

Sol–gel derived organic–inorganic hybrid materials: synthesis, characterizations and applications

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Abstract Organic/inorganic hybrid materials prepared by the sol–gel approach have rapidly become a fascinating new field of research in materials science. The explosion of activity in this area in the past decade has made tremendous progress in both the fundamental understanding of the sol–gel process and the development and applications of new organic/inorganic hybrid materials. Polymer–inorganic nanocomposite present an interesting approach to improve the separation properties of polymer material because they possess properties of both organic and inorganic such as good permeability, selectivity, mechanical strength, and thermal and chemical stability. Composite material derived by combining the sol–gel approach and organic polymers synthesis of hybrid material were the focus area of review. It has also been demonstrated in this review that a more complete understanding of their structure–property behavior can be gained by employing many of the standard tools that are utilized for developing similar structure–property relationships of organic polymers. This review article is introductory in nature and gives introduction to composite materials/nanocomposite, their applications and the methods commonly employed for their synthesis and characterization. A brief literature survey on the polysaccharide templated and polysaccharide/protein dual templated synthesis of silica composite materials is also presented in this review article.

Keywords Nanocomposites · Thermal properties · Sol–gel method · Hybrid material · Silica precursor

1 Introduction

There is an enormous demand for novel materials to meet the recent technological breakthroughs. Many of the well-established materials, such as metals [1] ceramics [2–4] or plastics [5, 6] cannot fulfill all technological desires for the various new applications. Mixtures of materials can show superior properties compared with their pure counterparts. Composites are formed by the incorporation of a basic structural material into a second substance, the *matrix* e.g., inorganic fiber-reinforced polymers [7–9] and lightweight materials [10, 11] with advanced mechanical properties. Composites of organic and inorganic are of special interest having characteristics in between the two original phases or even new properties. Due to the possibility of designing properties by the hybridization of the organic and inorganic components, multifunctional materials [12, 13] can be created. Such materials have the possibility of their processing as thin films thus they can lead to property improvements of cheaper materials by a simple surface treatment, e.g., scratch resistant coatings [14–16]. Based on the molecular or nanoscale dimensions of the building blocks, light scattering in homogeneous material can be avoided and the optical transparent nanocomposites materials suitable for optical applications [17–20] can be produced. While in most cases phase separation is avoided, phase separation of organic and inorganic components is used for the formation of porous materials [21, 22]. Material properties of composite materials are usually changed by modification of the composition on the molecular scale to result smart materials, such as materials that react to environmental changes or switchable systems for example electroactive materials [23, 24], electrochromic materials [25–27], sensors [28–30], membranes [31, 32], and biohybrid materials [33–35].

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Organic/inorganic composite materials have been extensively studied for a long time. When inorganic phases in organic/inorganic composites become nanosize, they are called nanocomposites. Inorganic nanoscale building blocks include nanotubes, layered silicates (e.g., montmorillonite, saponite), nanoparticles of metals (e.g., Au, Ag), metal oxides (e.g., TiO_2 , Al_2O_3), semiconductors (e.g., PbS, CdS), and so forth, among which SiO_2 is viewed as being very important. Therefore, polymer/silica nanocomposites have attracted substantial academic and industrial interest. In fact, among the numerous inorganic/organic nanocomposites, polymer/silica composites are the most commonly reported in the literature. They have received much attention in recent years and have been employed in a variety of applications. Organic or inorganic polymerization generally becomes necessary if at least one of the starting moieties is a precursor. In addition, considerable efforts have been devoted to the design and controlled fabrication of polymer/silica colloidal nanocomposites particles with tailored morphologies in recent years. The colloids represent a relatively new category of nanocomposites. A better understanding of the parameters governing sol–gel chemistry, and the development of suitable processing methods has led to the design of new materials with interesting properties in the past decade'. Sol–gel chemistry not only offers an access to ceramics and glasses with improved or new properties. The very mild reaction conditions, particularly the low reaction temperatures, also allow incorporating organic moieties in inorganic materials. This led to a conceptually novel class of materials composed of both inorganic and organic groupings.

Organic groups in sol–gel derived materials can serve different purposes:

1. During the preparation of purely inorganic materials, they can control the reaction rates of the reactants, the rheology of the sols, or the homogeneity and microstructure of the derived gels. They are degraded during calcinations to get purely inorganic materials.
2. The organic groups can be retained to modify or functionalize the oxidic material. The final material therefore is composed of inorganic (oxidic) structures cross-linked or substituted by organic groups.

Consequently, most reviews have a strong focus on the chemical background of the material synthesis or intend to elaborate on common structural principles and just mention potential or claimed few applications. Several comprehensive reviews on the research activities in the field of organic/inorganic hybrid materials by the sol–gel approach have been published describing the basic chemistry behind the preparation, different chemistry pathways as well as of the parameter influencing the processing techniques and in most of review attention to

sol–gel processing of organic–inorganic hybrid material along with some specific applications such as nano coating, photo catalysts, gas sensor etc. were discussed [36–49]. But no review, specifically discusses about biopolymer–silica nanocomposites materials based on sol–gel process are reviewed so far. This subject related to polysaccharide template organic–inorganic silica composite material has so far never been reviewed. The aim of this review is to summarize the recent developments in this field based mainly on the literature. Therefore, this review will give a general brief overview of the sol gel technique for the synthesis of organic–inorganic nanocomposites material followed by a brief discussion of their characterization, properties, and applications. A brief literature survey on the polysaccharide/protein dual templated synthesis of silica composite materials is also presented in this review article. There seems to be a strong need to increase the public knowledge about the sol gel derived biopolymer–silica nanocomposites and its achievements.

2 Natural origins

Many natural materials consist of inorganic and organic building blocks distributed on the (macro)molecular or nanoscale where 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 e.g., bone, or nacre. Bones, teeth and shells are typical biocomposites which consists of an organic polymer matrix reinforced by inorganic deposits. The biological hybrid inorganic–organic materials are formed at ambient temperatures, an aqueous environment, a neutral pH where plethora of complex geometries results. Mimicking [50, 51] such structures is the current research interest.

