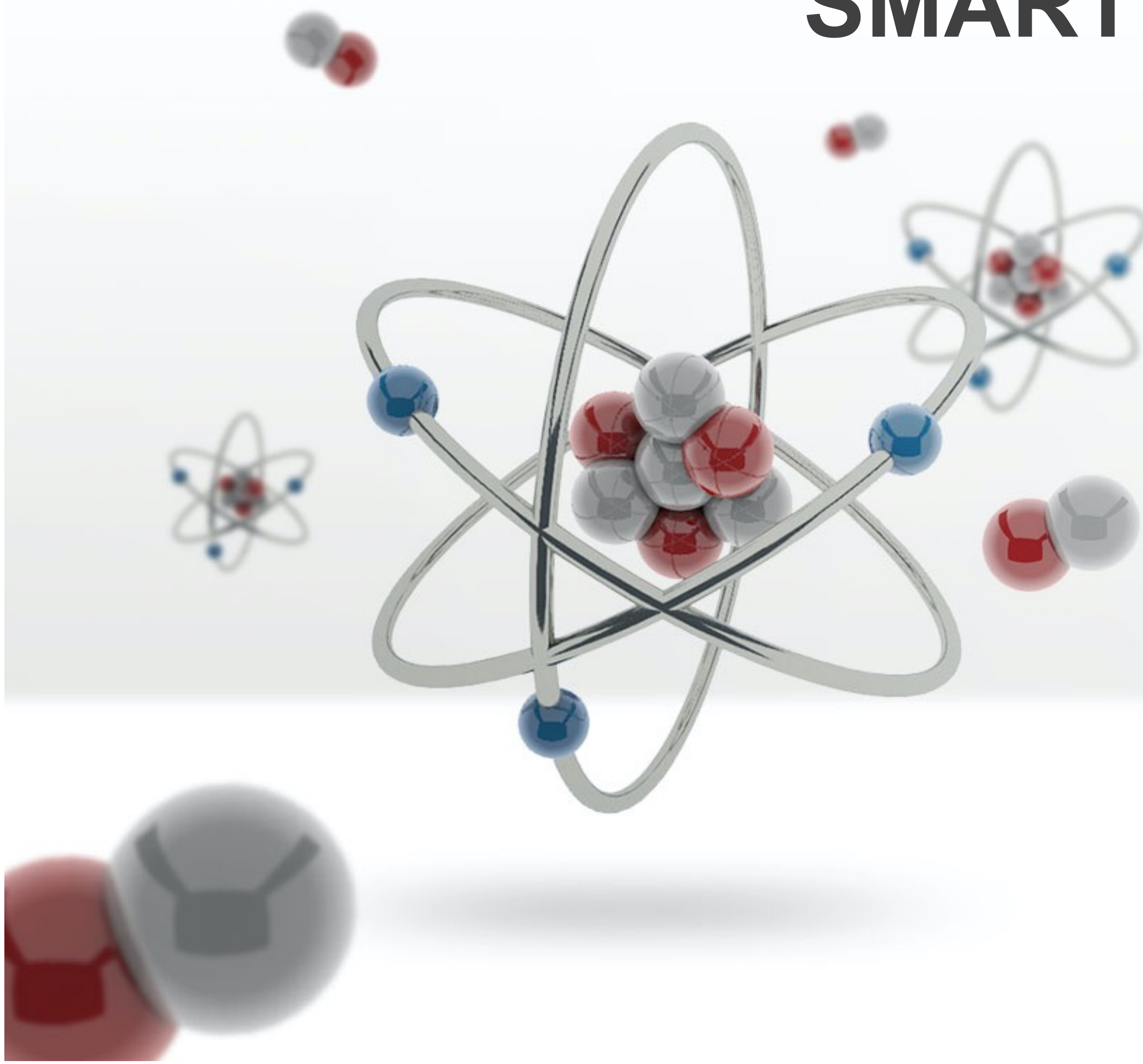
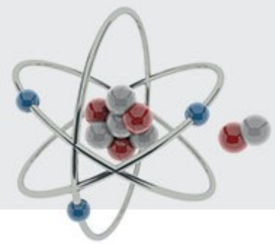
SMART HYBRID MATERIALS



UNIT 1: INTRODUCTION OF HYBRID MATERIALS

Objectives



Unit 1: Introduction of Hybrid Materials

Definition

Classification

- Class I: weak interaction
- Class II: strong interaction

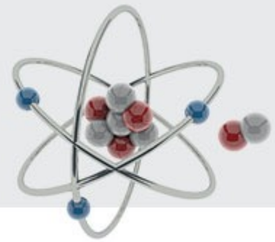
Advantages

Fabrication process

- Sol-gel Process
- Building Block

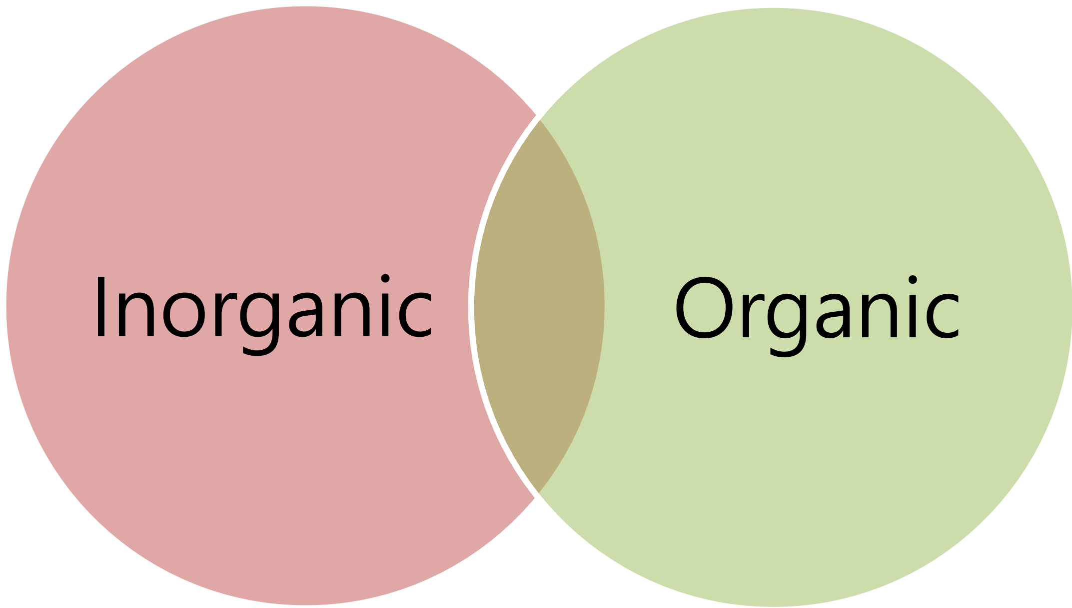
Characterization methods

I.1 Definition



" A hybrid material is a material that includes two moieties blended on the molecular scale"

