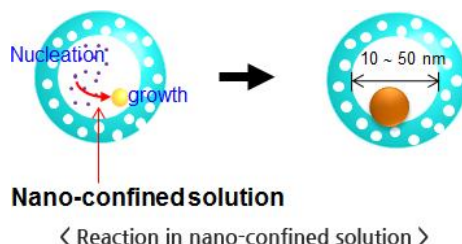


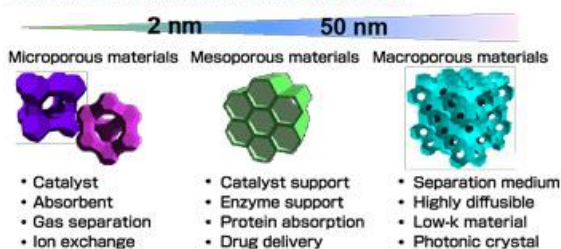
Unit-3 Reactions in nanospace

Chemical reactions in a confined nanospace can be very different from those in solution. Imine formation between molecular amines and an aldehyde inside a molecularly imprinted receptor was promoted strongly by the binding. Although how well the amine fit in the binding pocket and its electronic nature both influenced the reaction, the freedom of movement for the amine was the most important factor determining the binding-normalized reactivity.



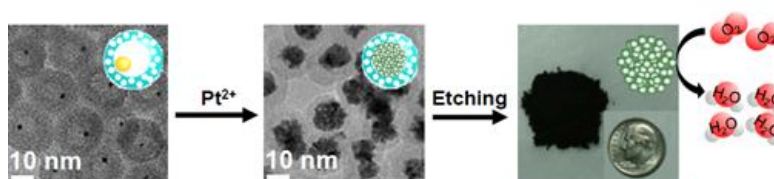
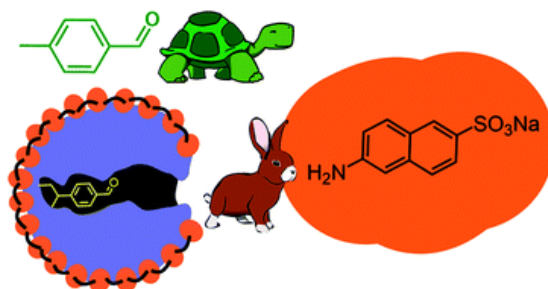
Functions of nanospace materials

Classification of nanospace materials by space size



Various functions depending on nanospace size

Function enhancement by integration of nanospace with different sizes



< Pt templated growth in nano-confined solution >

Nanoconfinement

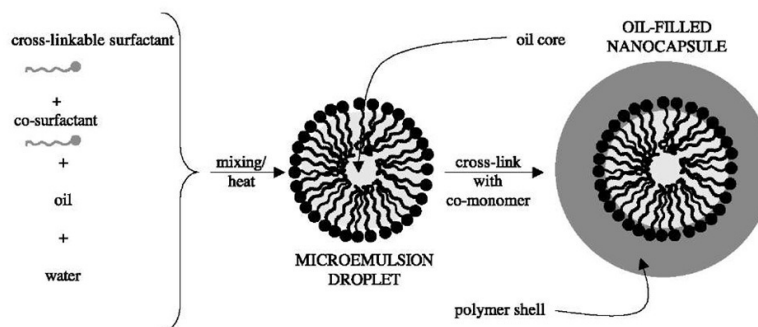
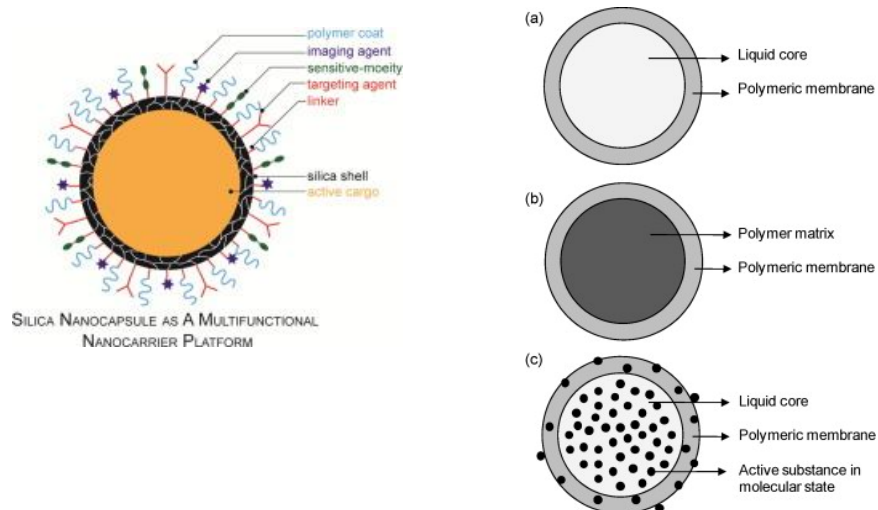
Nanoconfinement is receiving increasing interest in the field of energy storage and has been applied to different metal hydride systems in order to improve their properties for hydrogen storage. Modified hydrogen sorption kinetics and thermodynamics of metal hydrides have been achieved by nano size effects. In case of metal complex hydrides, in addition to kinetic limitations, competing side reactions and stable intermediates during de/rehydrogenation processes are obstacles for a practical utilization.

The Ions in Nanoconfinement app empowers users to simulate ions confined between material surfaces that are nanometers apart, and extract the associated ionic structure.

