Institute Core Course for BTech Program

IC250: Materials Chemistry II

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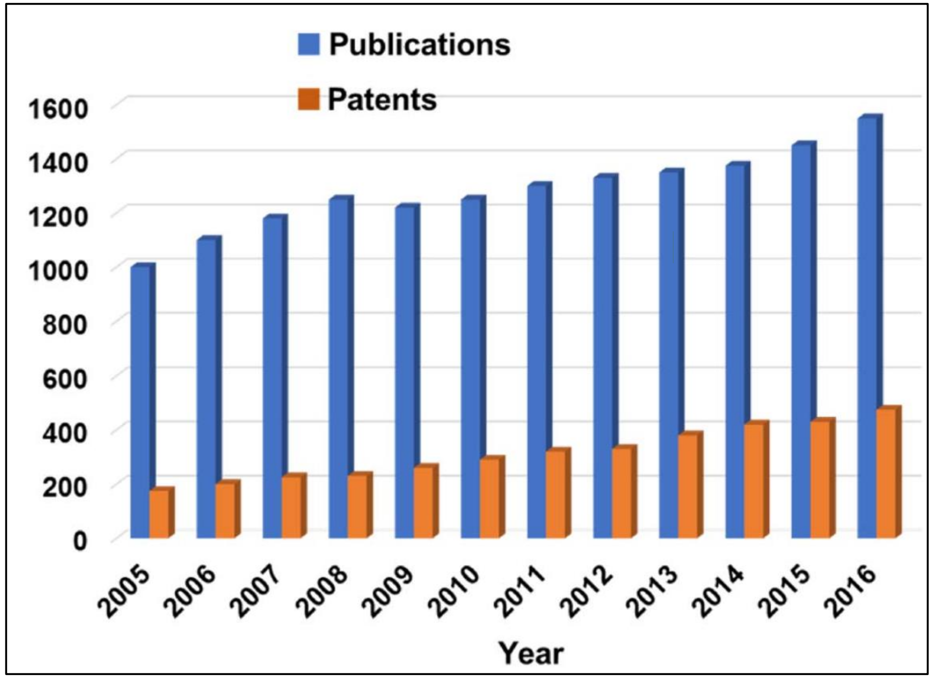
Hybrid Materials

Introduction

- Recent technological breakthroughs and the desire for new functions generate an enormous demand for novel materials.
- Scientists and engineers realized early on that mixtures of materials can show superior properties compared with their pure counterparts.
- One of the most successful examples is the group of composites which are formed by the incorporation of a basic structural material into a second substance, the matrix.
- Usually the systems incorporated are in the form of particles, whiskers, fibers, lamellae, or a mesh.

Introduction

- Most of the resulting materials show improved mechanical properties and a well-known example is **inorganic fiber-reinforced polymers**.
- The structural building blocks in these materials which are incorporated into the matrix are predominantly inorganic in nature.

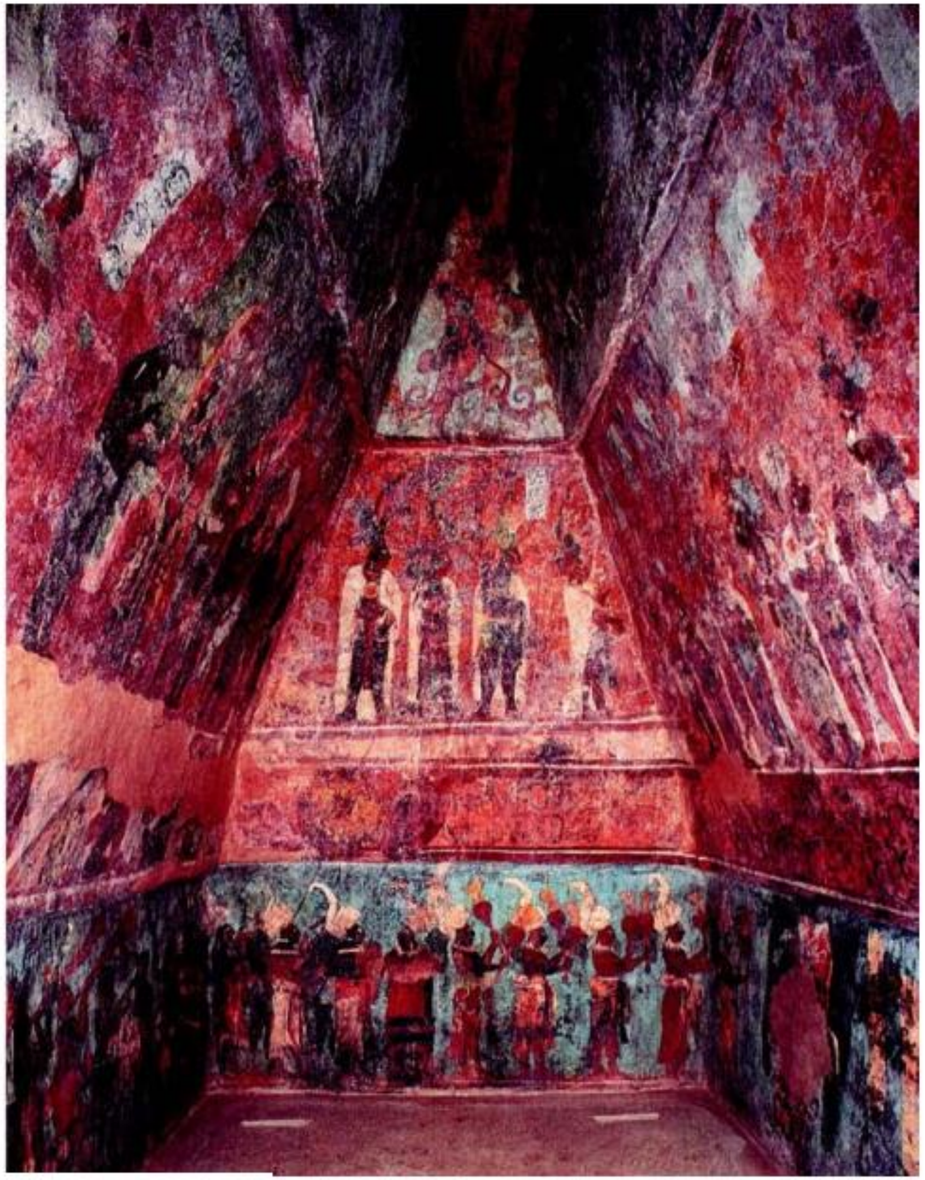


Natural Origins

- Many natural materials consist of inorganic and organic building blocks distributed on the (macro)molecular or nanoscale.
- In most cases the inorganic part provides mechanical strength and an overall structure to the natural objects while the organic part delivers bonding between the inorganic building blocks and/or the soft tissue.
- Typical examples of such materials are bone, or nacre.

Nacre also known as mother of pearl, is an organic-inorganic composite material produced by some molluscs as an inner shell layer; it also makes up the outer coating of pearls.

Development of Hybrid Materials



- Mayan wall paintings like this at Bonampak are twelve centuries old.
- This so-called Maya blue pigment is a hybrid organic-inorganic material formed by indigo dye molecules entrapped in a palygorskite clay mineral, a synergic nanocomposite material that has passed with excellent marks the test of centuries.

Development of Hybrid Materials

- Inorganic–organic hybrids can be applied in many branches of material chemistry because they are simple to process and are amenable to design on the molecular scale.
- Currently there are four major topics in the synthesis of inorganic–organic materials:

a) their molecular engineering

b) their nanometer and micrometer-sized organization

c) the transition from functional to multifunctional hybrids

d) their combination with bioactive components.

Hybrid Materials and Nanocomposites

- **A hybrid material is a material that includes two moieties blended on the molecular scale.**
- Commonly one of these compounds is inorganic and the other one organic in nature.