Apart from the use of inorganic materials as fillers for organic polymers such as rubber, in recent years, sol–gel method [52] of composite synthesis has attracted many researchers in particular the silicon based sol–gel process [53–59]. This process is similar to an organic polymerization starting from molecular precursors resulting in a bulk material under ambient conditions. Some similarities to sol–gel chemistry are shown by the stable metal sols and colloids, such as gold colloids [60].

3 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. The term hybrid material is used for many

different systems spanning a wide area of different materials, such as crystalline highly ordered coordination polymers [61, 62] and amorphous sol–gel compounds [63, 64], where the materials with and without interactions between the inorganic and organic units may result. In addition to the bonding characteristics, structural properties [65–70] also distinguish between various hybrid materials.

4 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. Commonly the term nanocomposites is used if discrete structural units in the respective size regime are used and the term hybrid materials is more often used if the inorganic units are formed in situ by molecular precursors, for example applying sol–gel reactions. Examples of discrete inorganic units for nanocomposites are nanoparticles [71–73], nanorods [74, 75], carbon nanotubes [76–78] and galleries of clay minerals [79, 80]. Usually a nanocomposite is formed from these building blocks by their incorporation in organic polymers.

4.1 Synthetic strategies

In principle two different approaches can be used.

4.1.1 Building block approach

In this approach building blocks at least partially keep their molecular integrity throughout the material formation and typical properties of these building blocks usually survive the matrix formation.

4.1.2 In situ formation of the components

In this method well-defined discrete molecules are transformed to multidimensional structures, which often show totally different properties from the original precursors.

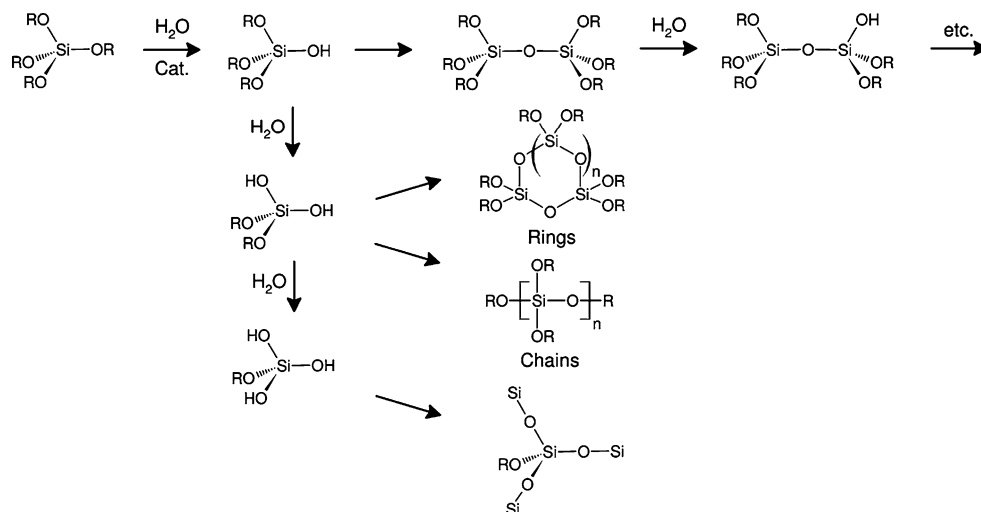
4.1.3 In situ formation of inorganic materials

Many of the classical inorganic solid state materials are formed using solid precursors and high temperature processes [81], which are often not compatible with the presence of organic groups because they are decomposed at elevated temperatures and sol–gel process is a suitable alternative, however this often does not lead to the thermodynamically most stable structure but to kinetic products, which has some implications for the structures obtained [51].

4.1.3.1 Sol–gel process Sol–gel reactions have been extensively studied for several decades as a method to prepare ceramic precursors and inorganic glasses at relatively low temperatures. The major advantage of the sol gel process is that mild conditions, such as relatively low temperature and pressure, are used in this type of processing of ceramics. The sol–gel process has been widely used to create novel organic–inorganic composite (hybrid) materials, which were termed “ceramers” by Wikes et al. [82] and “ormosils” or “ormocers” by Schmidt et al. [83] in the past decade. The goal to carry out the sol–gel reaction in the presence of organic molecules that are typically polymeric and contain functional groups to improve their bonding to the ceramic like phase are observed in case of composite material. This is found to be one of the very useful novel reinforcement techniques, which can generate reinforcing particles within a polymer matrix. Moreover, these novel hybrid sol–gel materials are normally nanocomposites and have the potential for providing unique combinations of properties that cannot be achieved by other materials [84].

Sol–gel process [53, 54] is chemically related to an organic polycondensation reaction in which small molecules form polymeric structures by the loss of substituent. As is well-known, the sol–gel process can be viewed as a two-step network forming process, In the first steps of this reaction oligo- and polymers as well as cyclics are formed subsequently resulting in colloids that define the sol. And in second step the Solid particles in the sol afterwards undergo cross linking reactions and form the gel (Fig. 1). Most of the interest in this method is concentrated on metal-organic alkoxides, especially silica, since they can form an oxide network in organic matrices. The most common silica precursor is TEOS because it is readily purified and has a relatively slow and controllable rate of reaction [84]. Many factors influence the kinetics of the hydrolysis and condensation reactions in the sol–gel process, which include the water/silane ratio, catalyst, temperature, the nature of solvent, and so forth. The sol–gel process surpasses the traditional blending method since it can subtly control the morphology or surface characteristics of the growing inorganic phase in the polymer matrix by control of these reaction parameters. The poor reactivity of silicon is generally activated by using acid or base catalysts. The pH used has an effect on the kinetics which is usually expressed by the gel point of the sol–gel reaction [85, 86]. The reaction is slowest at the isoelectric point of silica (between pH 2.5 and pH 4.5 depending on different parameters) and the speed increases rapidly on changing the pH. Besides the reaction conditions, structure of silica precursor has a strong influence on the kinetics of the reaction. Generally, larger substituents decrease the reaction time due to steric hindrance. In addition, the