β -sheet nanocrystals confined to a few nanometres achieve higher stiffness, strength and mechanical toughness than larger nanocrystals. We illustrate that through nanoconfinement, a combination of uniform shear deformation that makes most efficient use of hydrogen bonds and the emergence of dissipative molecular stick-slip deformation leads to significantly enhanced mechanical properties.

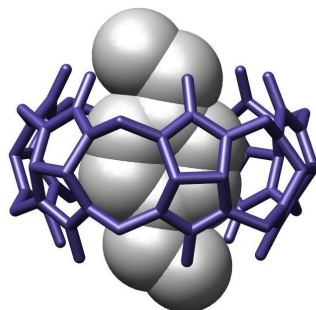
Nanocapsule

A nanocapsule is a nanoscale shell made from a nontoxic polymer. They are vesicular systems made of a polymeric membrane which encapsulates an inner liquid core at the nanoscale. Nanocapsules have many uses, including promising medical applications for drug delivery, food enhancement, nutraceuticals, and for self-healing materials. The benefits of encapsulation methods are for protection of these substances to protect in the adverse environment, for controlled release, and for precision targeting. Nanocapsules can potentially be used as MRI-guided nanorobots or *nanobots*, although challenges remain.



Cavitands

A cavitand is a container shaped molecule. The cavity of the cavitand allows it to engage in host–guest chemistry with guest molecules of a complementary shape and size. Examples include cyclodextrins, calixarenes, pillararenes and cucurbiturils.

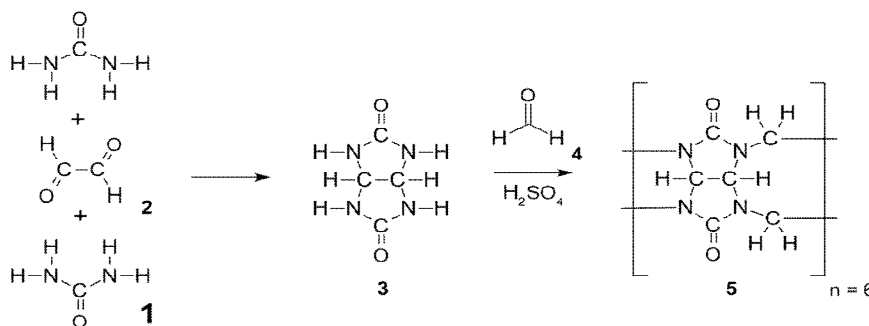


Applications

- A cavitand cucurbituril bound with a guest p-xylylenediammonium
- Specific cavitands form the basis of rigid templates onto which *de novo* proteins can be chemically linked. This *template assembled synthetic protein* (TASP) structure provides a platform for the study of protein structure.
- Silicon surfaces functionalized with tetraphosphonate cavitands have been used to singularly detect sarcosine in water and urine solutions.

Cucurbiturils

Cucurbiturils are macrocyclic molecules made of glycoluril (=C₄H₂N₄O₂=) monomers linked by methylene bridges (-CH₂-). The oxygen atoms are located along the edges of the band and are tilted inwards, forming a partly enclosed cavity. The name is derived from the resemblance of this molecule with a pumpkin of the family of Cucurbitaceae.

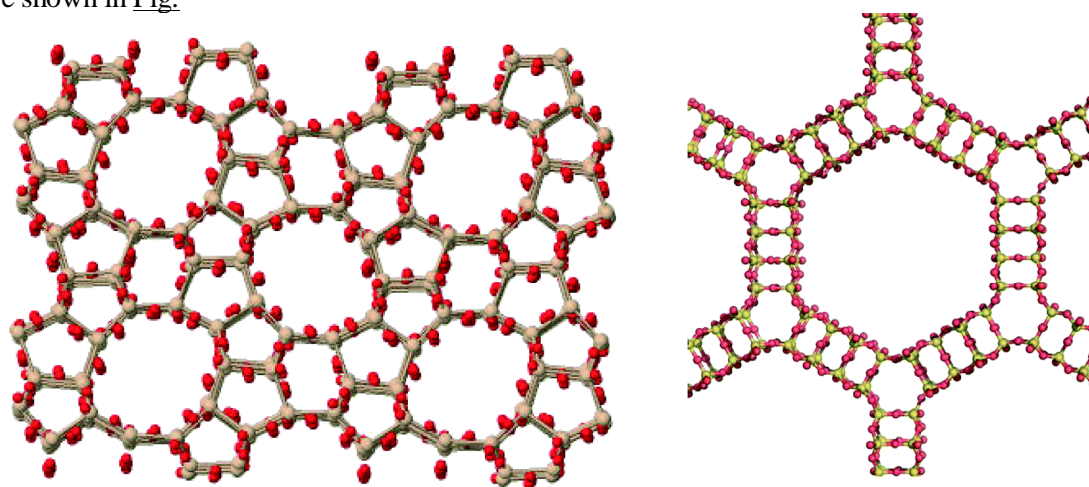


Cucurbiturils are amidals (less precisely amins) and synthesized from urea **1** and a dialdehyde (e.g., glyoxal **2**) via a nucleophilic addition to give the intermediate glycoluril **3**. This intermediate is condensed with formaldehyde to give hexamer cucurbituril above 110 °C. Ordinarily, multifunctional monomers such as **3** would undergo a step-growth polymerization that would give a distribution of products, but due to favorable strain and an abundance of hydrogen bonding, the hexamer is the only reaction product isolated after precipitation.