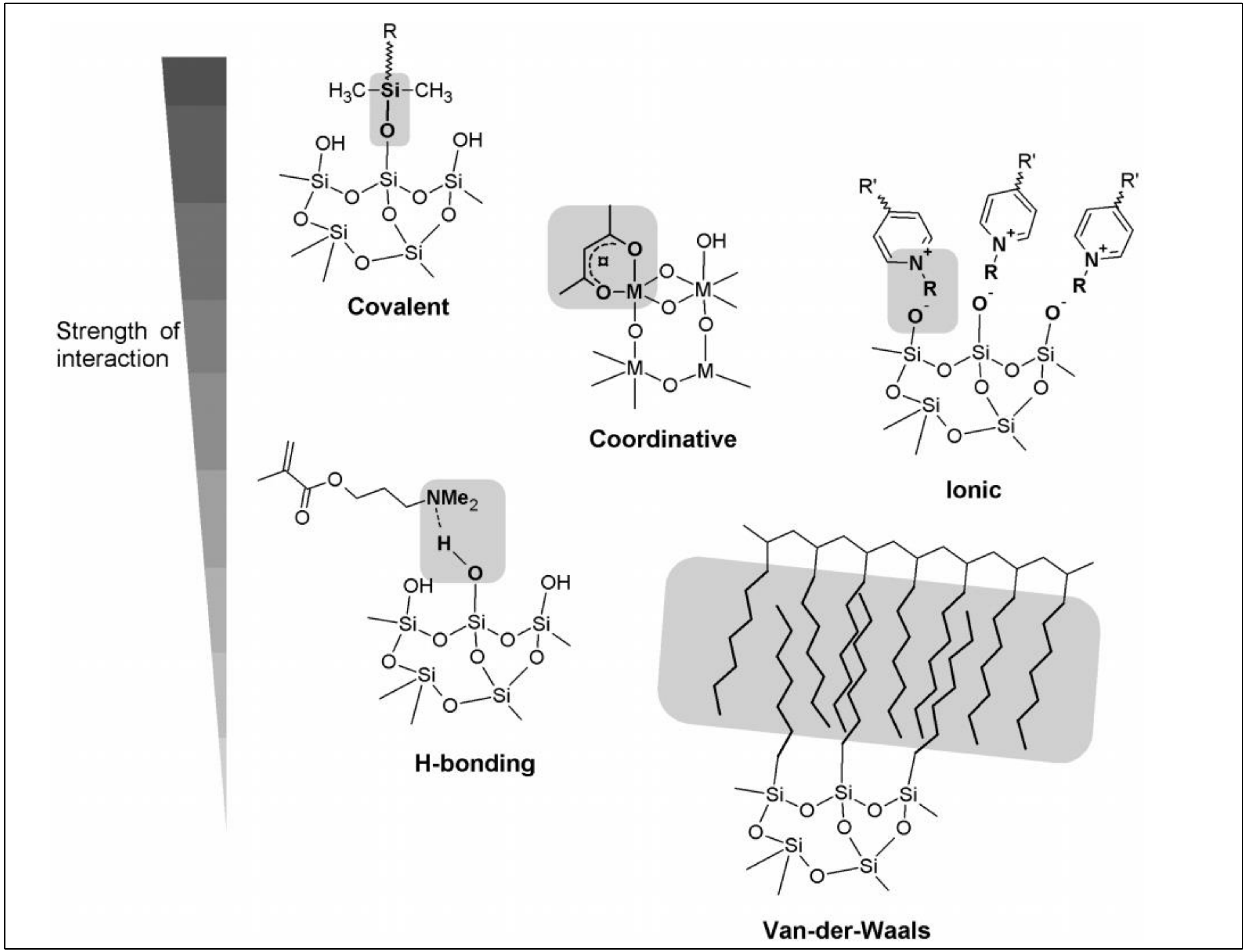
Different possibilities of composition and structure of hybrid materials.

Matrix:	crystalline ↔ amorphous
	organic ↔ inorganic
Building blocks:	molecules ↔ macromolecules ↔ particles ↔ fibers
Interactions between components:	strong ↔ weak

Different Types of Hybrid Materials

- Depending upon possible interactions connecting the inorganic and organic species the hybrid materials can be distinguished into two types:
- ***Class I* hybrid materials** are those that show weak interactions between the two phases, such as van der Waals, hydrogen bonding or weak electrostatic interactions.
- ***Class II* hybrid materials** are those that show strong chemical interactions between the components.

Different Types of Hybrid Materials



Different Types of Bonding Strength

Type of interaction	*Strength [kJ mol^{-1}]*	*Range*	*Character*
van der Waals	ca. 50	Short	nonselective, nondirectional
H-bonding	5–65	Short	selective, directional
Coordination bonding	50–200	Short	directional
Ionic	50–250[a]	Long	nonselective
Covalent	350	Short	predominantly irreversible

Different Types of Hybrid Materials

- In addition to the bonding characteristics, structural properties can also be used to distinguish between various hybrid materials:

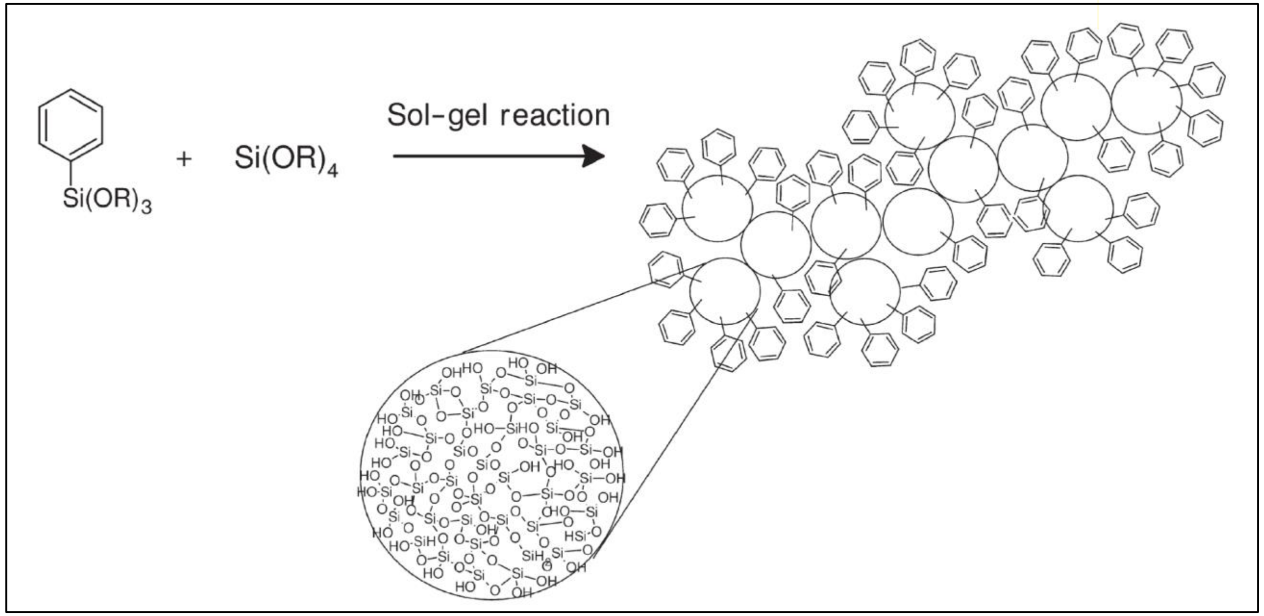
  a) Network Modifier

  b) Network Builder

  c) Network Functionalizer

Network Modifier:

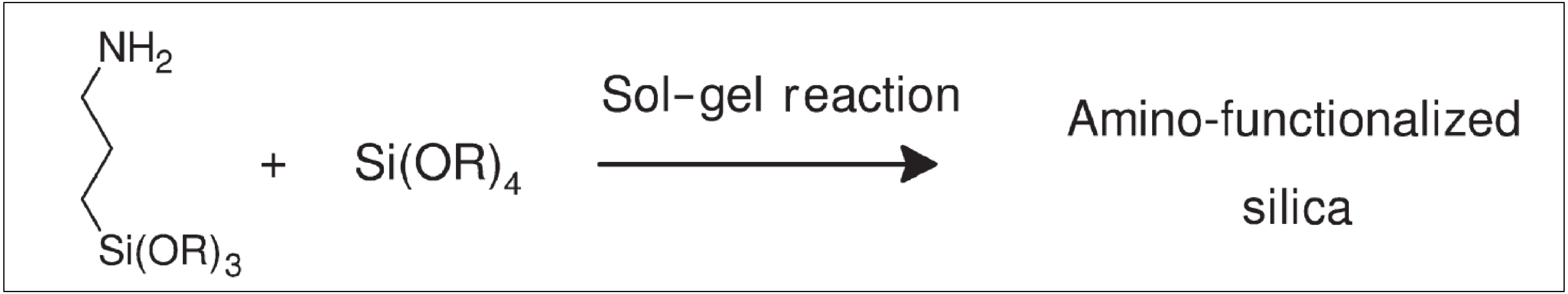
- An organic moiety containing a functional group that allows the attachment to an inorganic network, e.g. a trialkoxysilane group can act as a network modifying compound because in the final structure the inorganic network is only modified by the organic group.