Mechanical properties



Bonding

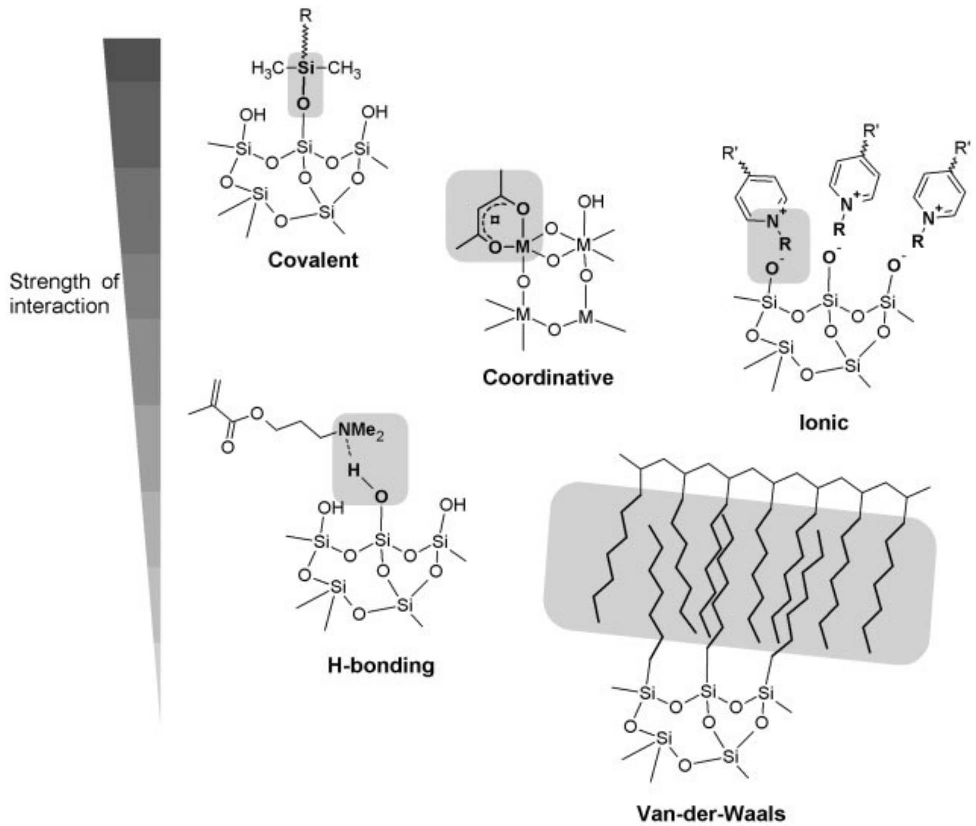
An overall structure

Superior properties

I.2 Classification

Class I

- Weak interactions

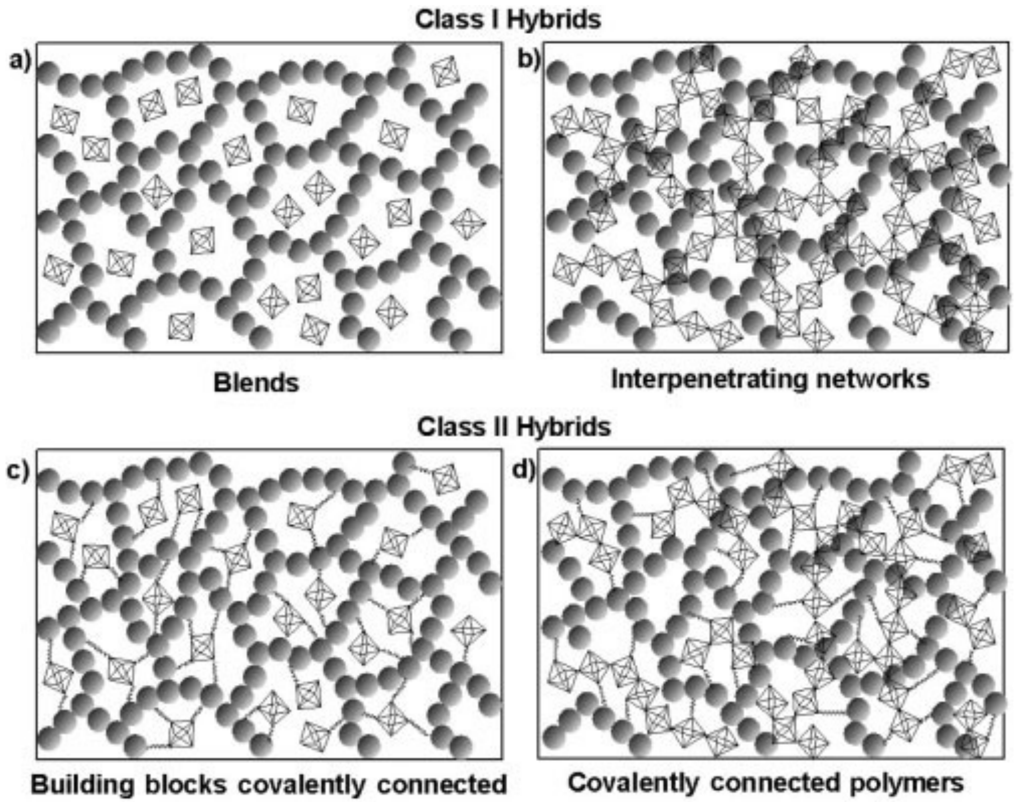


Class II

- Strong interactions

Selected interactions typically applied in hybrid materials and their relative strength.