Decreasing the temperature of the reaction to between 75 and 90 °C can be used to access other sizes of cucurbiturils including CB[5], CB[7], CB[8], and CB[10]. CB[6] is still the major product; the other ring sizes are formed in smaller yields. The isolation of sizes other than CB[6] requires fractional crystallization and dissolution. CB[5], CB[6], CB[7], and CB[8] are all currently commercially available. The larger sizes are a particularly active area of research since they can bind larger and more interesting guest molecules, thus expanding their potential applications.

Zeolites

Zeolites are crystalline aluminosilicates (or silicates) with regular arrangements of micropores, high surface areas, and exchangeable cations. Ordered mesoporous silica materials are amorphous silica materials with a regular arrangement of mesopores that results in very high surface areas. Zeolites and mesoporous silica are both readily modifiable using well-known silanol organofunctionalization methods. Representative zeolite and mesoporous silica structures are shown in Fig.



a) Silicalite (MFI framework)

b) MCM-41

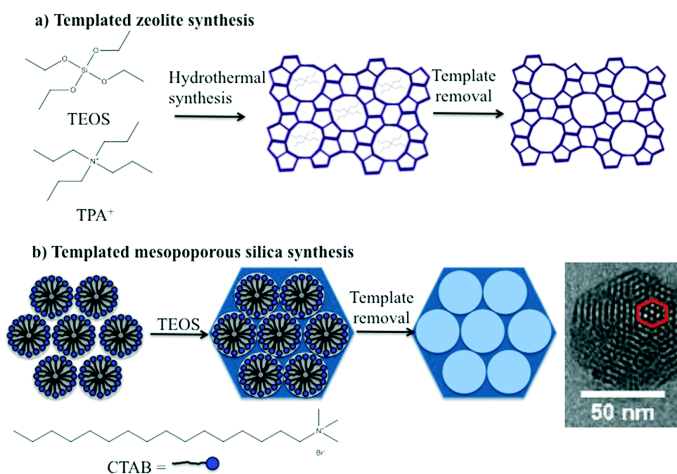
In recent years, there has been a great deal of interest in zeolites and mesoporous silica nanomaterials in which the particle or crystal size of these porous materials is less than approximately 100 nm. Thus, zeolites and mesoporous silica nanomaterials have two dimensions on the nanoscale – the particle size and the pore size. There have been several review articles focused on the synthesis and applications of nanoscale zeolites and mesoporous silica nanoparticles.

Recently there has been growing interest in the green synthesis of porous nanomaterials such as zeolites and mesoporous silica. The principles of green chemistry were introduced in the early 1990's and articulate the objective of reducing (and/or eliminating) negative environmental impacts by decreasing waste or increasing efficiency of chemical processes or syntheses. For example, the porosity in zeolites and mesoporous silica nanomaterials is typically produced using a structure-directing organic template or surfactant that is subsequently removed *via* calcination or solvent extraction leading to potential negative environmental impacts, such as high energy use and the release of toxic by-products. Greener synthetic routes to zeolites include recycling methods, low-cost or degradable templates, template-free synthesis methods, microwave synthesis, and solvent-free or ionic liquid-mediated syntheses.

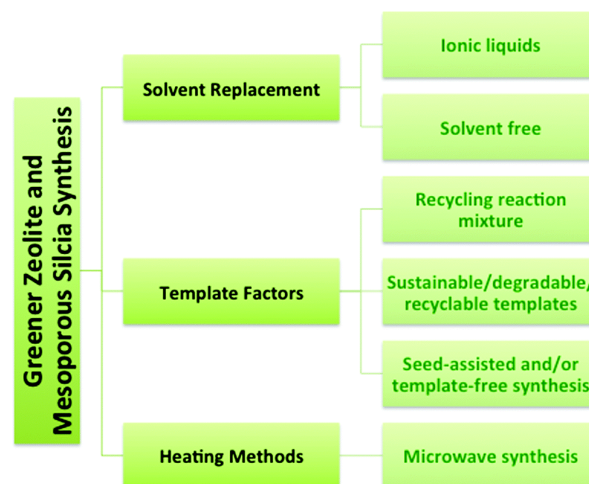
The environmental applications of zeolites and mesoporous silica nanomaterials include environmental catalysis, renewable energy applications, such as biomass conversion and adsorption of environmental contaminants. One of the concerns with the use of zeolite or mesoporous silica adsorbents is the increased cost of these materials compared to more common adsorbents, such as activated carbon. A major factor in the cost is the use of a template, which is ultimately removed to afford the void space. Therefore, the development and implementation of greener synthetic methods for preparing these materials may help address a critical issue in the commercialization of zeolite and mesoporous silica for adsorption applications.

Interest in the toxicity of zeolite and mesoporous silica nanomaterials stems from the concern that as zeolite and mesoporous silica nanomaterials are more widely used in industry and in commercial products, environmental and human exposures will increase dramatically. Crystalline silica dusts have been extensively studied and it is well-established that prolonged exposure leads to silicosis, lung cancer and autoimmune diseases in humans. Recently, there have been a number of studies of the biological toxicity of zeolite and mesoporous silica nanomaterials and the key results will be presented. In this review article, three major areas with respect to zeolite and mesoporous silica nanomaterials and the environment will be reviewed. The first area is the synthesis of zeolite and mesoporous silica nanomaterials using greener synthetic routes. The second area is the largely unrealized commercial potential of these porous nanomaterials for environmental applications and the third area is biological toxicity.