Different Types of Hybrid Materials

Network Functionalizer:

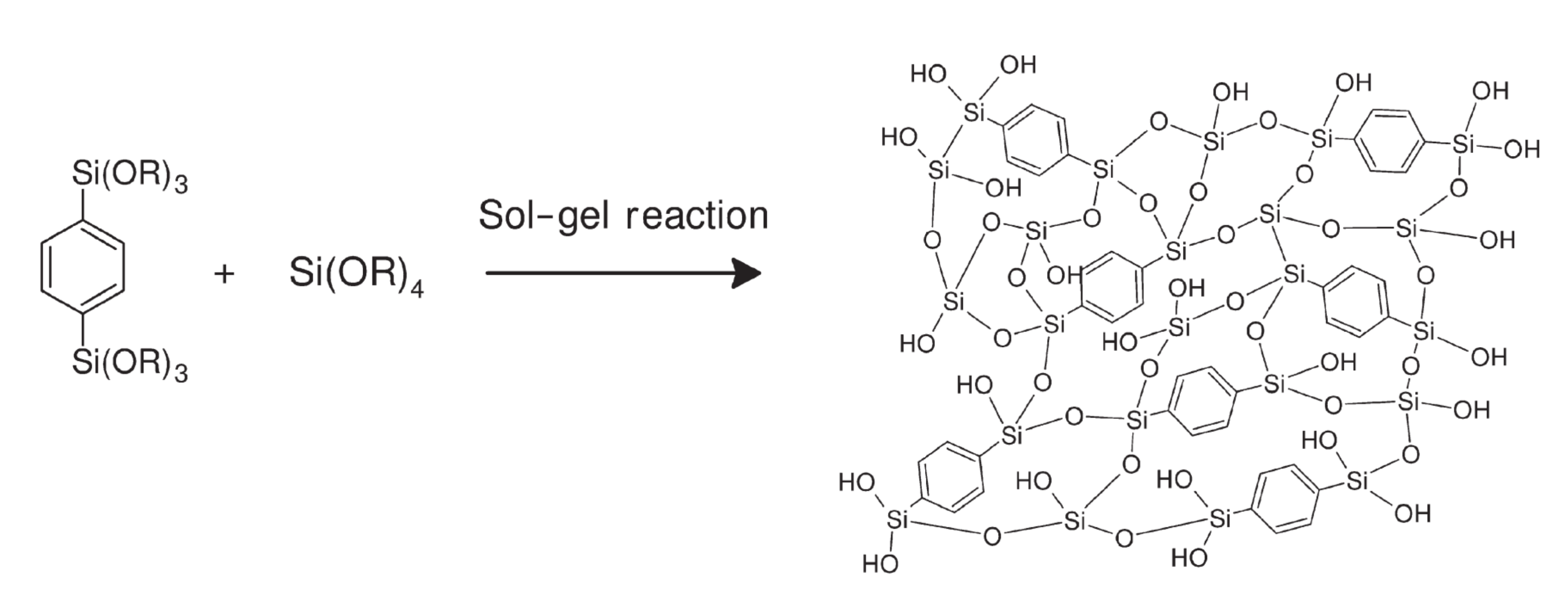
- If a reactive functional group is incorporated the system is called a network functionalizer.



Different Types of Hybrid Materials

Network Builder:

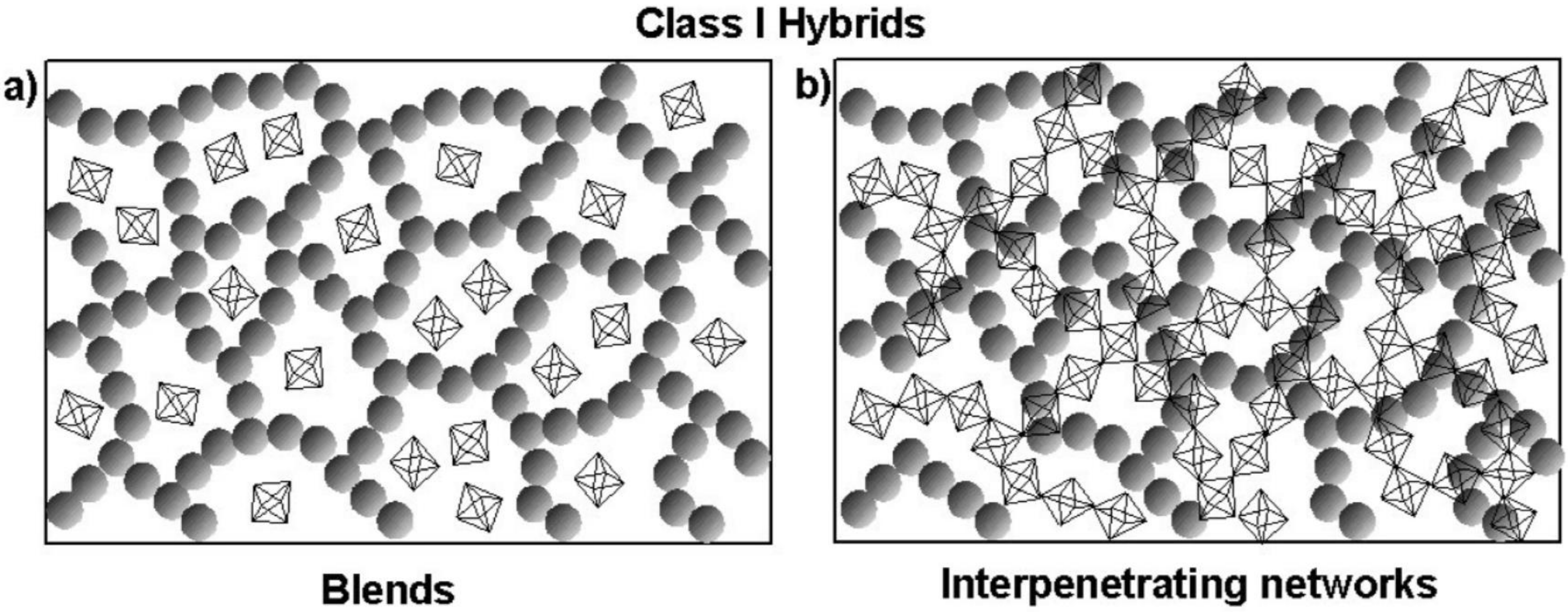
- The situation is different if two or three of such anchor groups modify an organic segment; this leads to materials in which the inorganic group is afterwards an integral part of the hybrid network.