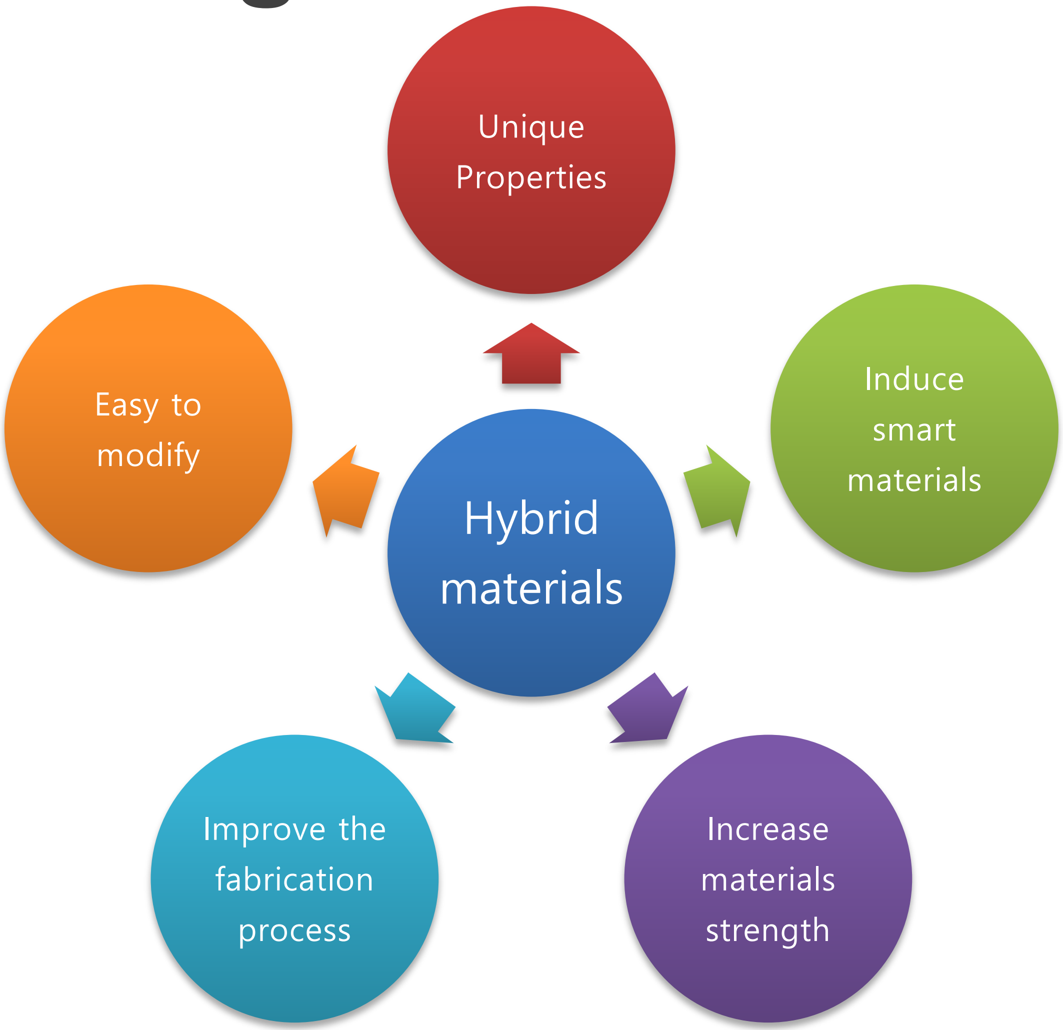
I.2 Classification

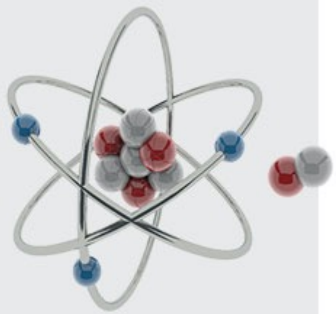


- Entrapped by physical interaction
- Entrapped inside the cross-linked polymer matrix

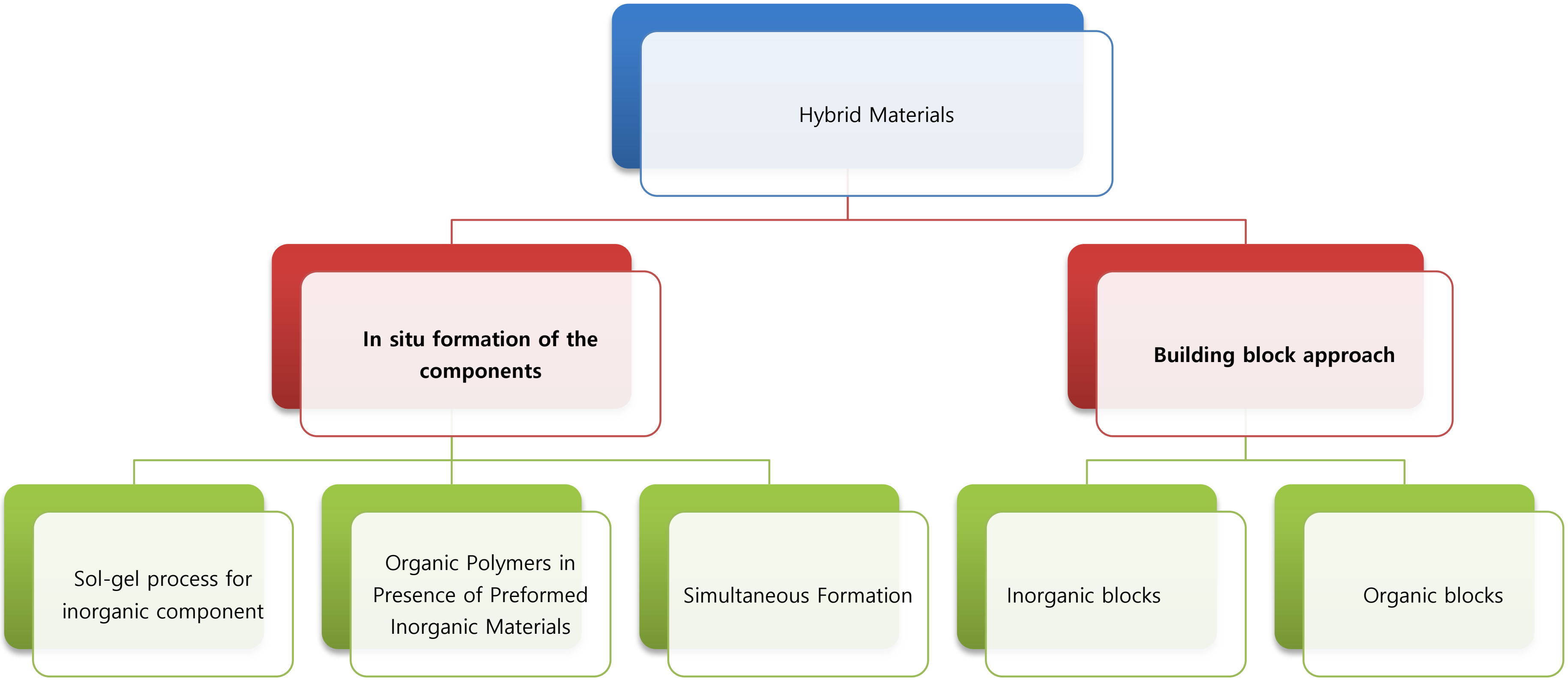
- Inorganic building blocks covalently bond with organic polymers
- Inorganic and organic polymers cov alently bond together

I.3 Advantages





I.4. Synthetic Strategies



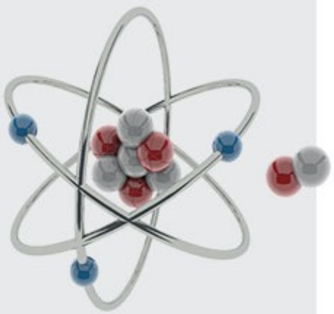
I.4.1 *In situ* formation of the components

Definition: based on the chemical transformation of the precursors used throughout material's preparation.