Fig. 1 Reaction steps in sol–gel process based on tetraalkoxysilanes



substituents play a major role in the solubility of the precursor in the solvent. Water is required for the reaction and if the organic substituents are quite large usually the precursor becomes immiscible in the solvent. The pH plays a major role in the mechanism and for the microstructure of the final material. Applying acid-catalyzed reactions an open network structure is formed in the first steps of the reaction leading to condensation of small clusters afterwards [87], while the base-catalyzed reaction leads to highly crosslinked sol particles already in the first steps [88]. This leads to variations in the homogeneity of the final materials. Commonly used catalysts are HCl, NaOH or NH_4OH , but fluorides [89] can be also used as catalysts leading to fast reaction times. If tetraalkoxysilanes are used as precursors, two water molecules per starting compound are necessary to form completely condensed SiO_2 . A lower $\text{H}_2\text{O}/\text{Si}$ ratio leads to an alkoxide containing final material (Figs. 2, 3).

Acid catalysis results in a faster hydrolysis of TEOS and in an open weakly ramified polymer-like structure. In contrast, slower hydrolysis and faster polycondensation were observed in the case of base catalysis leading to compact colloidal particles. Large spherical particles are expected in the case of base-catalyzed reaction, while linear chain growth is expected via acid catalysis. It has been shown that basic catalysis usually yields opaque composites with phase dimensions well above 100 nm and more generally in the micrometer range. These materials can definitely not be considered as nanocomposites. The transparent nanocomposites with characteristic morphology sizes below 100 nm are generally obtained, if alternatively acid catalysis is used in place of base catalysis. Therefore, the polymer/silica nanocomposites prepared by sol–gel processes are generally obtained by acid-catalysis [37].

Jones et al. [90] has published the document in which they define various terms related to the structure and

processing of inorganic, polymeric, and inorganic–organic hybrid materials from precursors, through gels to solid products. These important definitions are intended to assist the reader who is unfamiliar with sol–gel processing, ceramization, and related technologies and materials, and to serve as a guide to the use of standard terminology by those researching in these areas.

Some other sol–gel processes include

1. *Nonhydrolytic sol–gel process*: In this process the reaction between metal halides and alkoxides is used for the formation of the products [91, 92]. The alkoxides can be formed during the process by various reactions.
2. *Sol–gel reactions of non-silicates*: Metal and transition-metal alkoxides [93, 94] are generally more reactive towards hydrolysis and condensation reactions compared with silicon. The metals in the alkoxides are usually in their highest oxidation state surrounded by electronegative—OR ligands which render them susceptible to nucleophilic attack. M–C bonds in metal alkoxides are not stable enough to survive the sol–gel conditions and therefore, other mechanisms have to be employed for preparing inorganic–organic metal oxide materials in a one-step approach. Thus organically functionalized bi and multidentate ligands [94] are used that show a higher bonding stability during the sol–gel reaction and, in addition, reduce the speed of the reaction by blocking coordination sites.

4.2 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 where the molecules have to endure the pH of the environment. Hence,

Fig. 2 Differences in mechanism depending upon the type of catalyst used in silicon based sol–gel process

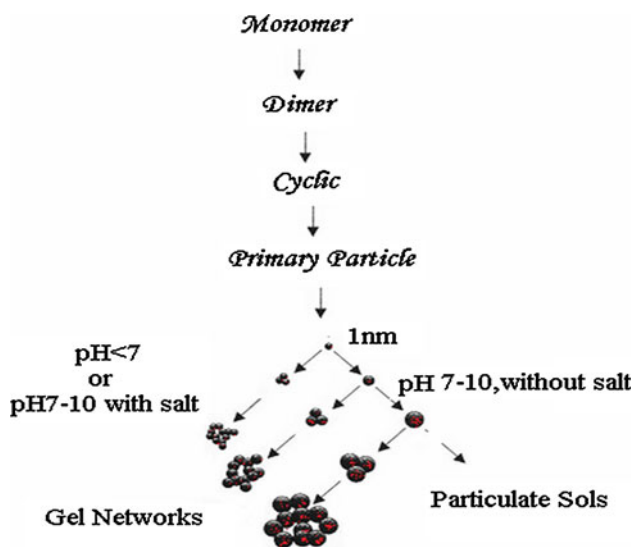
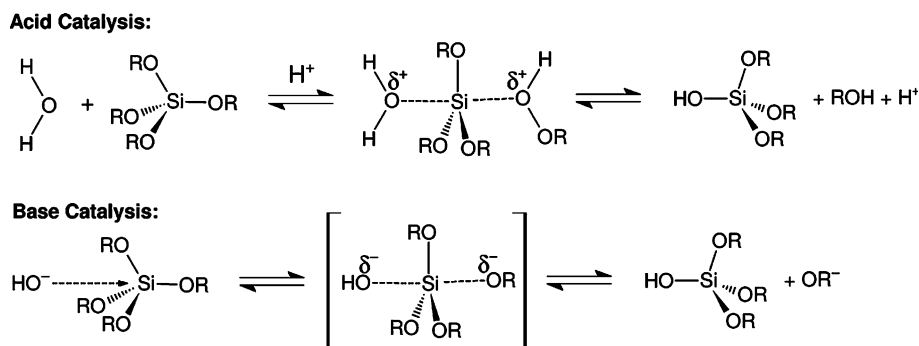


Fig. 3 Polymerization behavior of silica precursor

functional organic groups that can be hydrolyzed are not tolerated, but a partial tolerance for the pH can be obtained by carrying out the reaction in a buffer solution especially if biological molecules, such as enzymes, are to be entrapped in the gel [95]. Physical entrapment has the disadvantage that sometimes the materials obtained are not stable towards phase separation or leaching because of differences in polarity.