Different Hybrid Materials

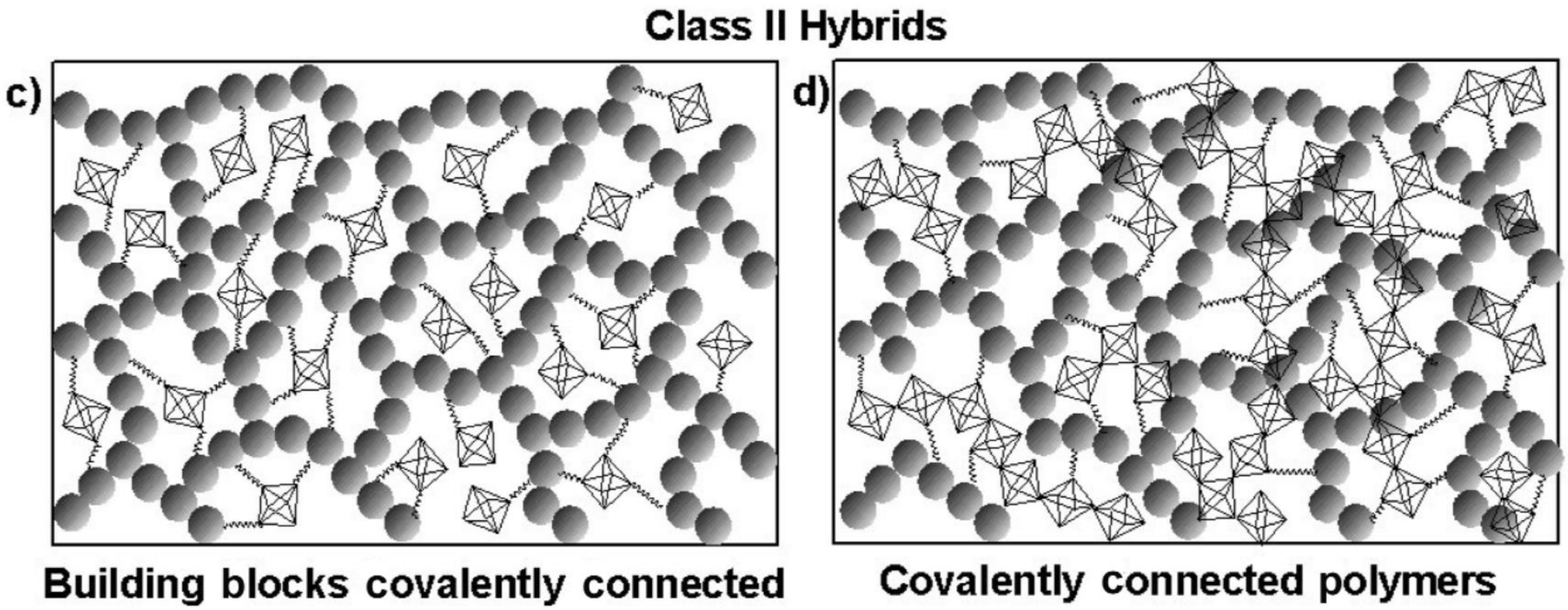
- **Blends** are formed if no strong chemical interactions exist between the inorganic and organic building blocks.
- One example for such a material is the combination of inorganic clusters or particles with organic polymers lacking a strong (e.g. covalent) interaction between the components.
- If an inorganic and an organic network interpenetrate each other without strong chemical interactions, so called interpenetrating networks (IPNs).
- Both materials mentioned belong to ***Class I*** hybrids.

Different Types of Hybrid Materials



Different Types of Hybrid Materials

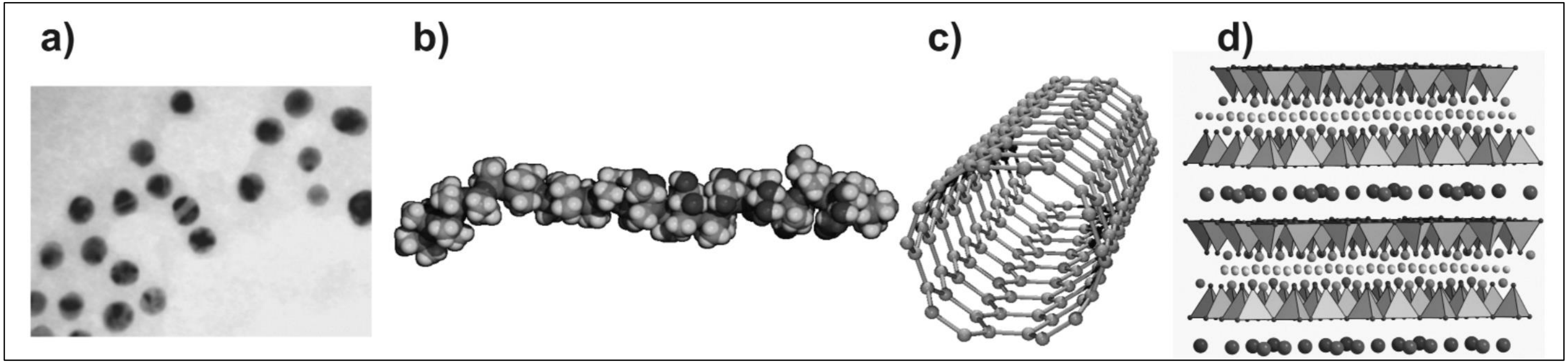
- ***Class II*** hybrids are formed when the discrete inorganic building blocks, e.g. clusters, are covalently bonded to the organic polymers or inorganic and organic polymers are covalently connected with each other.



Different Types of Hybrid Materials

What is the difference between inorganic–organic hybrid materials and inorganic–organic nanocomposites?

- The term nanocomposite is used if one of the structural units, either the organic or the inorganic, is in a defined size range of 1–100 nm.
- There is a gradual transition between hybrid materials and nanocomposites.



Advantages of Combining Inorganic and Organic Species

- The most obvious advantage of inorganic–organic hybrids is that they can favorably combine the often dissimilar properties of organic and inorganic components in one material.

Properties	*Organics (polymers)*	*Inorganics (SiO_2, transition metal oxides (TMO))*
Nature of bonds	covalent [C—C], van der Waals, H-bonding	ionic or iono-covalent [M—O]
T_g	low (−120 °C to 200 °C)	high (≫200 °C)
Thermal stability	low (<350 °C–450 °C)	high (≫100 °C)
Density	0.9–1.2	2.0–4.0
Refractive index	1.2–1.6	1.15–2.7
Mechanical properties	elasticity plasticity rubbery (depending on T_g)	hardness strength fragility

Properties	*Organics (polymers)*	*Inorganics (SiO_2, transition metal oxides (TMO))*
Hydrophobicity	hydrophilic	hydrophilic
Permeability	hydrophobic ±permeable to gases	low permeability to gases
Electronic properties	insulating to conductive redox properties	insulating to semiconductors (SiO_2, TMO) redox properties (TMO) magnetic properties
Processability	high (molding, casting, film formation, control of viscosity)	low for powders high for sol–gel coatings

Advantages of Combining Inorganic and Organic Species

- Opportunity to invent an almost unlimited set of new materials with a large spectrum of known and as yet unknown properties.
- Possibility to create multifunctional materials.
- Probably the most intriguing property of hybrid materials that makes this material class interesting for many applications is their processing.
- Material properties of hybrid materials are usually changed by modifications of the composition on the molecular scale.
- Formation of smart materials.

Synthetic Strategies towards Hybrid Materials

- In principle, two different approaches can be used for the formation of hybrid materials:

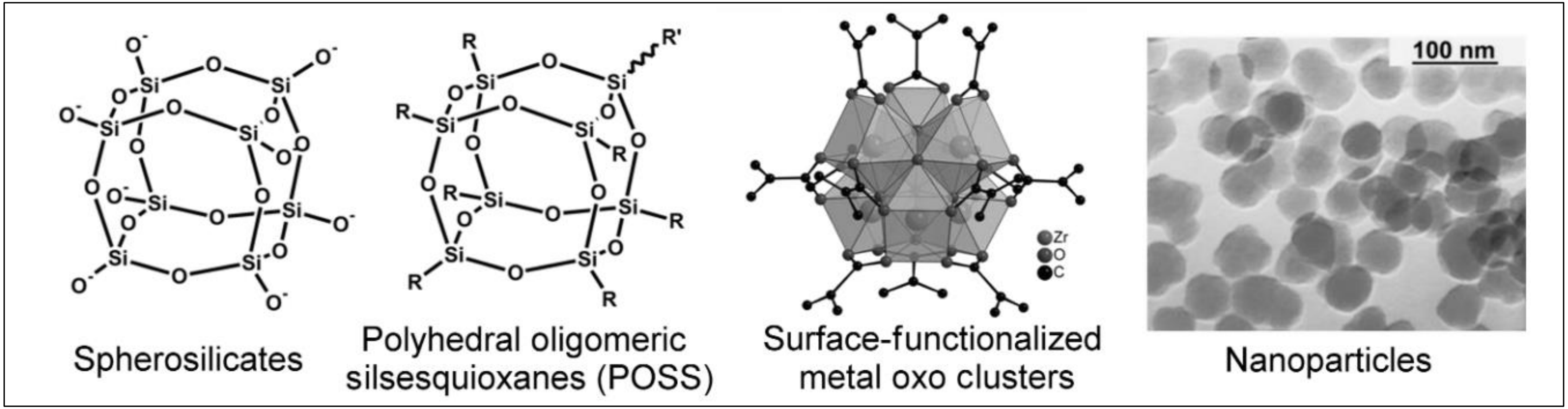
a) Building block approach

b) In situ formation of the component

Building Block Approach:

In this case, well-defined preformed building blocks are applied that react with each other to form the final hybrid material in which the precursors still at least partially keep their original integrity.