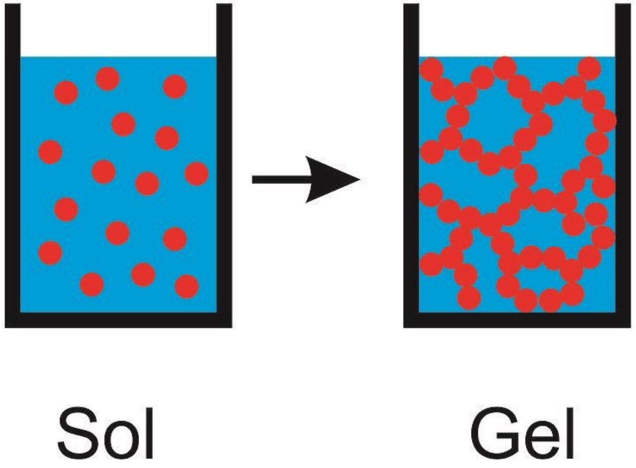
Hybrid materials by Sol-gel Process

=> What is the sol-gel process???

The sol-gel process (gelation): a change from a liquid state to a gel state through poly- condensation reactions

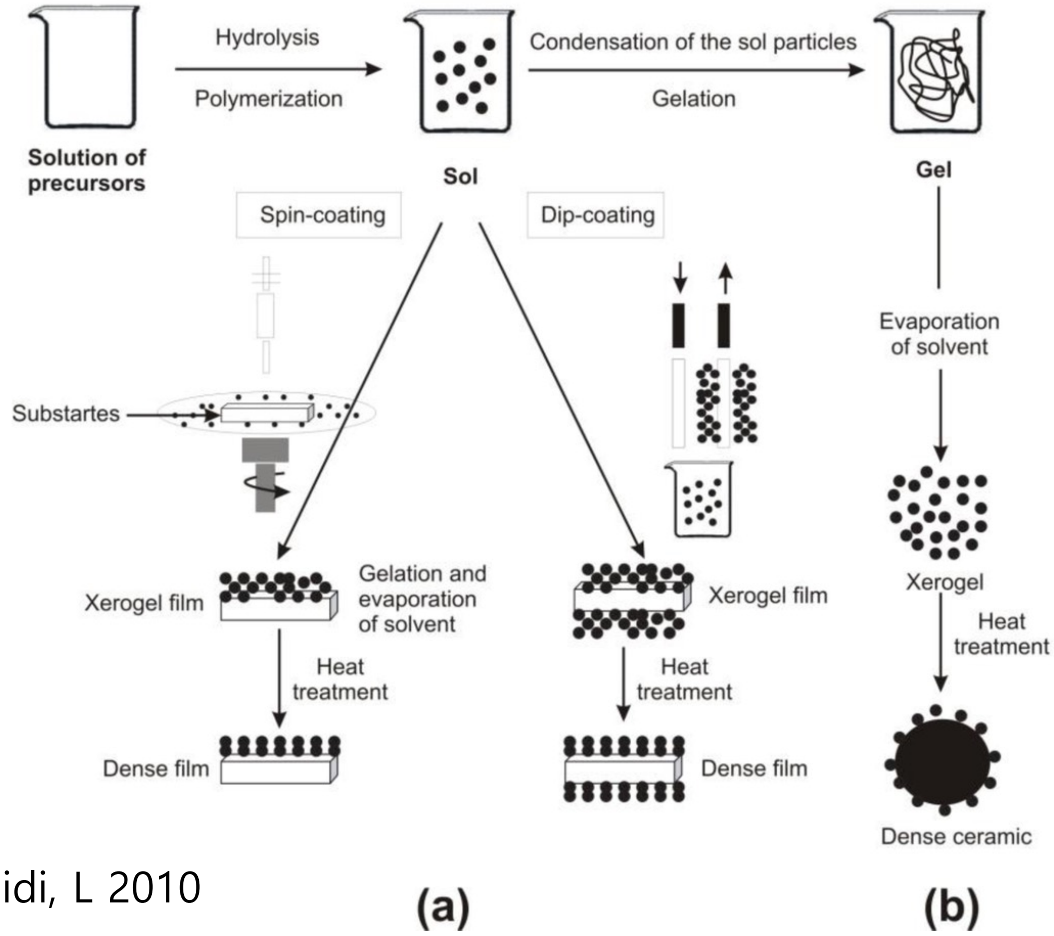


A sol is a stable dispersion of colloidal particles or polymers in a solvent.
The particles may be amorphous or crystalline.
Typical size few nm.



A gel consists of **a three dimensional conti nuous network of the sol particles,** which encloses a liquid phase.

Sol-gel Process



Znaidi, L 2010

Classifications:

- Silicon based sol-gel process
- Non hydrolytic sol-gel

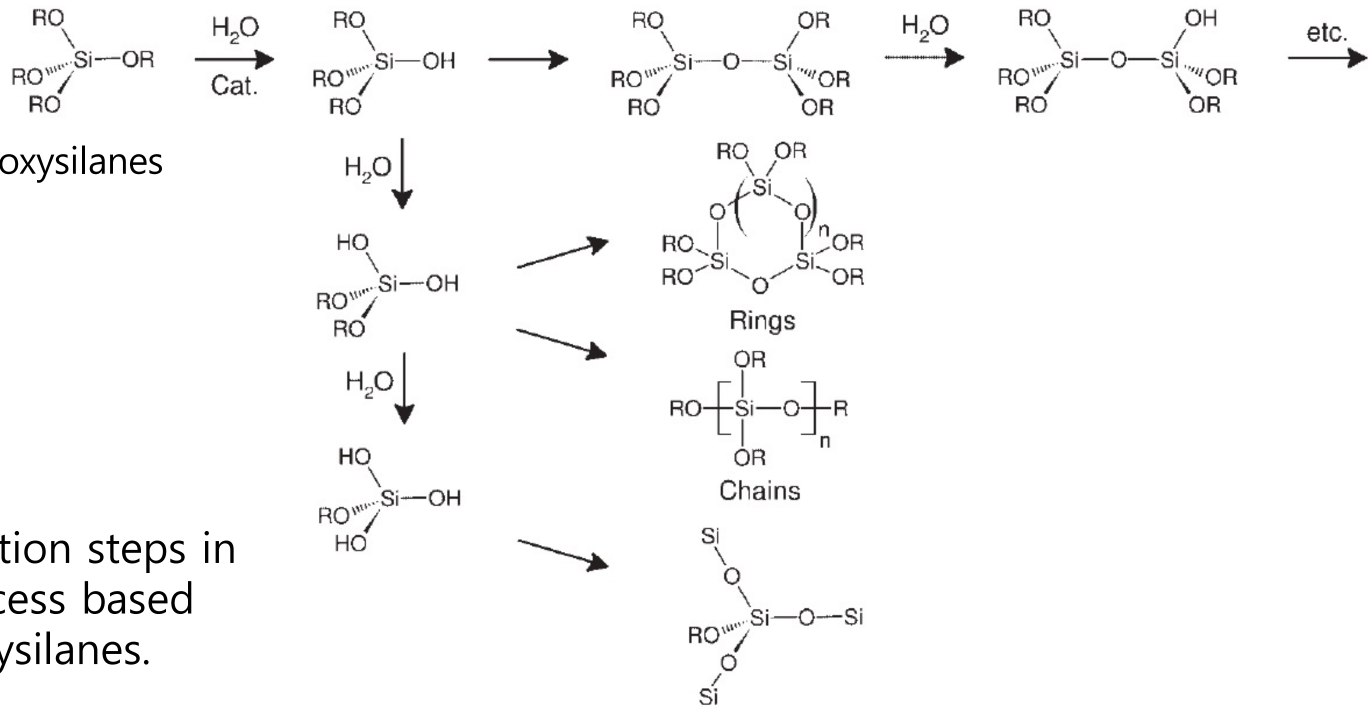
Silicon based Sol-gel Principle

$R_{4-n}Si - X_n$ —Hydrolysis→ $R_{4-n}Si - OH$ —Condensation→ $R_{4-n}Si - O - SiR_{4-n}$

as precursors with n=1-4, X as –OR′ or halo gen

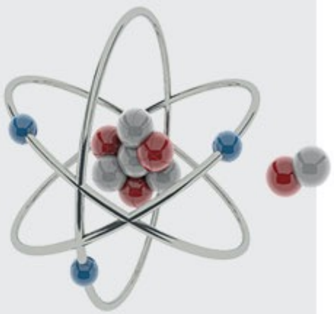
Unstable silanols

Undergo crosslink and form a gel



tetrialkoxysilanes

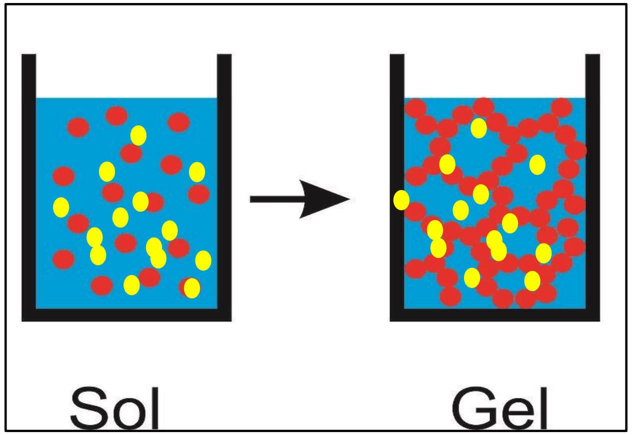
Fundamental reaction steps in the sol–gel process based on tetrialkoxysilanes.



How to make a hybrid materials?

Adding organic molecules into Sol

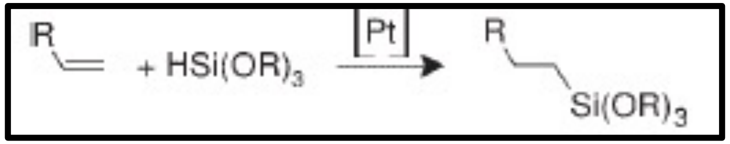
Organic Molecules
Inorganic Molecules



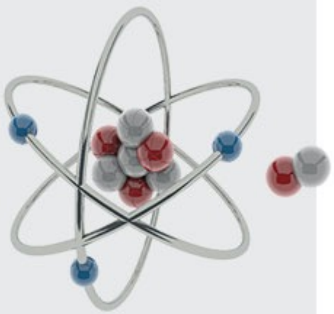
OM is entrapped in the formed network

Disadvantages: Phase separation and leaching due to the different polarity

Need: Modify the organic part with trialkoxysilanes to co-conden sation process



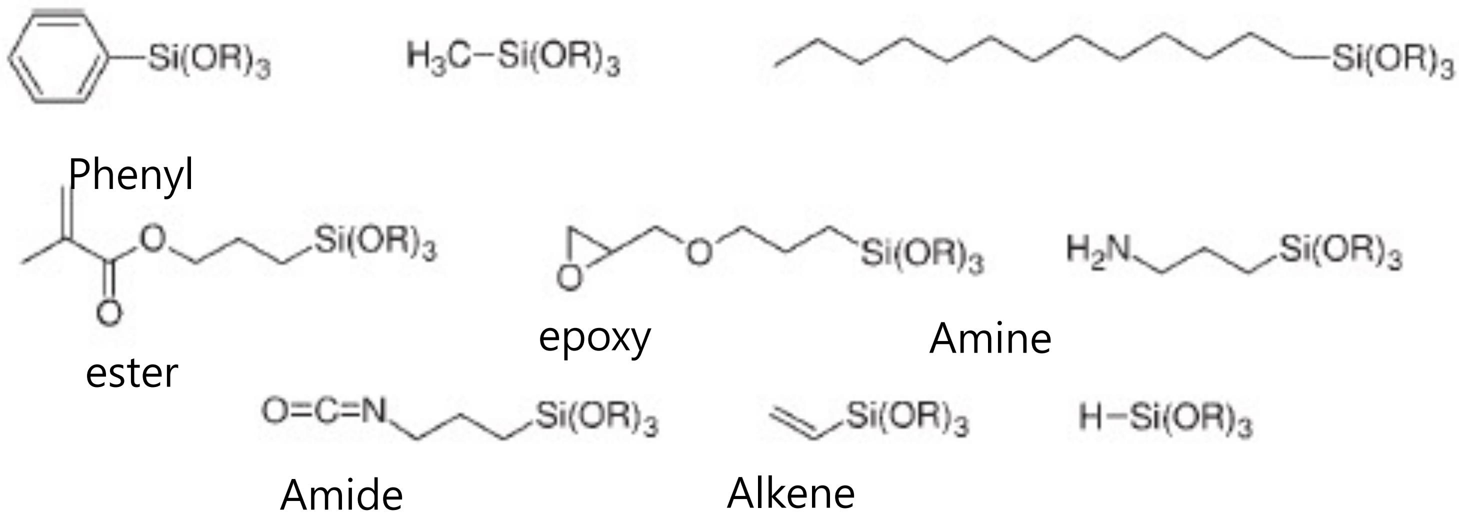
reaction between an unsaturated bond and a trialkoxysilane

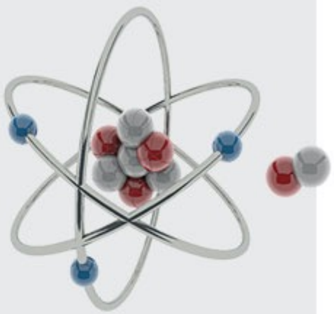


How to make a hybrid materials?

The functional group incorporated changes the properties of the final material

For examples:





How to make a hybrid materials?