Chemical modification of organic compounds with trialkoxysilane groups [96] can partially avoid such problems due to co-condensation during the formation of the sol–gel network and thus development of covalent linkages to the network.

Though the formation of homogeneous materials with a chemical link between the inorganic and organic component is the preferred route, a controlled phase separation between the entrapped organic molecules and the sol–gel material is necessary for the preparation of mesoporous materials [97]. Besides the entrapment of organic systems, precursors with hydrolytically stable Si–C bonds can also be used for co-condensation reactions with tetraalkoxysilanes. In addition, organically functionalized

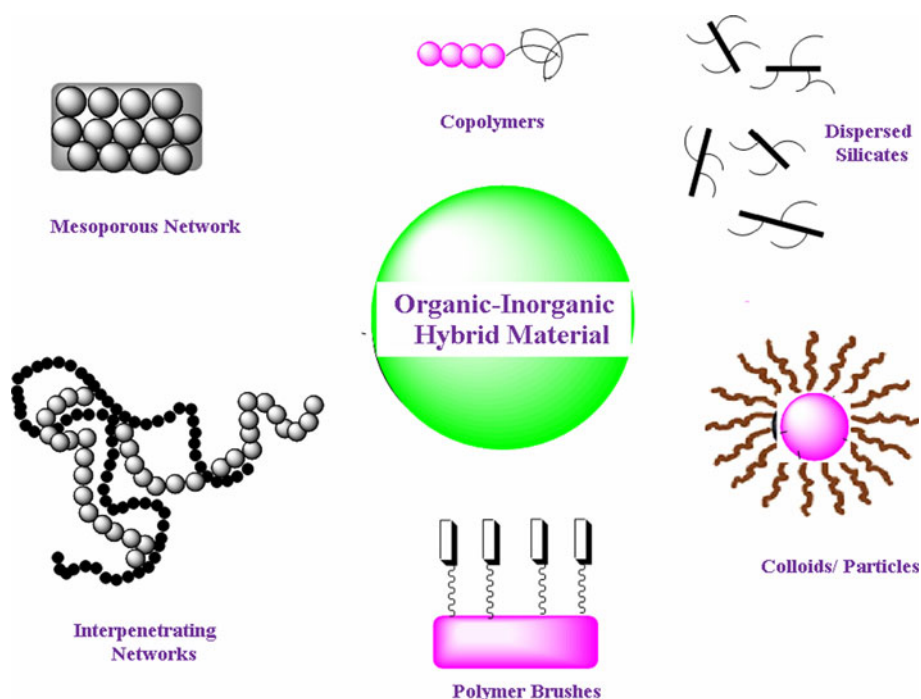
trialkoxysilanes [98, 99] can also be used for the formation of 3-D silsesquioxanes (general formula $\text{R-SiO}_{1.5}$) materials. Because of the stable Si–C bond, the organic unit can be included within the silica matrix without transformation.

In addition, the functional group incorporated changes the properties of the final material, for example fluoro-substituted compounds can create hydrophobic [100] and lipophobic materials [101]. Additional reactive functional groups can be introduced to allow further reactions such as amino, epoxy or vinyl groups.

4.3 Composite materials derived by combining the sol–gel approach and organic polymers

The sol–gel processes show mild reaction conditions and a broad solvent compatibility thus results in the formation of the inorganic network in presence of a preformed organic polymer [102] or to carry out the organic polymerization before, during [36] or after the sol–gel process [97]. The properties of the final materials are determined by the properties of the inorganic and organic component, by the phase morphology and the interfacial region between the two components. Covalent linkages can be formed if functional groups that undergo hydrolysis and condensation reactions are covalently attached to the organic monomers. Some typically used monomers that are applied in homo or copolymerizations are Hydroxyethylmethacrylate (HEMA) [103], vinyl pyridine [104], dimethylacetamide, glycidoxypropyl trialkoxysilane [105], methacryloyl trialkoxysilane etc. [106]. Well-defined organic polymers have been attached to inorganic copolymers, particles, surfaces, glassy networks and interpenetrating polymer networks to prepare organic/inorganic hybrid materials. Additionally, polymers of controlled size, composition, and architecture have been used as shape templates in the synthesis of Mesoporous inorganic networks (Fig. 4). Hybrid organic–inorganic nanocomposites have been synthesized by using polymer such as poly (tetramethylene oxide) and poly(oxazolines).

Fig. 4 Examples of organic/inorganic hybrid materials



4.3.1 Organic building blocks

Beside the inorganic building blocks, organic building blocks can also be used for the formation of composite materials. Typical examples are oligo- [107] and polymers [108, 109] as well as biological active molecules like enzymes [110].

4.3.2 Small molecules

The mild conditions of the sol–gel process permit the introduction into the inorganic network of any organic molecule that consists of groups which do not interfere with these conditions. In recent years functional hybrid composites have been the particular focus of interest. Organic dyes [111], nonlinear optical groups [112, 113], or switchable groups [114] are only a small selection of molecules which have already been used to prepare hybrid materials and nanocomposites.

4.3.3 Macromolecules

Oligo- and polymers as well as other organic macromolecules often show different solubility in specific solvents compared with their monomers. For homogeneous materials, an appropriate solvent for both the inorganic and the organic macromolecules is of great benefit [115, 116]. A particularly interesting group of macromolecules are block copolymers [117], consisting of a hydrophilic and a hydrophobic segment [118–120].