Synthetic Strategies towards Hybrid Materials



In situ formation of the component:

- Contrary to the building block approach the in situ formation of the hybrid materials is based on the chemical transformation of the precursors used throughout materials' preparation.

Synthetic Strategies towards Hybrid Materials

- Some methods of in situ formation of inorganic materials are:

  a) Sol-Gel Process

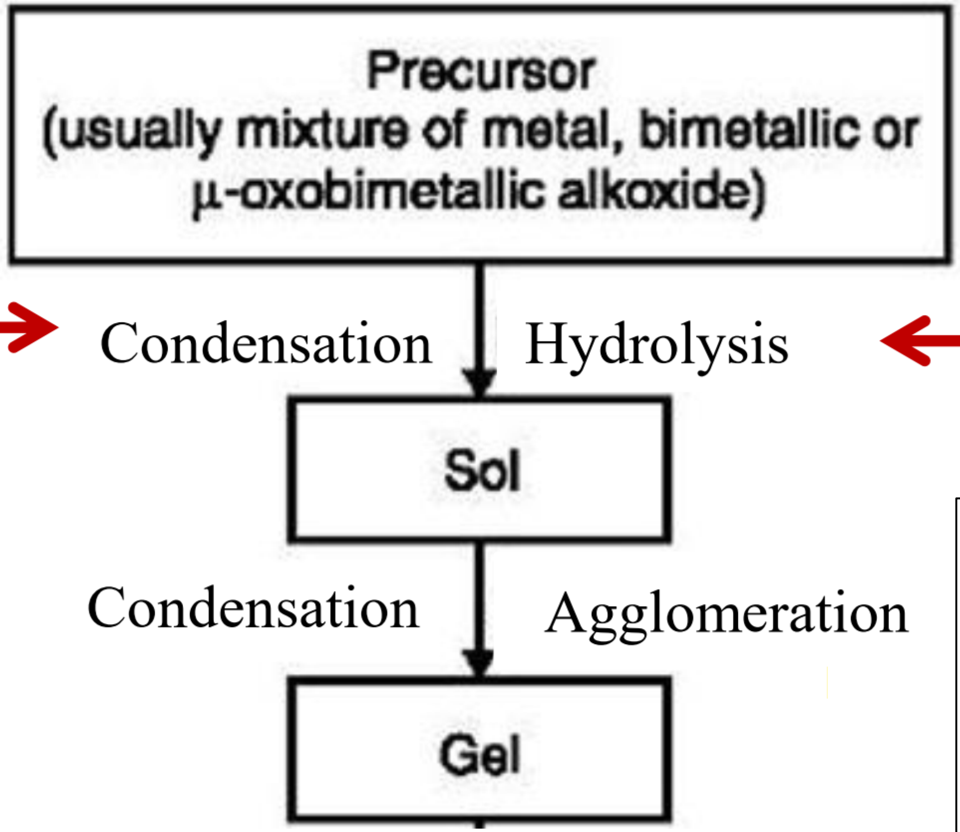
  b) Nonhydrolytic Sol-Gel Process

  c) Sol-Gel Reactions of Non-Silicates

a) Sol-Gel Process:

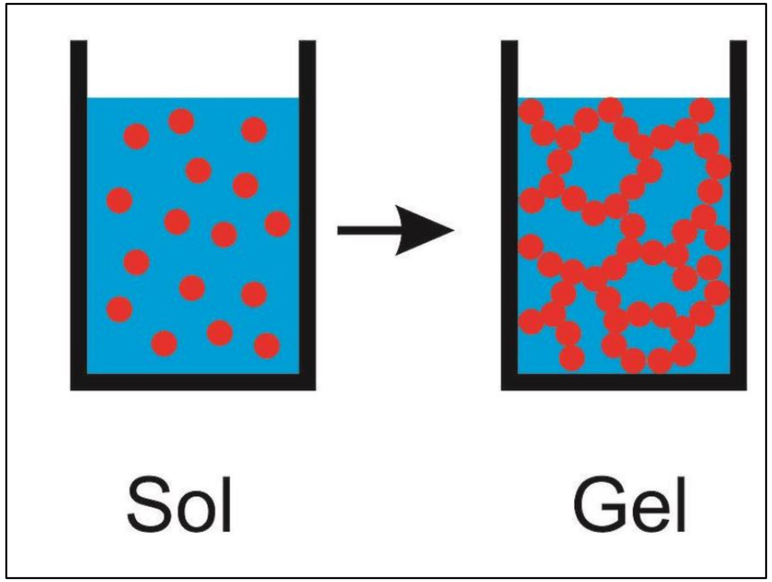
- This process is chemically related to an organic polycondensation reaction in which small molecules form polymeric structures by the loss of substituents.
- Usually the reaction results in a three-dimensional (3-D) cross-linked network.