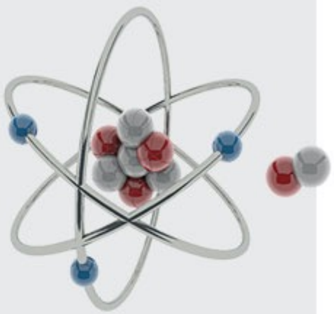
Sol-gel approaches + Organic polymers

→ carry out the inorganic network forming process in presence of a preformed organic polymer

→ carry out the organic polymerization before, during or after the sol–gel process.

Advantages:
- Mild reaction conditions
- Solvent compatibility

Properties:
- Not only based on O and IO components
- By the phase morphology
- By the interfacial region

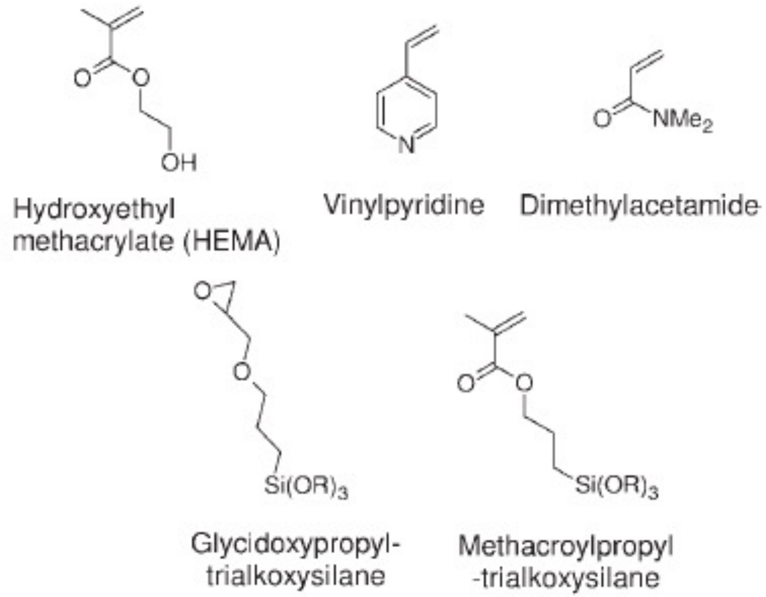


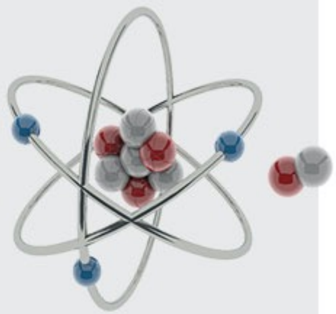
Sol-gel approaches + Organic polymers

Problems: Phase separation due to immiscible of organic polymers with alcohols as products of sol-gel approach.

Solutions:

Polymer contains functional groups which compatible with sol-gel process or interaction with inorganic networks





I.4.2 Formation of Organic Polymers in presence of Preformed In-organic materials

Preformed Inorganic+ Organic polymers

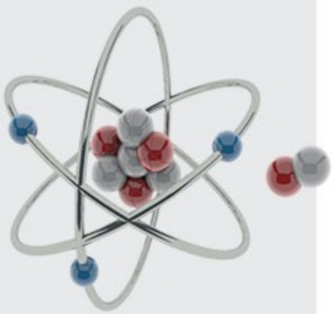
To overcome the incompatibility of the two species.

Inorganic Particles

- Pretreated with silane coupling agents
- Pretreated with surfactants

3D network Inorganic Particles

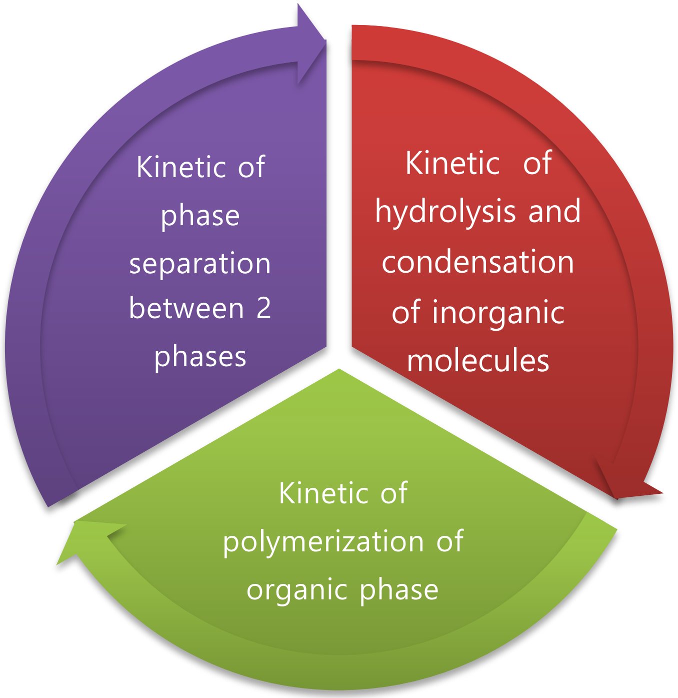
- Porous and layered inorganic materials is used
- 2D inorganic layers intercalate with organic molecules
- The host-guest hybrid materials: directly thread or *in situ*



I.4.3 Hybrid Materials by Simultaneous Formation of Both Components

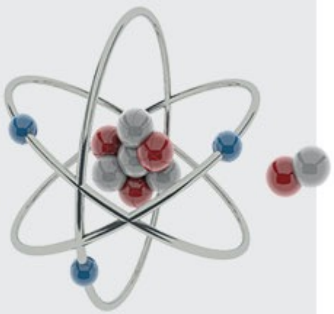
Simultaneous formation ➔ homogeneous interpenetrating networks.

Precursor (sol-gel) + **monomer** (polymerization)+ W/WO **solvents**



Problems

The sensitivity of many organic polymerization processes for sol–gel conditions or the composition of the materials formed



I.5. Building Block Approach

Well defined:
- Molecules
- Nanostructures
- Size and shape
- A tailored structure and composition

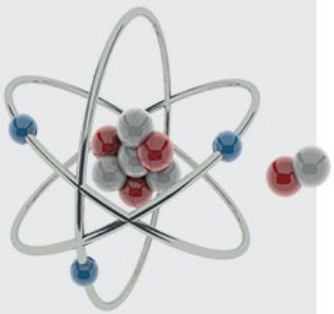
Inorganic Building Block

+

Organic Building Block

→ Hybrid Materials

Interacting properties
E.g.: Conductivity, thermal.