The synthesis of zeolites and mesoporous silica nanomaterials are distinctly different but do share some common characteristics. Zeolites are commonly synthesized under hydrothermal conditions in an autoclave using an organic template or structure directing agent, commonly a tetraalkylammonium cation, such as tetrapropylammonium cation (TPA^+) (Fig). The zeolite structure forms around the organic template, which is subsequently removed by a high temperature calcination process that ultimately leads to the desired porosity. The key to producing nanoscale zeolites is careful control of the zeolite nucleation process. Many methods for the synthesis of mesoporous silica are based on the Stöber method which was introduced in the 1960's for preparation of colloidal solutions of nonporous silica. The Stöber method was modified by the incorporation of a surfactant into the synthesis which lead to the formation of ordered pores. The size of the pores and the pore structure were varied by judicious choice of surfactant and/or modifying the concentration of surfactant, respectively. The particle size was also varied by adjusting reactant concentrations. Similar to zeolites, the porosity is a result of removal of the surfactant either by extraction or high temperature calcination (Fig. 2B).

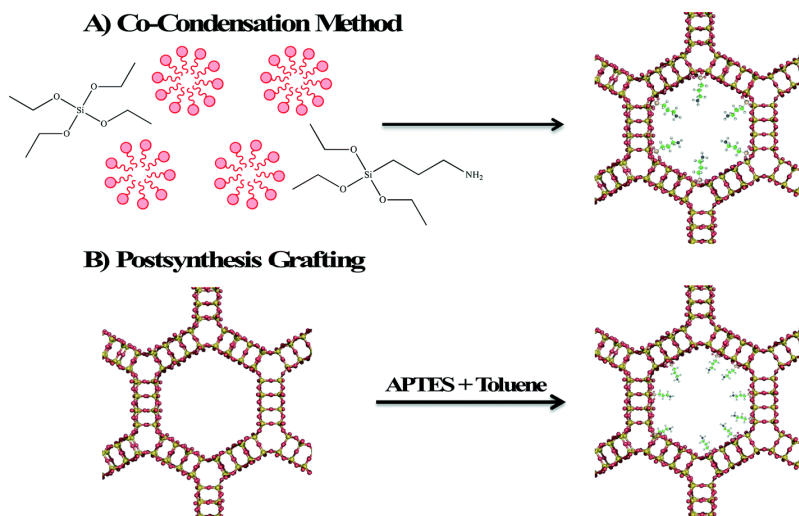


The syntheses of zeolites and mesoporous silica are inherently challenging from a green chemistry perspective because of the reliance on organic templates or surfactants that are ultimately removed by calcination at high temperature to combust the template, or extraction using an organic solvent. The financial and energy costs associated with template removal are high as well as the environmental cost associated with the formation of greenhouse gases during calcination of the organic template and the toxicity of the amphiphilic surfactants, such as cetyltrimethylammonium bromide (CTAB). Synthetic strategies (Fig) will be described here that have been developed to improve the zeolite and mesoporous silica syntheses with respect to green chemistry criteria. The green strategies can be organized into three main categories: solvent, template, and heating. One obvious focus is on synthetic methods that do not require a template or use a recyclable, inexpensive or renewable template. Other strategies for greener syntheses of zeolites and mesoporous silica nanomaterials involve replacing the solvent, developing solvent-free methods and using microwave heating.



Zeolites and mesoporous silica are both considered excellent adsorbents for environmental contaminants due to their high surface areas and readily modifiable surface properties. Surface modification of zeolite and mesoporous silica nanomaterials enhances their adsorption properties by providing a better surface for ionic (electrostatic) interaction or by providing binding sites for chelation of heavy metals. Two methods are employed in surface functionalization of zeolites and mesoporous silica with an organosilane. In the first method shown in Fig. 5A, called co-condensation, the organosilane, aminopropyltriethoxysilane (APTES) is added with the silicon source (often tetraethylorthosilicate, TEOS) so that functionalization occurs simultaneously with formation of the framework.

The second method (shown in Fig. 5B) is postsynthesis grafting in which the calcined porous material is modified by heating an organosilane reactant and the porous material in an aprotic solvent, such as toluene. Due to the larger pore size and surface area, mesoporous silica materials exhibit greater adsorption capacities relative to zeolites. In the rest of this section, the focus will be on the development of mesoporous silica adsorbents.



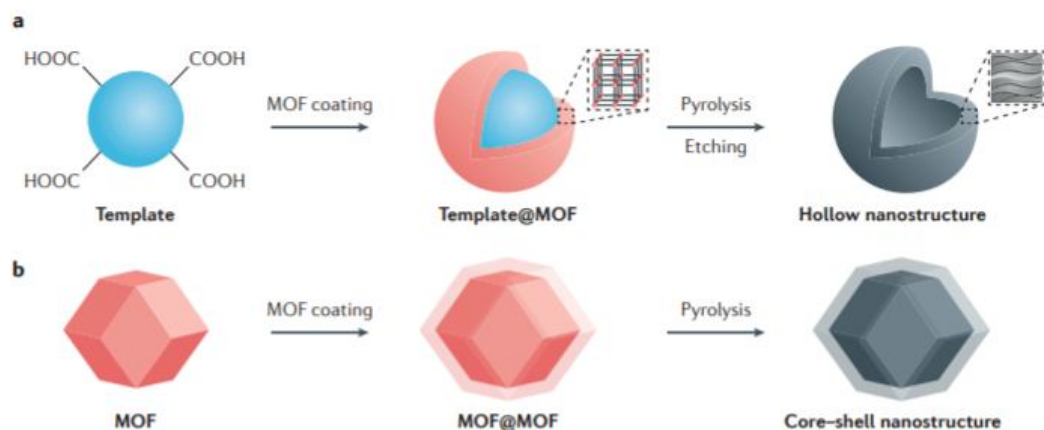
M.O.Fs

The distinct crystalline and porous structures and tailored compositions of metal–organic frameworks (MOFs) make them outstanding templates and precursors to create nanostructures by high-temperature pyrolysis. Many MOF-derived nanostructures have excellent chemical and mechanical stabilities, large specific surface areas, adjustable pore structures and various functionalities. A timeline showing some of the breakthroughs in the study of the morphology, composition and application of MOF-derived nanostructures is shown in FIG. 1. In the first report of MOF-derived nanostructures, pristine carbons were synthesized by the thermal transformation of MOF precursors. Subsequently, metal oxides, metal chalcogenides, metal phosphides, metal carbides and metal nanoparticles have been produced using MOFs as the starting materials. Early studies also revealed that under the harsh and high-temperature conditions of pyrolysis, MOFs tend to collapse, and their original morphologies are damaged, leading to bulk materials with featureless morphologies.