Sol-Gel Process

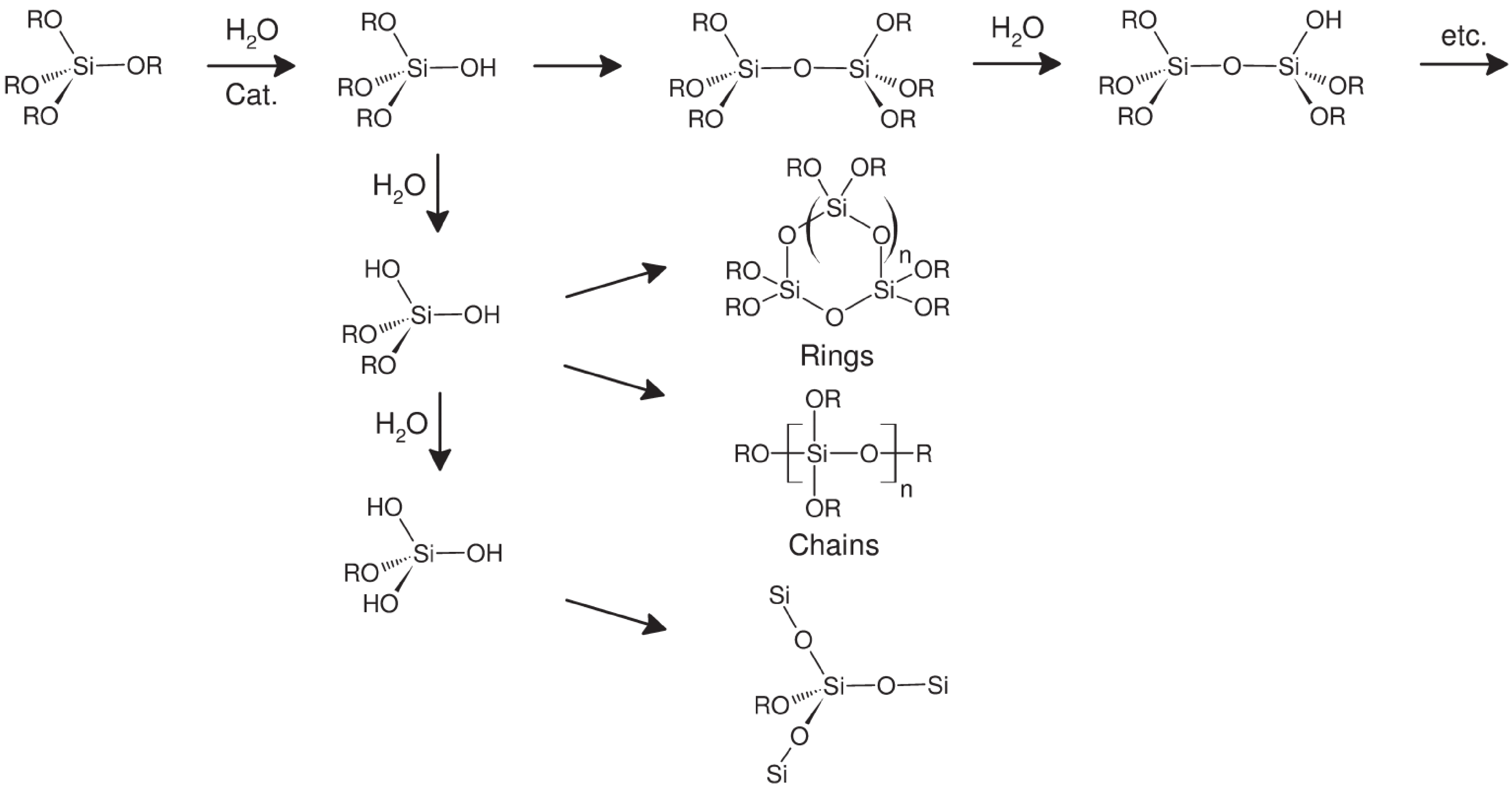


Step 2 → Condensation | Hydrolysis ← Step 1

Condensation | Agglomeration

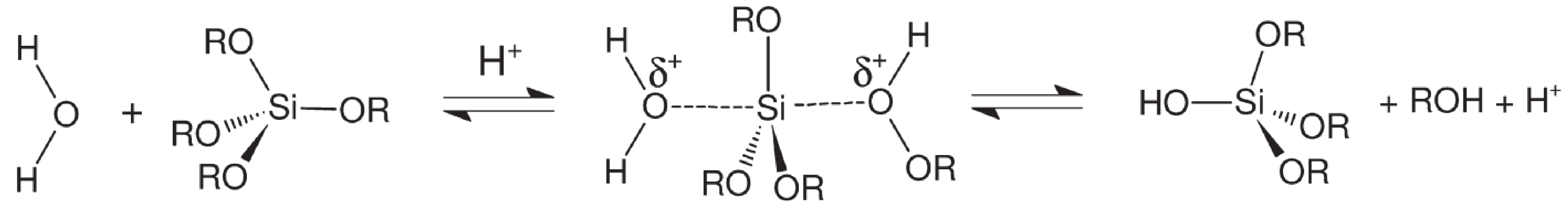


Synthetic Strategies towards Hybrid Materials

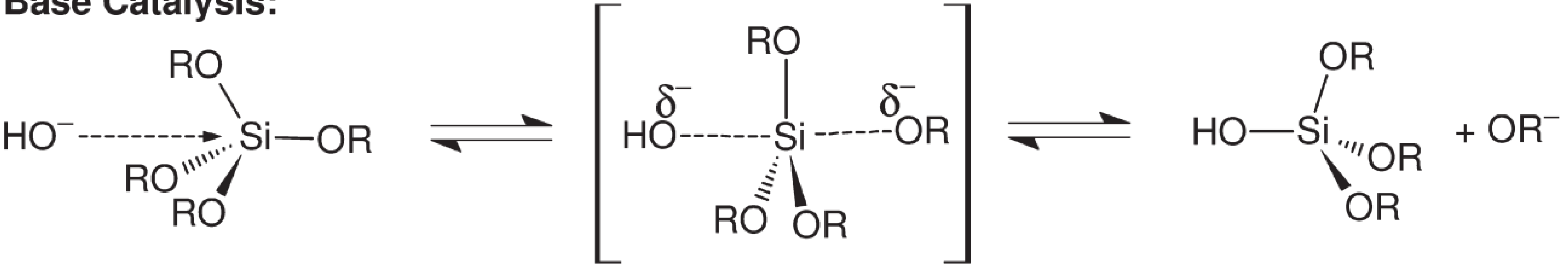


Synthetic Strategies towards Hybrid Materials

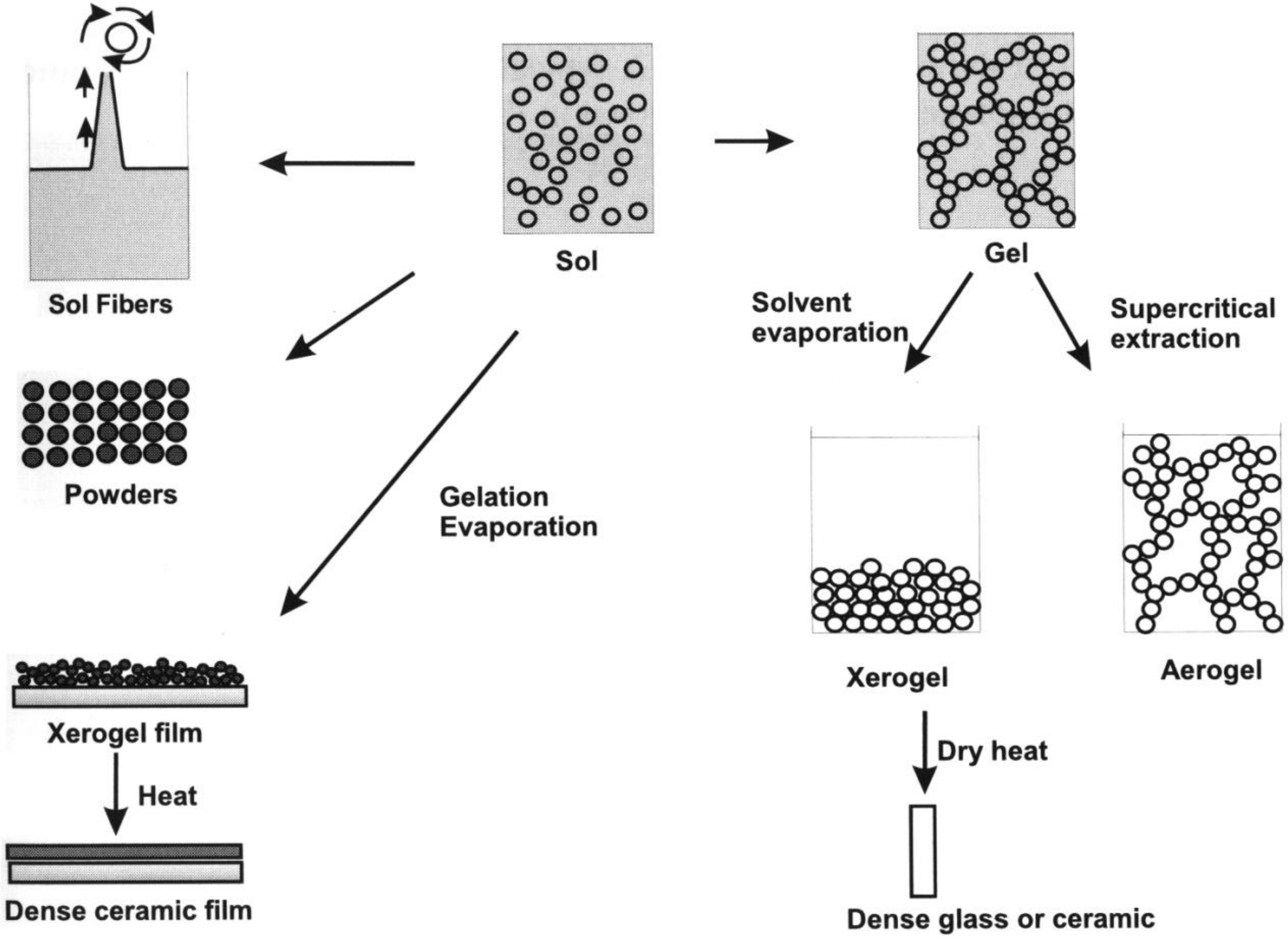
Acid Catalysis:



Base Catalysis:



Synthetic Strategies towards Hybrid Materials



Synthetic Strategies towards Hybrid Materials

b) Nonhydrolytic Sol-Gel Process:

- In this process the reaction between metal halides and alkoxides is used for the
- formation of the products.
- The alkoxides can be formed during the process by various reactions.
- Usually this process is carried out in sealed tubes at elevated temperature but it can also be employed in unsealed systems under an inert gas atmosphere.