I.5.1 Inorganic Building Block

Inorganic building block = cluster compounds of various compositions

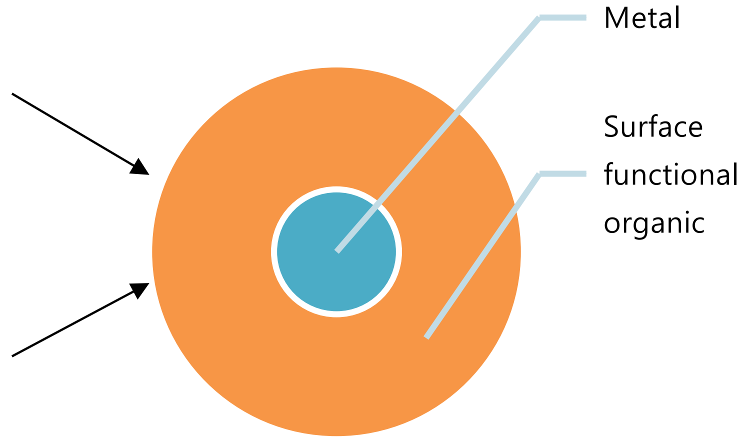
Cluster = agglomerates of pure metal or metal mix with other elements

Problems: Metal clusters are not stable => make a larger particles

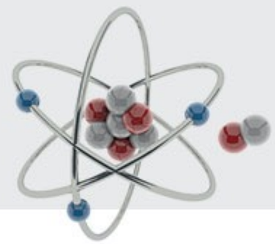
Requires

post-synthesis modification

In situ functionalization



I.5.1 Inorganic Building Block

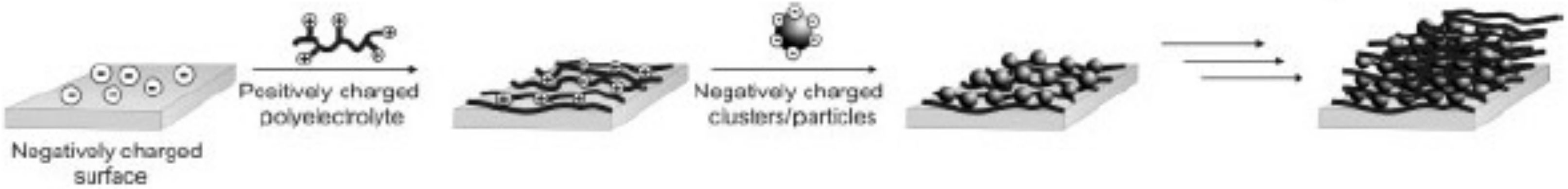


Types: Clusters –Nanoparticles – Metal oxides

Post-synthesis modification:

Step 1: Forming nanoparticles/clusters → Step 2: Functionalization with organic groups

For examples:



Layer by layer using electrostatic force

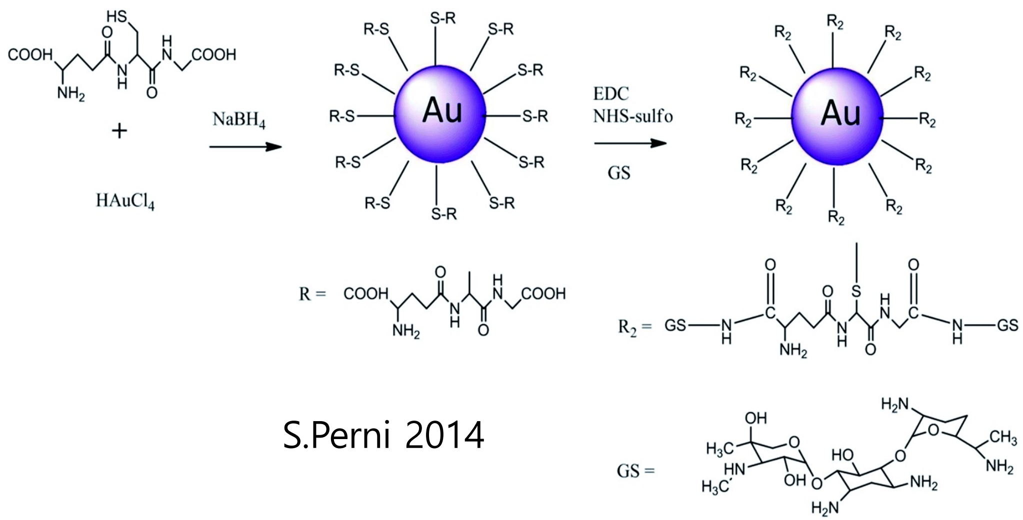
I.5.2 Inorganic Building Block

In presence of functional organic groups

Formation of inorganic nanoparticles

In situ functionalization:

For examples:



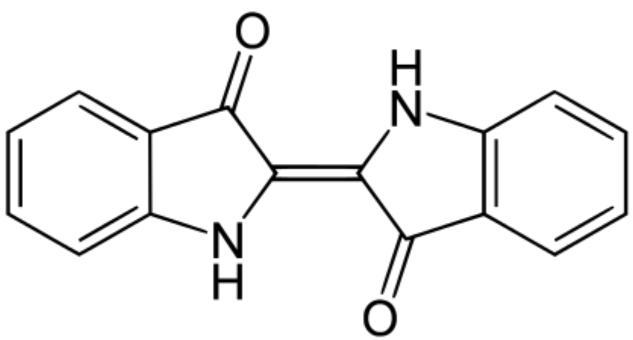
S.Perni 2014

I.5.3 Organic Building Block

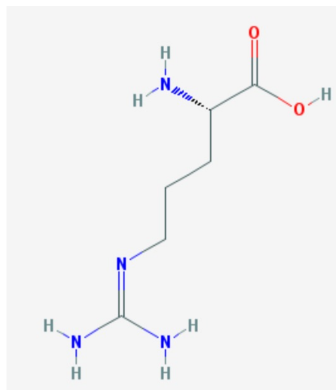
Small molecules | Macromolecules | Particle and particle-like structure