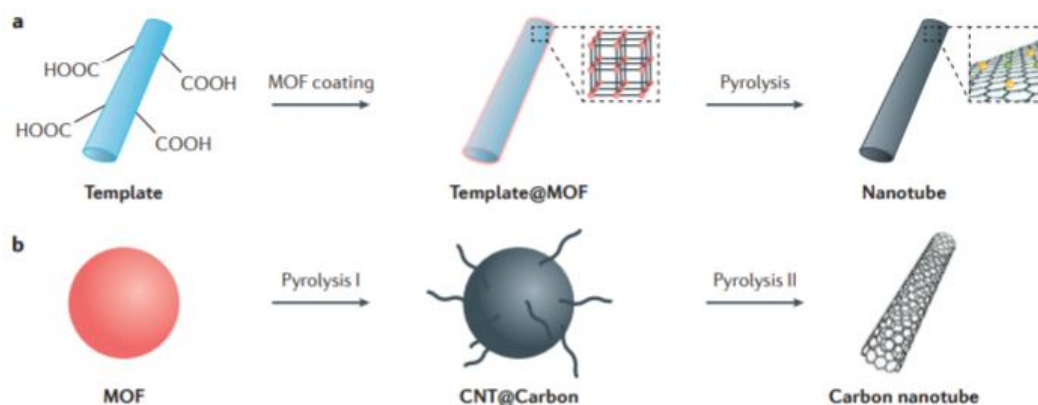
More recently, by selecting appropriate MOF precursors and applying control strategies, this pyrolysis method has enabled the rational design of MOF-derived nanostructures with a range of morphologies. These MOF-derived nanostructures have shown great potential for applications such as gas storage and separation, sensing, catalysis, and energy storage and conversion. The recognition of the importance of morphology in the enhancement of the performance of these nanomaterials in some of these applications has been the main driver of research in this field⁸. Compared with other synthetic approaches to produce nanostructures, the pyrolysis of MOFs, which have periodic crystalline structures and porosities, not only affords precise control of the size, shape, composition and structure but also allows the integration of diverse functionalities in one step. Most synthetic methods to prepare nanostructures from MOF precursors involve a templating strategy and morphology-preserved transformations. In this regard, these MOF-templated strategies can be categorized into self-templating and external-templating methods.

The self-templating method involves pyrolysis of MOF-only precursors, and the external-templating method uses MOF composites with external templates (for example, graphene, silica, carbon and metal oxides). Accordingly, a variety of MOF-derived nanostructures with diverse morphologies have been prepared, including 0D polyhedra, hollow and core–shell structures; 1D rods, hollow rods and tubes; 2D sheets, ribbons and sandwiches; and 3D arrays, frameworks and honeycomb-like structures. Heteroatom-containing MOF precursors, such as nitrogen-rich zeolitic imidazolate frameworks (ZIFs), can be used to prepare nanostructures doped with heteroatoms (for example, nitrogen, sulfur, boron and phosphorus). This approach can result in the modification of the electronic and geometric structures, provide more active sites and facilitate host–guest interactions. Another strategy to generate heteroatom-doped nanostructures is to encapsulate heteroatom precursors

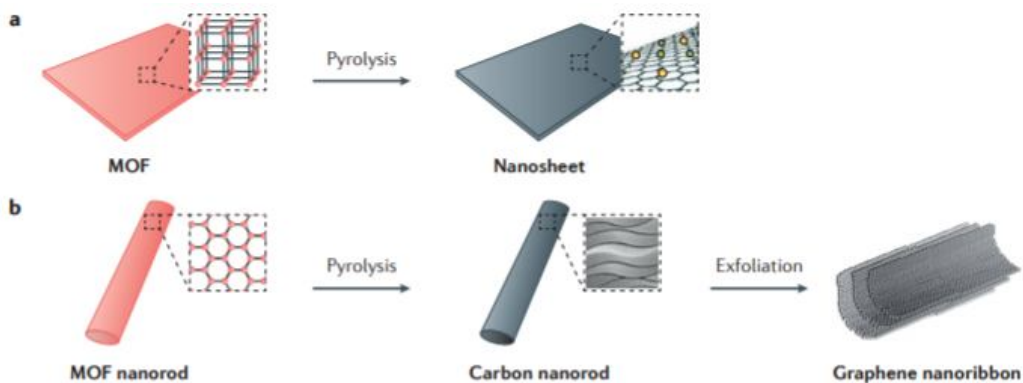
into the pores of MOFs. However, it is challenging to fabricate these nanostructures with well-controlled structural characteristics that influence, or even determine, their electronic, physical and chemical properties. Accordingly, controlling the morphologies of these nanostructures is an attractive way to regulate their properties.