4.3.4 Particles and particle-like structures

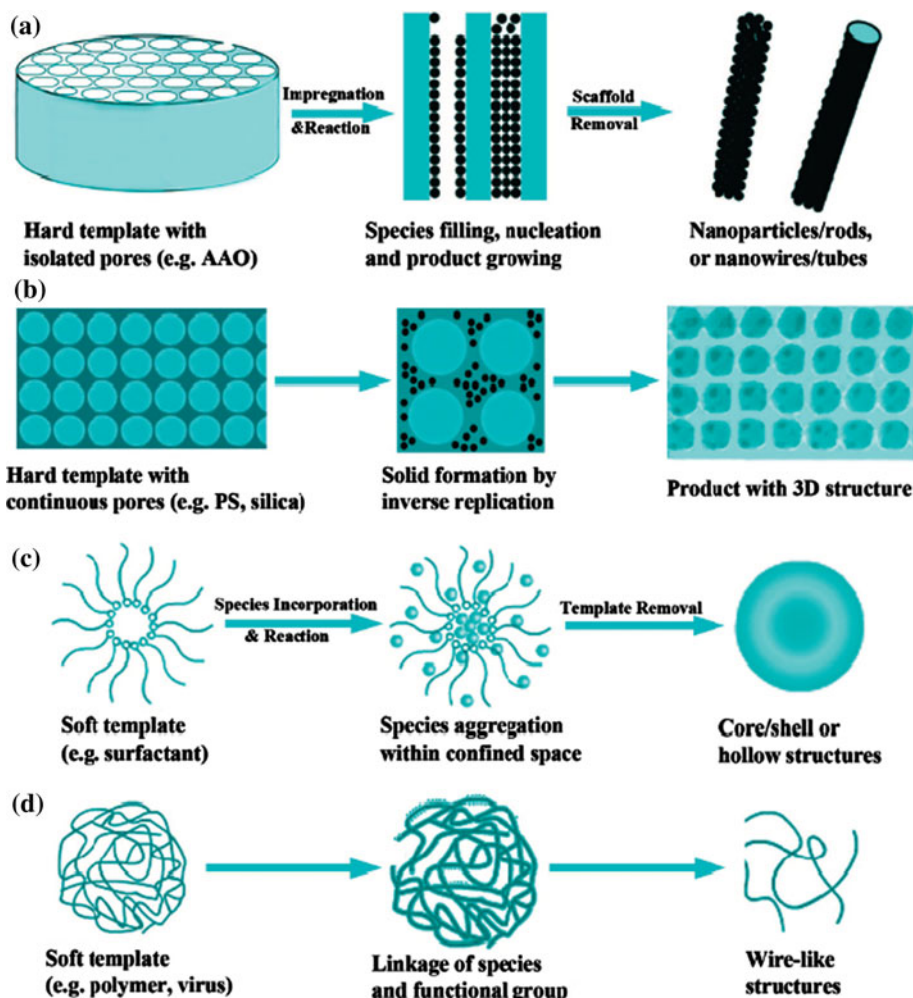
Organic colloids formed from physically or chemically crosslinked polymers can also be used as building blocks for inorganic–organic hybrid materials and nanocomposites [121].

4.3.5 Template-directed synthesis of hybrid materials

Templates for the synthesis of hybrid materials can be preformed structures such as dendrimers [122] or nanoparticles [123] that form 2-D or 3-D ordered structures or polymers [124]. Furthermore the supramolecular self-organization of single molecules into larger 2-D and 3-D structures can also be employed as a template. After removal of the template which commonly occurs by calcination at temperatures above 450 °C, the materials are purely inorganic in nature.

Concept of the template synthesis was illustrated in Fig. 5 [125]. The overall process generally involves the following procedures: (a) precursors combine with templates by impregnation or incorporation; (b) solid species form through reaction, nucleation and growth; and (c) product is obtained after template removal. Templates can be employed to various synthetic techniques such as sol–gel synthesis, chemical vapour deposition, thermal decomposition, electro deposition, solvothermal preparation, and so on. The connectivity of the pores or channels strongly influences the structure of the resulting solid product in case of hard templates. In the case of

Fig. 5 Schematic depiction showing some typical examples of the hard and soft template synthesis of electrode materials with diverse morphologies (Adapted from Ref. [111]. Reprinted with permission from ACS Publishing Group, Copyright (2011))



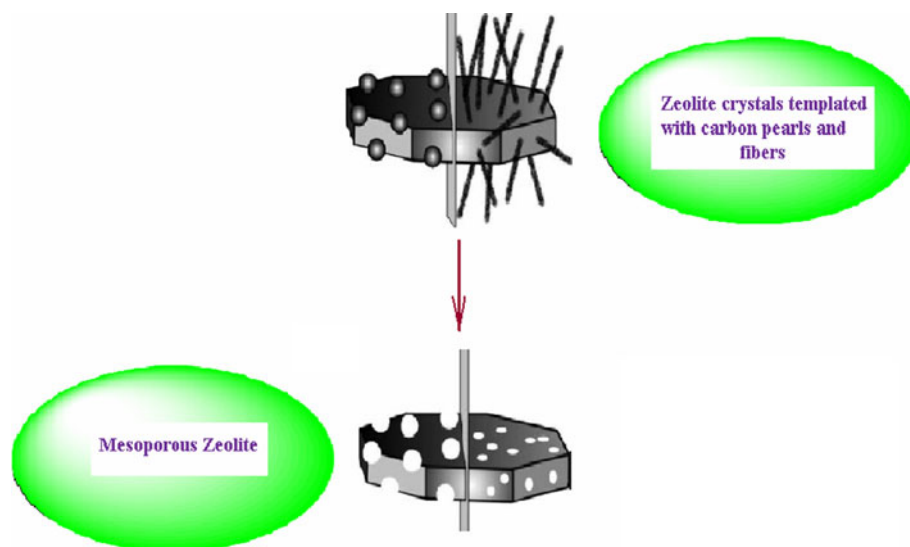
nonconnected porous templates such as AAO membranes and MCM-41 silica, solid product forms inside the isolated pores, replicating the shape of the void space in templates. As a result, aligned structures such as 1D nanotubes and nanowires are usually obtained after removing the template scaffold (Fig. 5a). The templates that consist of a continuous pore system such as porous carbons or silica gels generally lead to an inverse replica of the mold structure after template isolation, thus resulting in frameworks with interconnected 3D pores (Fig. 5b) [126]. The AAO membranes are most widely used hard templates because of their facile preparation and controllable pore size [127]. A series of inorganic electrode materials including metals [128, 129], metal oxides [130, 131] and hydroxides [132–134], lithium metal oxide [135], and composite metal oxide [136] are obtained by applying AAO template synthesis.