Non-hydrolytic sol–gel process:

$$\text{M-Cl} + \text{M-OR} \longrightarrow \text{M-O-M} + \text{R-Cl}$$

In situ formation of alkoxides:

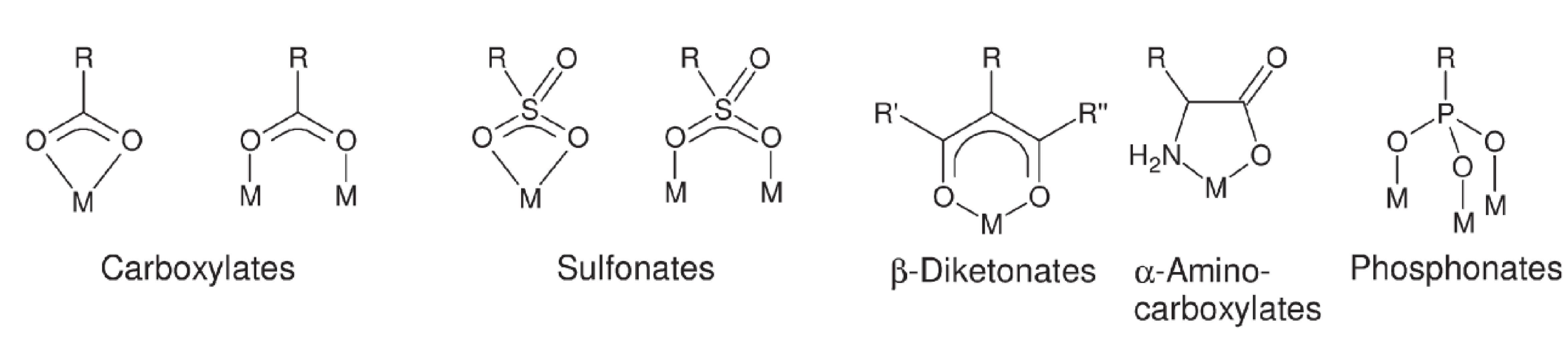
$$\text{M-Cl} + \text{R-O-R} \longrightarrow \text{M-OR} + \text{R-Cl}$$

$$\text{M-Cl} + \text{R-OH} \longrightarrow \text{M-OR} + \text{HCl}$$

Synthetic Strategies towards Hybrid Materials

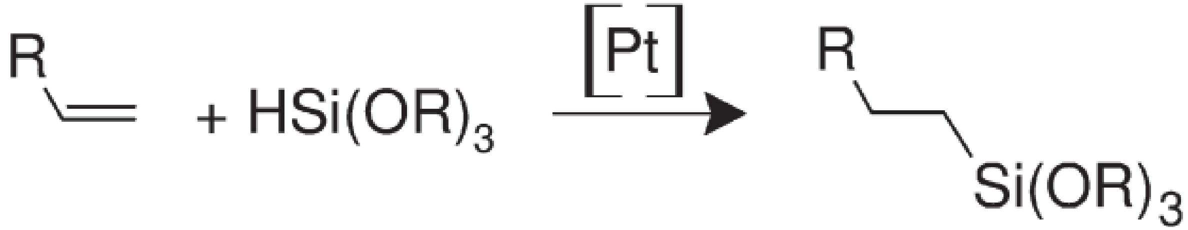
c) Sol-Gel Reactions of Non-Silicates:

- Use of organically functionalized bi- and multi-dentate ligands that show a higher bonding stability during the sol–gel reaction and, in addition reduce the speed of the reaction by blocking coordination sites.



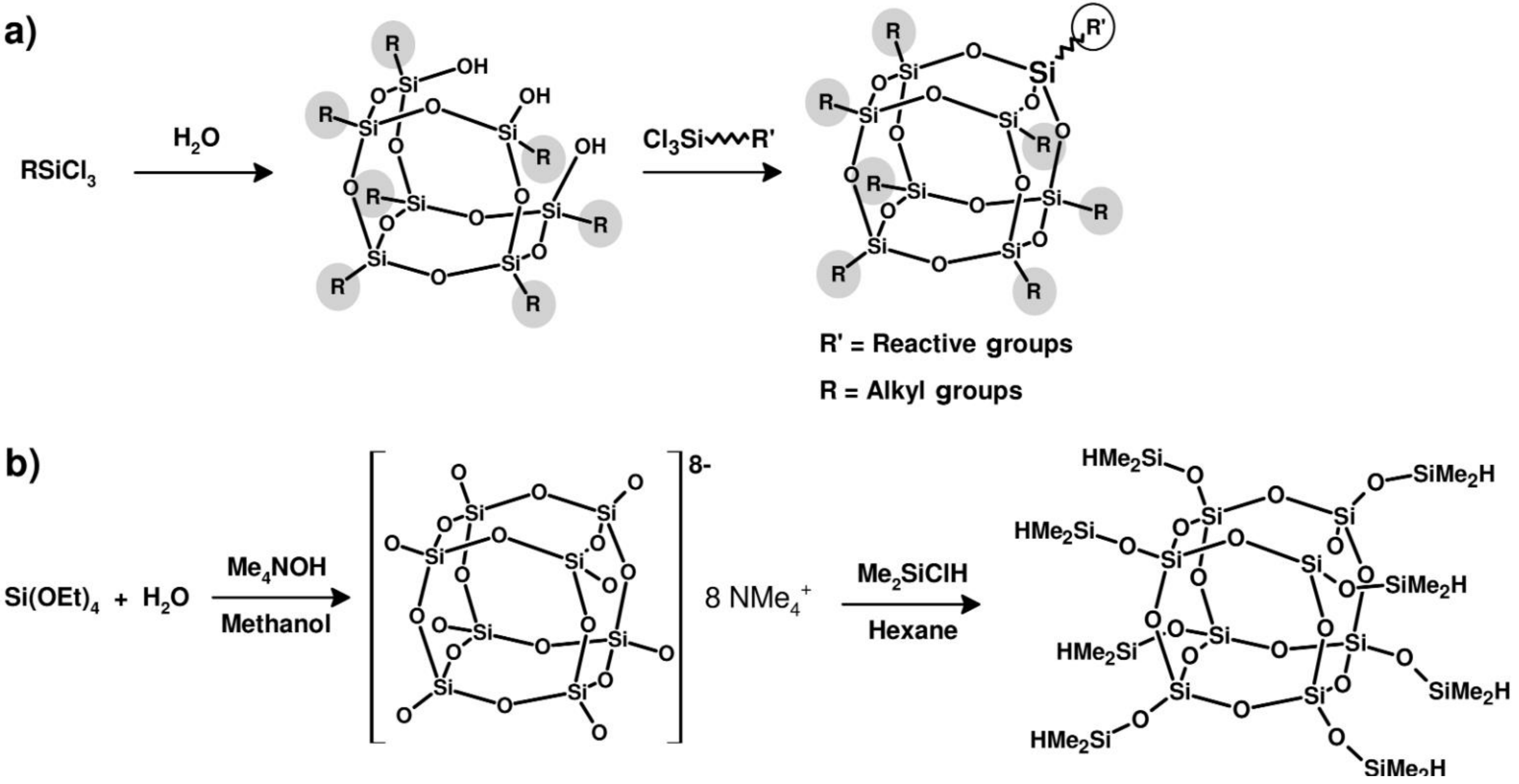
Hybrid Materials by the Sol–Gel Process:

- Organic molecules other than the solvent can be added to the sol and become physically entrapped in the cavities of the formed network upon gelation.
- Physical entrapment has the disadvantage that sometimes the materials obtained are not stable towards phase separation or leaching because of differences in polarity.
- Trialkoxysilane groups are typically introduced by a platinum catalyzed reaction between an unsaturated bond and a trialkoxysilane.