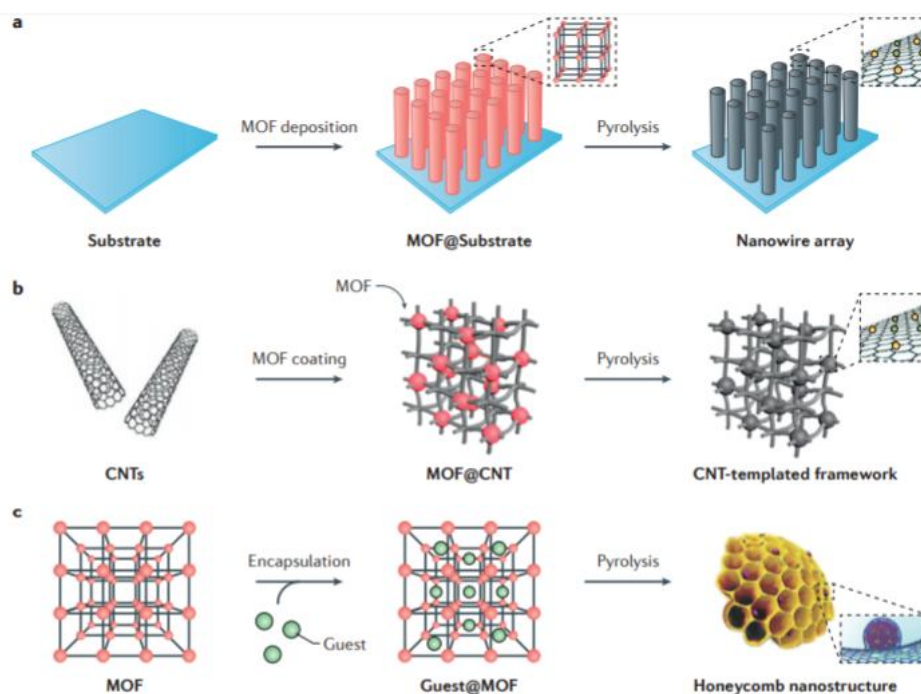
Synthetic strategies for the construction of 0D MOF-derived nanostructures. a | An external template is commonly used to grow a metal–organic framework (MOF) shell. The template@MOF composite produces a hollow nanostructure after pyrolysis and removal of the template. Insets show a MOF (left) and stacked graphene (right). b | A MOF is used as the template for the construction of a MOF@MOF composite, and a core–shell nanostructure is produced after pyrolysis. Red, MOF; blue, template; grey, MOF-derived nanostructure.



Representative strategies for constructing 1D MOF-derived nanostructures. a | An external template is coated with a metal–organic framework (MOF) to produce a template@MOF composite. Subsequent pyrolysis and template removal results in the formation of 1D nanotubes. Insets show a MOF (left) and heteroatom-encapsulated nanotube (right). b | MOF precursors may be directly pyrolysed into carbon nanospheres with carbon nanotubes (CNTs) generated in situ and directly attached to the nanospheres. These CNT@carbon nanostructures are completely transformed into 1D CNTs with further pyrolysis. Red, MOF; blue, template; grey, MOF-derived nanostructure.



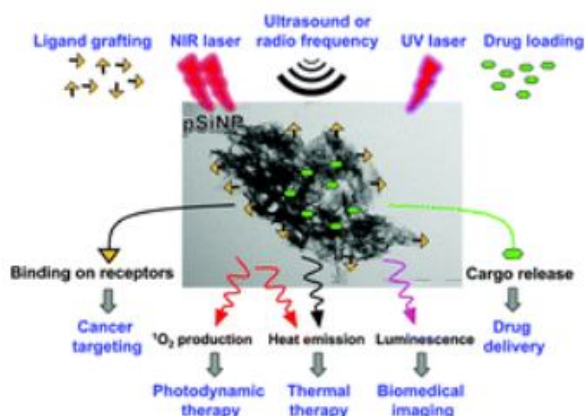
Strategies for the construction of 2D MOF-derived nanostructures. a | A nanosheet is made from a 2D metal–organic framework (MOF) precursor, and the original morphology of the MOF is retained. Insets show a MOF (left) and heteroatom-encapsulated nanosheets (right). b | A MOF nanorod is used to generate a carbon nanorod by a morphology-preserved thermal transformation process. Subsequent exfoliation creates 2D several-layered graphene nanoribbons. Insets show a MOF and stacked graphene sheets within the carbon nanorod. Red, MOF; grey, MOF-derived nanostructures.



Strategies for the construction of 3D MOF-derived nanostructures. a | On a conductive substrate, metal–organic frameworks (MOFs) are grown and produce a template@MOF nanoarray. Subsequent pyrolysis of the template@MOF nanoarray generates a 3D nanowire array. Insets show a MOF (left) and heteroatom-encapsulated nanowire (right). b | Carbon nanotubes (CNTs) can be used to create a CNT-crosslinked-MOF composite, which is further transformed into a CNT-crosslinked 3D framework upon pyrolysis. Inset shows heteroatom-encapsulated carbon. c | Guests are introduced into the pores of a MOF to produce a guest@MOF composite. Pyrolysis of this composite produces honeycomb-like nanostructures. Red, MOF; blue, substrate; grey, MOF-derived nanostructure.