For soft templates, they function as structure-directing agents that assist in the assembly of reacting species. Because of either the unique anisotropic structures or the functionality of their subunit groups soft templates are facile for controlled fabrication of nanomaterials. Typical examples are

surfactants, long-chain polymers, and viruses. Under a certain condition, these materials are assembled into the form of aggregating entities such as micelle/vesicle aggregates or liquid crystal phase, which restrict and direct the growth of a guest structures [137]. Precursor species react in the confined space of surfactant micelles (Fig. 5c) or on the surface of polymer/virus chains (Fig. 5d), as driven by self-assembly or interaction between functional groups [138, 139]. After separating the template, sphere like or wirelike structures can be fabricated, following the basic shape of the aggregates. Porous nanostructures are obtained during such a “nanocasting” process [140] in many cases. The main strategy of this synthesis route is based on the transcriptive and/or synergistic effect of the soft templates. Through the template synthesis route various lithium storage materials such as lithiated metal oxides (e.g., LiCoO_2 and LiMn_2O_4), carbons, tin-based oxides, and transition metal oxides (e.g., Fe_2O_3 , Co_3O_4 , NiO , VO_x , TiO_2 , MnO_2 , etc.) can be obtained.

Meanwhile, the template-prepared electrode materials usually possess controlled nanostructures with different size, shape, and dimension. For example, 1D nano/

Fig. 6 Zeolitization process resulting in micro/mesoporous composite in the presence of carbon templates



microarrays, 2D films, and 3D interconnected and ordered porous structures have been obtained by using different types of templates. The related novel structures and morphologies of these templated materials may facilitate the Li^+ intercalation and lithium transition reactions, and electrochemical properties that are superior to those of their bulk counterparts can be expected.

Several groups have employed Mesoporous carbon blacks as templates to prepare nanosized zeolites, which possess both micro and mesoporous properties [141–143]. To introduce mesopores into Zeolite materials, templating with carbon as fibers and spheres in the Zeolite synthesis has been performed. Carbon black pearls, carbon nanotubes, or carbon nanofibers are impregnated with a Zeolite precursor solution and subjected to hydrothermal treatment. The Zeolite crystals grew around the carbon template and finally the template was burned in a subsequent calcination step producing intracrystalline pores during the hydrothermal treatment. A schematic representation of the formation of composites based on carbon templates is given in Fig. 6.

Another approach generates closed packed arrays created by sub micrometer sphere-air pore systems by applying gravity sedimentation, vertical deposition, centrifugation, and flow of solvent through polystyrene or silica colloid spheres [144–147]. In addition, macroporous materials with inorganic components, polymers, metal or carbon frameworks were produced by introducing monomers, metal nanocrystals or carbon into the air macropore systems, followed by extraction or etching [126, 148–150]. The uniform introduction of materials into the air pore system is challenging as the surfaces are not available in the narrow and relatively inaccessible interstitial regions of colloidal spheres and such arrays are relatively fragile and easily disrupted. In order to obtain high-quality macroporous materials, efforts must be made to overcome these obstacles.

Another possibility of preparation of materials with bimodal porosity involves the use of various substrates with a templating function. Valtchev [151–153] by using a silica-containing vegetal template, such as leaves and stems of *Equisetum arvense* Zeolite Beta macrostructures with hierarchical porosity were prepared. The Zeolite readily crystallized in the vegetal tissues with the Zeolite nucleation induced by the highly reactive biomorphic silica deposited on the epidermal surface of the plant. Once the Zeolite/vegetal composites were formed and upon calcination, they were transformed into a pure Zeolite macrostructures retaining all features of the vegetal template but exhibiting hierarchical porosity (Fig. 7). This approach demonstrates the possibility of directing the macro-morphological and the nanolevel organization of the composite materials by controlling the type of biotemplates. The analysis of the zeolite/vegetal composite and all-zeolite replica showed that material with hierarchical porosity was obtained, and both the leaves and the stems of the *Equisetum arvense* were transformed into micro-/mesoporous and micro-/meso-/macroporous structures, respectively. Thus, the biotemplates controlled both the macro morphology and nanolevel organization of the materials.

Biopolymers/silica composites represent a new category of environmentally safe materials for applications to explore. Use of synthetic polymers is related to environmental problems due to use of organic solvents in the process as well as due to the crisis of petrochemical industry-related plastics. Materials produced in this way are not biodegradable and their production costs are high.