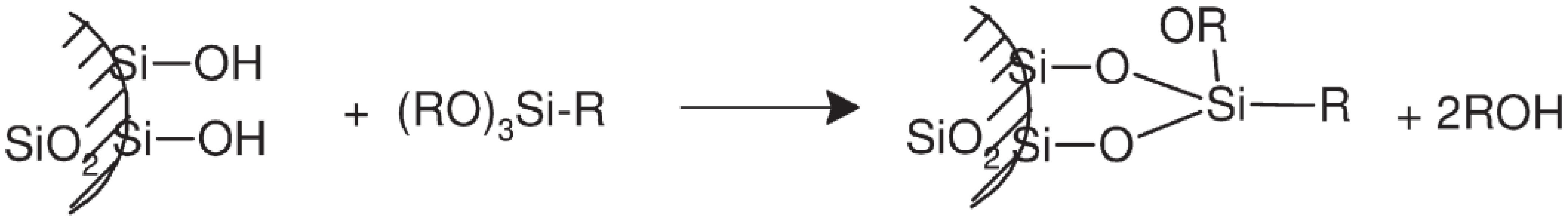
Silica Gel through Sol–Gl Process

Building Block Approach:

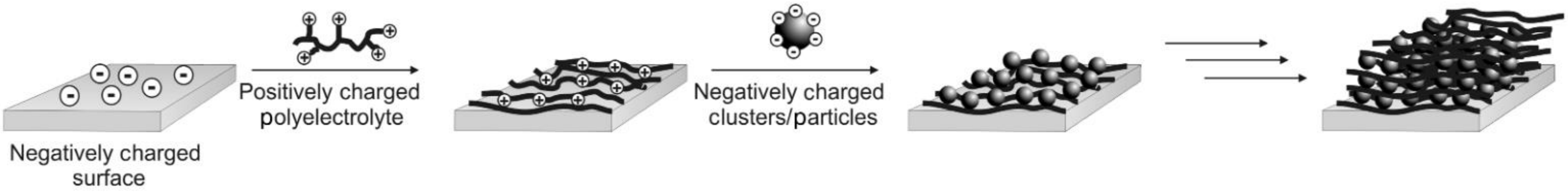


Synthetic Strategies towards Hybrid Materials

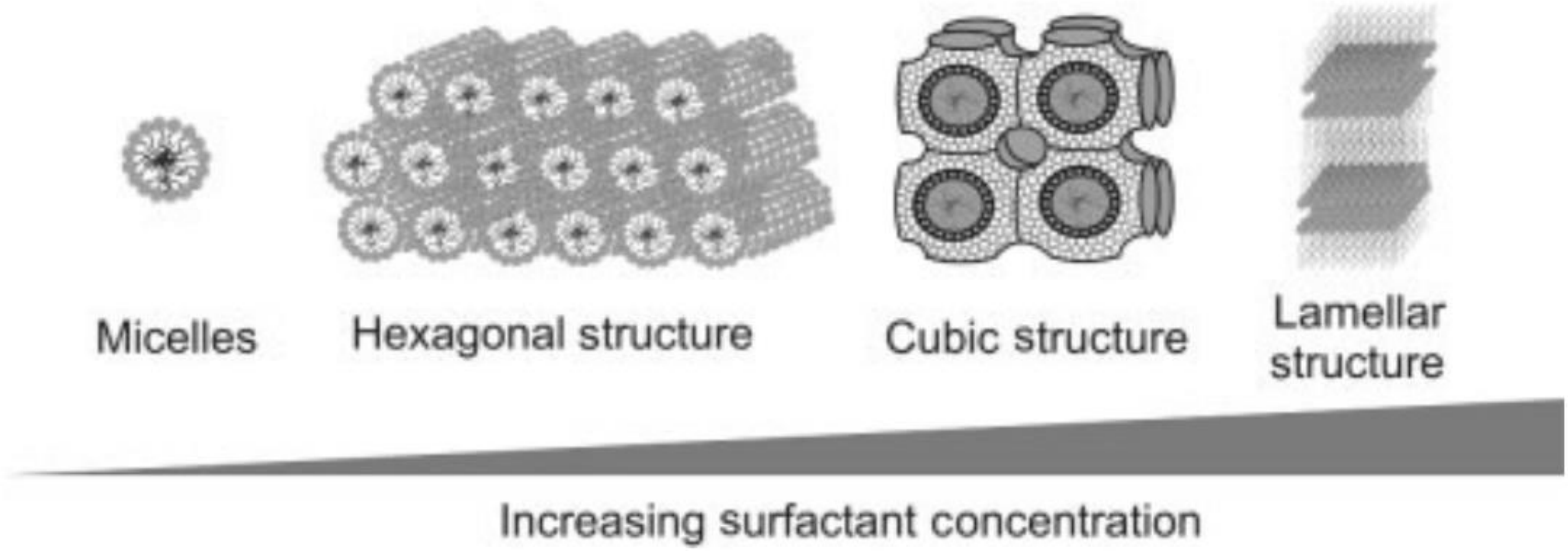
Post Synthetic Modifications:



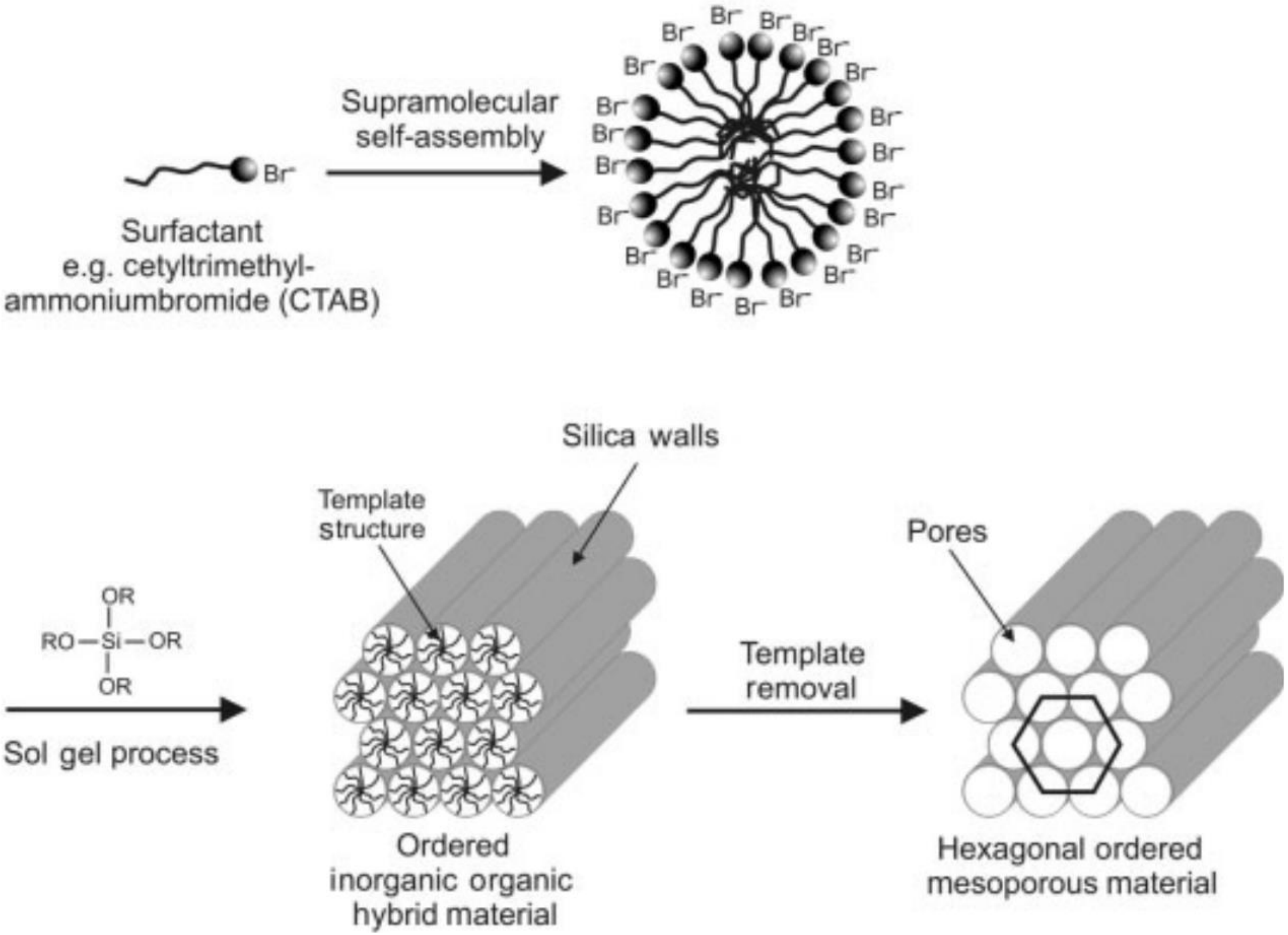
Principle of Layer-by-Layer Deposition:



Template Directed Synthesis of Hybrid Materials



Template Directed Synthesis of Hybrid Materials



Template Directed Synthesis of Hybrid Materials