Porous Silicon Nanoparticles

Nanoscience is a major part of biomedical research, due to material advances that aid the development of new tools and techniques to replace traditional methods. To this end, the potential of porous silicon nanoparticles (pSiNPs) has been examined, especially in areas of cancer treatment and diagnosis. The properties of pSiNPs such as their porous structure, high surface area and porous volume, biocompatibility and biodegradability offer real opportunities for focal therapies that can avoid the side effects caused by conventional methods. This review is focused on pSiNPs and their potential application in targeted anticancer drug delivery, and photodynamic and thermal therapies. In addition, the luminescence properties of pSiNPs are useful in bioimaging and diagnosis. Hence, the theranostic potential of pSiNPs is discussed herein.



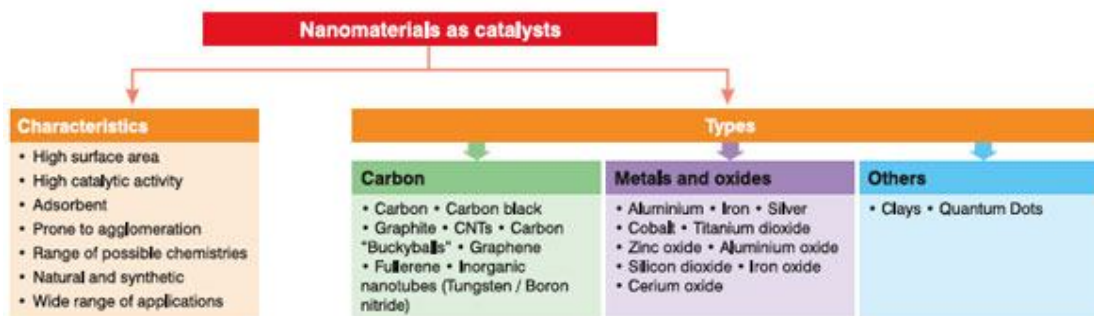
Porous silicon (por-Si) is a very promising material for such containers, as long as it corresponds to the conditions mentioned above. To use porous silicon as nanocontainers one should take into account its characteristics, including radial and axial pore dimensions, pore partition width, porosity, surface extension measure, chemical composition of por-Si surface, electronic state of por-Si surface. The chemical composition and electronic state of por-Si surface are important for researching the mechanisms of adsorption of a medicine, possible chemical interactions, and peculiarities of drug loading.

These parameters depend on the silicon wafer properties (the conductivity type, dopant concentration, structure imperfections, etc.) as well as the porous etching conditions (the electrolyte solutions composition, current density, etching time, etc.). Simultaneous taking into consideration all the factors is extremely difficult. In this regard, it is more reasonable to determine general principles of por-Si formation and dependences of por-Si parameters on the etching conditions to get por-Si with required characteristics.

Nanocatalysis

Nanocatalysis is a rapidly growing field which involves the use of nanomaterials as catalysts for a variety of homogeneous and heterogeneous catalysis applications. Heterogeneous catalysis represents one of the oldest commercial practices of nanoscience; nanoparticles of metals, semiconductors, oxides, and other compounds have been widely used for important chemical reactions. Although surface science studies have contributed significantly to our fundamental understanding of catalysis, most commercial catalysts, are still produced by "mixing, shaking and baking" mixtures of multi-components; their nanoscale structures are not well controlled and the synthesis-structure-performance relationships are poorly understood. Due to their complex physico-chemical properties at the

nanometer scale, even characterization of the various active sites of most commercial catalysts proves to be elusive.



A key objective of nanocatalysis research is to produce catalysts with 100% selectivity, extremely high activity, low energy consumption, and long lifetime. This can be achieved only by precisely controlling the size, shape, spatial distribution, surface composition and electronic structure, and thermal and chemical stability of the individual nanocomponents. In this article, the exciting opportunities of nanocatalysis in chemical and refining processes, as well as the challenges in developing nanostructured catalysts for industrial applications, are discussed.

The field of nanocatalysis (the use of nanoparticles to catalyze reactions) has undergone an explosive growth during the past decade, both in homogeneous and heterogeneous catalysis. Since nanoparticles have a large surface-to-volume ratio compared to bulk materials, they are attractive candidates for use as catalysts. In homogeneous catalysis, transition metal nanoparticles in colloidal solutions are used as catalysts. In this type of catalysis, the colloidal transition metal nanoparticles are finely dispersed in an organic or aqueous solution, or a solvent mixture.

The colloidal nanoparticle solutions must be stabilized in order to prevent aggregation of the nanoparticles and also to be good potential recyclable catalysts. Metal colloids are very efficient catalysts because a large number of atoms are present on the surface of the nanoparticles. The method that is used in synthesizing transition metal nanoparticles in colloidal solutions is very important for catalytic applications. The reduction method employed controls the size and the shape of the transition metal nanoparticles that are formed, which are very important in catalytic applications.

The different reduction methods that have been used to synthesize colloidal transition metal nanoparticles for homogeneous catalysis are summarized below. Chemical reduction of the precursor transition metal salt is the most widely used method of synthesizing transition metal nanocatalysts in colloidal solution. There are four other synthetic methods to prepare colloidal transition metal nanocatalysts that are not as commonly used. These synthetic methods include

- thermal, photochemical, or sonochemical reduction of the precursor transition metal salts
- ligand reduction and displacement from organometallic precursors
- metal vapor synthesis and
- electrochemical reduction of transition metal precursor salts. Stabilization of nanoparticles in the solution is necessary in order to prevent agglomeration and

aggregation. For catalytic applications, the choice of stabilizers plays an important role in

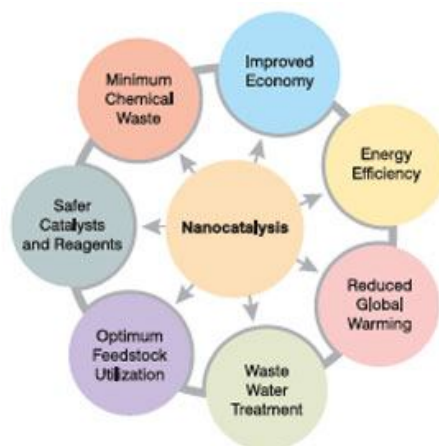
- Stabilization of nanoparticles in the solution is necessary in order to prevent agglomeration and aggregation. For catalytic applications, the choice of stabilizers plays an important role in determining the reactivity of nanoparticles. The above figure shows a schematic of synthesis of Pt-Clay nanocatalyst.