The modification of inorganic networks with small organic molecules

Good for sol-gel process derived by silicon based materials



indigo



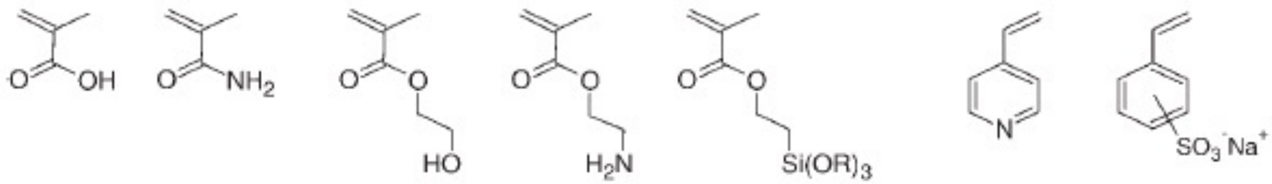
Nonlinear Organic Optical group

I.5.3 Organic Building Block

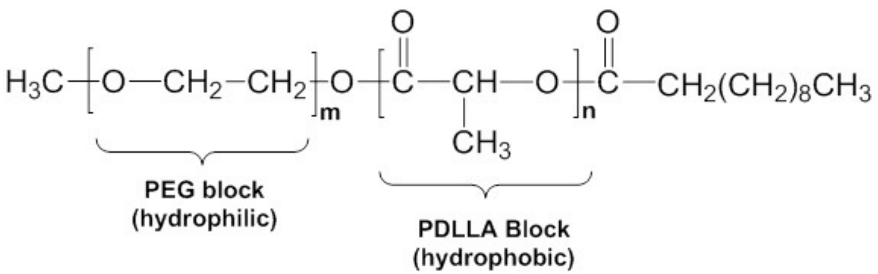
Macromolecules

Using macromolecules for inorganic networks

Typical monomer: form a homopolymer and compatibilize between 2 components



Block copolymer: consisting of a hydrophilic and a hydrophobic segments



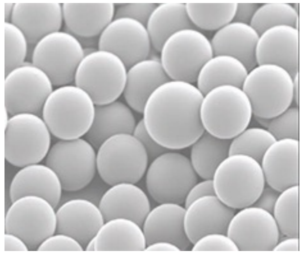
I.5.3 Organic Building Block

Particle and particle-like structure

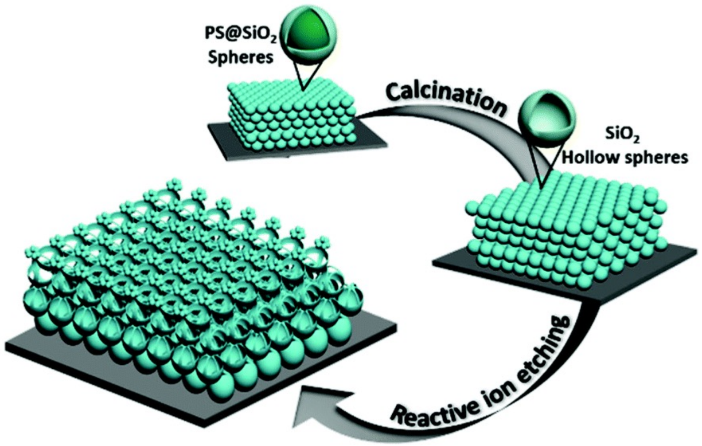
Organic colloids formed from physically or chemically crosslinked polymers

Easy to control size range: nanometer to micrometer

Latex colloids

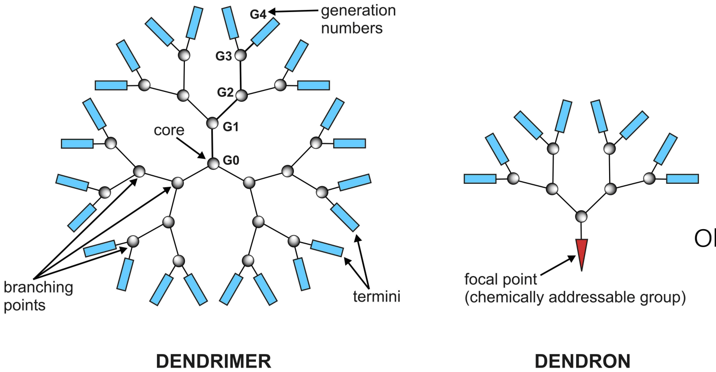


Thermo Frisher Scientific



Kuo Zhong 2016

Dendrimers

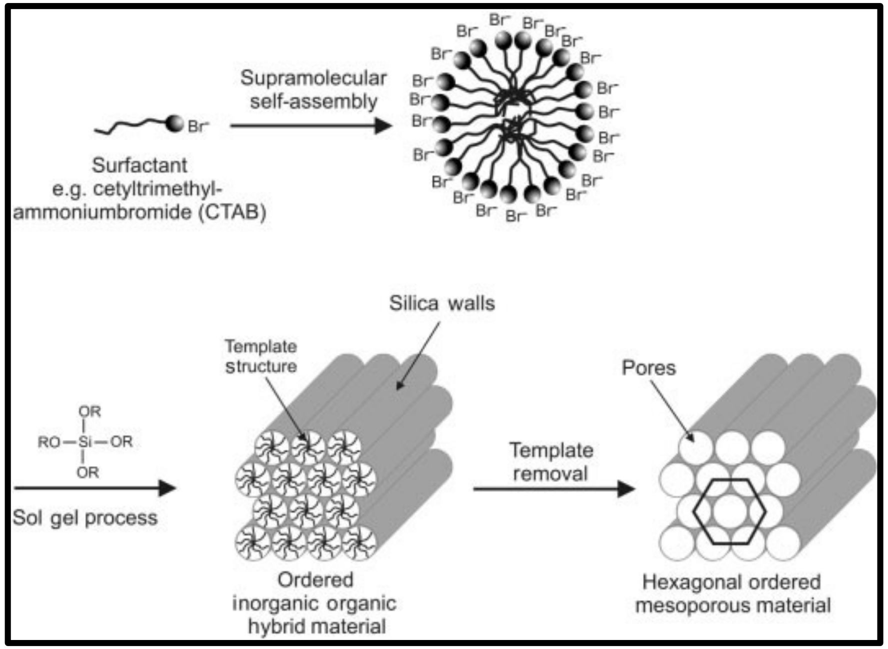


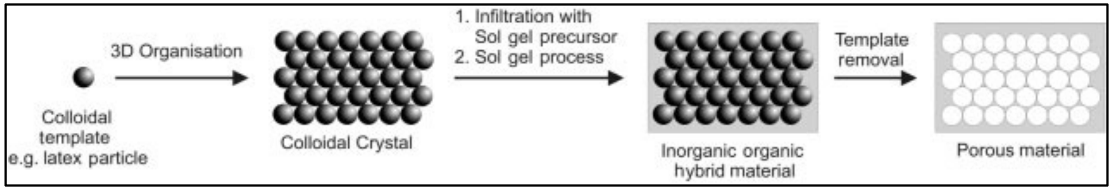
Oleg Lukin

I.6 Structural Engineering

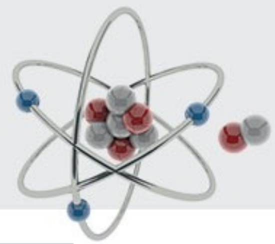
Design materials → Adapt to multi-applications → Best processing strategies

- Thin films and coatings using dip/spin coating
- Fibers using spinning techniques
- Bulk materials using pouring in forms and curing





I.7 Characterization of Materials



Scanning electron microscopy (SEM)	Produce high resolution images of a sample surface
X-ray photoelectron spectroscopy (XPS)	a surface sensitive analytical tool used to examine the chemical compositions and electronic state of the surface of a sample.
Transmission electron microscopy (TEM)	Give information about the inner structure of the specimen
Atomic force microscopy (AFM)	represents the topography of the sample.
X-ray diffraction	identify the different phases in a polycrystalline sample.
Thermal analysis techniques	Studies the weight changes of samples in relation to changes in temperature

Summary

Hybrid materials is the most modern materials in the recent

In this part of Introduction:

- Overview of critical issues in the synthesis
- The importance of the interface between the inorganic and
- organic materials
- Methods for fabrication is importance
- The structure, formation, processing and analysis is importance as well.