Use of polysaccharide as template in the template directed composite synthesis is of special interest as polysaccharides are economical, abundantly available biodegradable materials having diversified structure and characteristics. Cyclodextrin-based composites [154] are

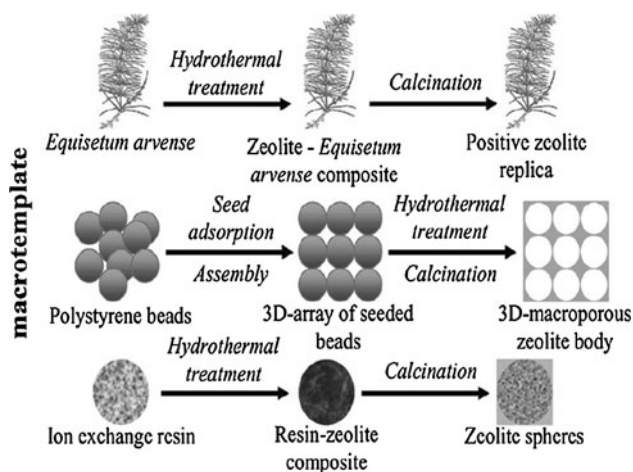


Fig. 7 General representation of the approaches used to obtain self-bonded zeolite macrostructures based on ion-exchange resin, polystyrene beads, and *Equisetum arvense* (Adapted from Ref. [139]. Reprinted with permission from Elsevier Publishing Group, Copyright (2011))

also considered as member of polysaccharide-composite family. There is a need to compare properties of composites with differing polysaccharide composition to make an optimal choice. Advancements in the field of materials research, specifically porous materials [155] have facilitated their use in a variety of applications such as catalysts [156–158], adsorbents, membranes, sensors, optical devices [159–162], drug carriers [163, 164], biomedical [165–168] and insulators.

4.3.6 Magnetic hybrid nanocomposite material

The synthesis of organic/inorganic hybrid materials composed of magnetic materials and polymers has gained increasing attention for emerging applications as sensors, imaging agents, storage media, and catalysis in biotechnology and microelectronics [169–176]. Advances in polymer science have demonstrated the ability to prepare a vast array of materials exhibiting controllable mechanical, thermal, and electroactive properties. However, the preparation of wholly organic polymeric materials possessing high magnetic moments and susceptibilities comparable to inorganic systems remains a challenge. To overcome this inherent problem, the synthesis of composites combining organic polymers and inorganic magnetic particles has been conducted to prepare hybrid materials with modular organic composition and functionality [177]. The hybridization of inorganic and organic materials on the nanoscale is often the smallest domain size possible to enable the retention of useful properties similar to the bulk state.

Numerous examples of magnetic nanocomposite materials have been investigated which combine different polymer and colloid forming chemistry. Emulsion and

dispersed media polymerizations have been utilized to encapsulate iron oxide nanoparticles into polymeric micro and nanospheres. These materials typically kinetically trap numerous iron oxide nanoparticles in polymeric matrices prepared by free radically polymerizable monomers [178–183]. Magnetic nanocomposites have also been prepared by loading of the organometallic, or metal salt precursors into homopolymer, or block copolymer thin films and inducing magnetic nanoparticle formation in the solid state [184–189]. This approach ensures intimate dispersion of magnetic nanoparticles in polymeric matrices with the potential for the selective placement of colloids into specific phase separated domains. Core-shell nanoparticles have also been explored where discrete magnetic nanoparticles are passivated with an organic shell of polymers. This general methodology enables the synthesis and functionalization of various magnetic nanoparticles with well-defined polymers. This controlled approach to preparing core-shell nanoparticles offers the potential to modify the properties of magnetic nanoparticles in a highly modular fashion by control of the copolymer shell structure and composition (Fig. 8).

4.3.7 Metallic magnetic nanoparticle from block copolymers

Nitrile containing block copolymers based on polysiloxanes and polystyrenes were synthesized by Riffle et al. to prepare magnetic cobalt nanoparticles [190–194]. ABA triblock copolymers incorporating poly(3-cyanopropyl)-methylsiloxane (PCPMS) prepared using anionic ring-opening polymerization was further chain extended with hexamethylcyclo-trisiloxane to yield PDMS-*b*-PCPMS-*b*-PDMS surfactants. Thermolysis of $\text{Co}_2(\text{CO})_8$ under varying conditions with these polysiloxanes copolymers yielded either super paramagnetic colloids of uniform size, or polydisperse ferromagnetic nanoparticles (Fig. 9). Ordered 2-D nanoparticle arrays were obtained after magnetic purification of polymer coated colloids.

4.3.8 Synthesis of iron oxide magnetic nanoparticles

Modified carboxylic acid containing copolymers have been investigated as an approach to prepare and stabilize iron oxide nanoparticles. Mihama et al. reported the copolymerization of an allyl-terminal poly(ethylene oxide) (PEO) macro monomer with maleic anhydride, followed by basic ring-opening, to yield a carboxylic acid functional surfactant (Fig. 10) [195]. The oxidation of ferric salts in air and hydrogen peroxide in the presence of this copolymer yielded a super paramagnetic nanoparticle, which was described as magnetite, but was likely Fe_2O_3 . The adsorption of lipases onto this polymer coated magnetic colloid afforded a

Fig. 8 Examples of magnetic hybrid nanocomposite materials prepared by encapsulation, coating of inorganic colloids with polymer shells, or dispersion within organic polymer thin films