A good stabilizer is one that protects the nanoparticles during the catalytic process, but does not neutralize the surface of nanoparticles resulting in loss of catalytic activity. The choice of a stabilizer to be used for capping the nanoparticles is usually a balancing act between passivation of the nanoparticle surface and the fraction of available sites for catalysis, and also affects the size and shape of the nanoparticles formed.

Heterogeneous metal nanocatalysts are prepared by adsorption of nanoparticles on to supports, which involves functionalization of supports to adsorb nanoparticles on to them and, fabrication of nanostructures on the supports by lithographic techniques.

Benefits of nanocatalysts in the chemical industry

- Increased selectivity and activity of catalysts by controlling pore size and particle characteristics
 - Replacement of precious metal catalysts by catalysts tailored at the nanoscale and use of base metals, thus improving chemical reactivity and reducing process costs
 - Catalytic membranes by design that can remove unwanted molecules from gases or liquids by controlling the pore size and membrane characteristics
- In view of the numerous potential benefits that can accrue through their use, nanostructured catalysts have been the subject of considerable research attention in recent times. Many applications and patents have also been realized adopting such nanostructured catalysts leading to significant process improvements as exemplified below.



Common Synthesis Methods for Colloidal Nanoparticles

Chemical Reduction Method

Important Characteristics: • Reduction of a metal salt in solution using reducing agents like alcohol, sodium borohydride, etc. • Precursor transition metal salts are reduced to form the transition metal nanoparticles

Thermal, Photochemical and Sonochemical Reduction Method

Important Characteristics: • Decomposition of the precursor organometallic salt to the zerovalent form • Reduction of precursor metal salt or degradation of an organometallic complex by radiation X-ray or gamma-ray and also UV-visible radiation by use of xenon or mercury lamp • Reduction of the precursor metal salt by an acoustic cavitation phenomena and growth of colloids in the sonicated liquid medium

Ligand Displacement Method

Important Characteristics: • Displacement of ligand in the organometallic complex (e.g. amine ligands are displaced by thiol ligands)

Condensation of Metal Vapor

Important Characteristics: • Evaporation of transition metal vapors at reduced pressure and subsequent co-condensation of these metals at low temperature with organic vapors • Nanoparticles are formed by nucleation and growth when the frozen metal/organic mixture is warmed to the point of melting • No precise control on size of the nanoparticles

Electrochemical Reduction Method

Important Characteristics: • Precursor metal ions are reduced at the cathode using a sacrificial anode as the metal source • The metal at anode is oxidized in presence of a quaternary ammonium salt which acts as both the electrolyte and the stabilizer

Important Applications of Nanocatalysis

Biomass

Application: *Biomass gasification to produce high syn gas and biomass pyrolysis for production of bio-oil*

Catalyst: Nano NiO catalyst supported on γ - Al₂O₃ microspheres of 3 μ m size

Application: *Production of biodiesel from waste cooking oil*

Application: *Green diesel production using Fischer-Tropsch Synthesis (FTS)*

Catalyst: • Nano Fe and Co powders (10-50 nm) are used as FTS catalysts in slurry reactors, promoted by other metals like Mn, Cu & alkalis • Produced by thermal plasma chemical vapor deposition (TPCVD) and cluster spray techniques • Minimize liquid-solid

diffusion resistance • Multi-walled carbon nanofilaments (MWCNF), produced by CO₂ sequestration via dry reforming for gas-to-liquid FTS, with the iron carbide content rendering catalytic activity

Oil, Gas & Fossil Fuels

• Paraffin Dehydrogenation • Naphtha Reforming • Selective Hydrogenation • Hydrodesulfurization

Application: Improved economic catalytic combustion of JP-10 aviation fuel using hydrocarbon fuel soluble nano catalyst

Catalyst: Hexanethiol monolayer protected Palladium clusters < 1.5 nm

Application: Hydrogen production by steam reforming of ethanol over nanostructured indium oxide catalysts

Catalyst: Mesoporous In₂O₃ prepared using Mobil Composition of Matter No. 41 (MCM-41) silica catalyst as templates with particle size of 2-3 nm and surface area of 107 m²/g to 173 m²/g

Application: Adsorptive desulfurization and bio desulfurization of fossil oils

Catalyst: Nano γ - Al₂O₃ (10 nm in width and 100-200 nm in length) with specific surface area of 339 m²/g

Application: Hydrodesulfurization of diesel

Catalyst: Synthesis of new NiMo/Al hexagonal, mesoporous structured nanocomposite catalyst by supercritical deposition method

Fuel Cells

Application: Core-shell nanocatalysts for fuel cell applications

Catalyst: Smooth and compact Pt shell for better oxygen reduction reactions in fuel cell applications

Application: In situ hydrogen production by reaction of ammonia and nanocatalysts

Catalyst: The dissociation catalyst is a mixture of nanometer size particles of Co-Ni-Cu-Zr catalyst deposited on high surface area of TiO₂ and 2% Pt deposited on alumina particles