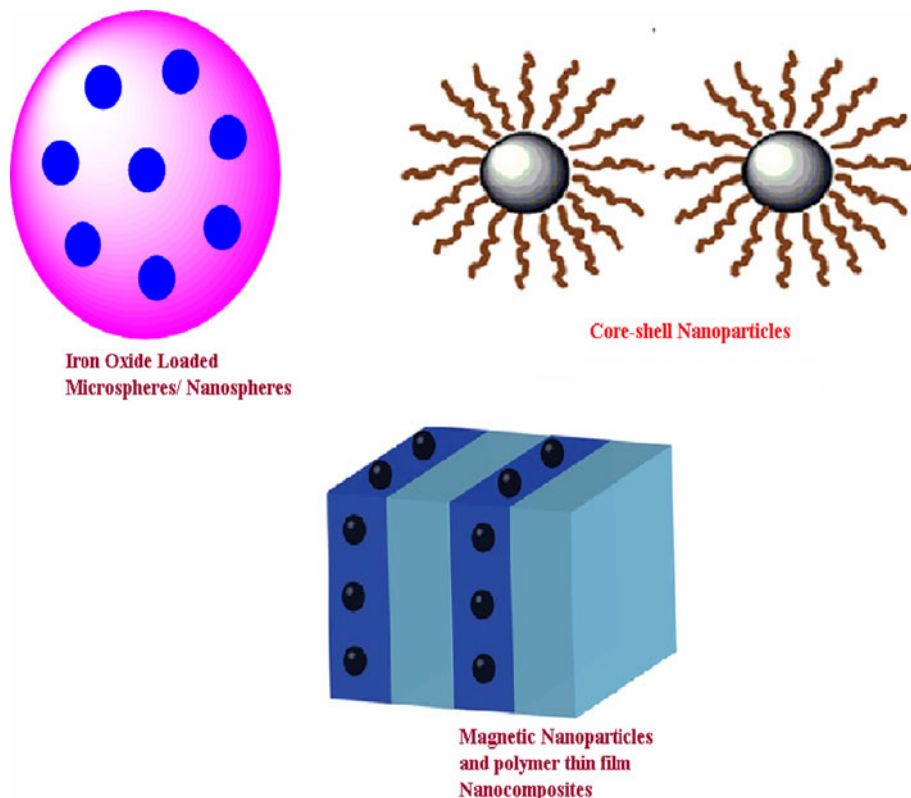
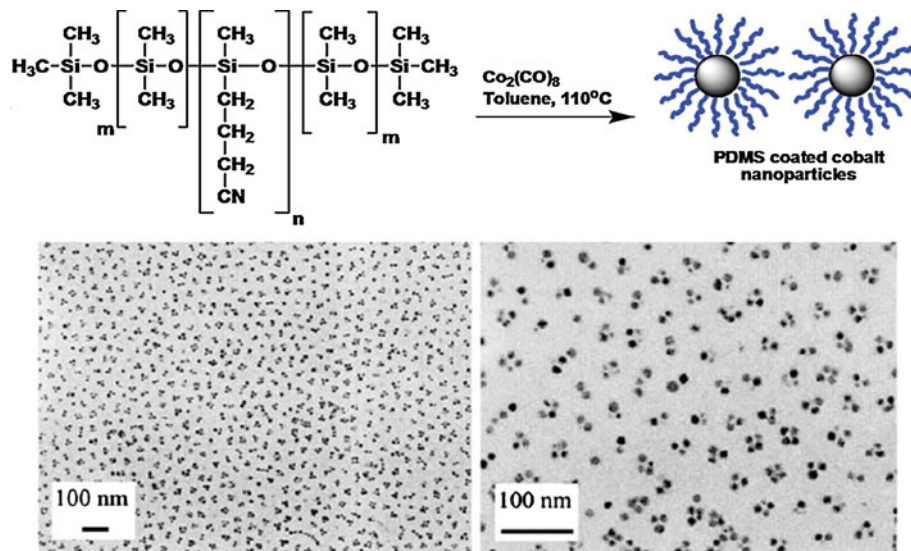


Fig. 9 Nitrile containing polysiloxanes surfactants used to prepare metallic cobalt nanoparticles (Adapted from Ref. [177]. Reprinted with permission from Elsevier Publishing Group, Copyright (2011))



catalytically active support for esterification that was recovered by application of a magnetic field.

5 Characterization of materials

Different characterization techniques for studying the properties of nanocomposites is been discuss. This section will focus on some important techniques often used for the investigation of polymer/silica nanocomposites. In this

section characterization based on chemical structure, microstructure and morphology, and thermal properties were undertaken. Nanocomposite properties are strongly depend on their composition, the size of the particles, interfacial interaction, etc. [196].

5.1 Characterization based on chemical structure

The chemical structure of polymer/silica nanocomposites is generally identified by FTIR and solid-state ^{29}Si NMR

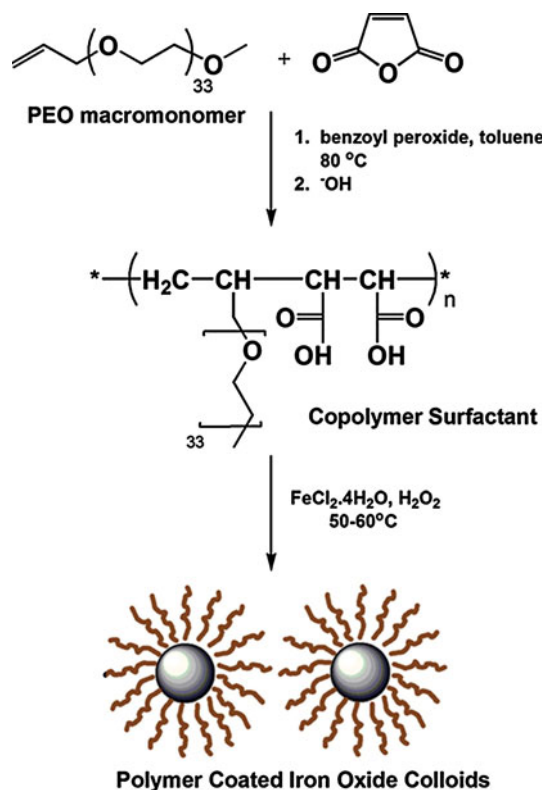


Fig. 10 Synthesis of PEO functional polymaleic acid copolymer surfactants and iron oxide colloids

spectra. FTIR spectrometry is widely used to prove the formation of nanocomposites especially for those prepared by the sol–gel reaction, in which a silica network can be formed. The major peak at about $1,100\text{ cm}^{-1}$ (varying with different samples in the range of $1,000\text{--}1,200\text{ cm}^{-1}$) that is attributed to the asymmetric stretching vibrations of Si–O–Si bonds of silica can be found in the hybrids. If the condensation reaction is not complete, Si–OH groups will also exist. The characteristic absorption bands of the hydrolysis product of TEOS in the (polyimide)PI/SiO₂ hybrids are as follows [197]. The FTIR spectrum shows absorption bands due to –OH bond stretching at $3,480\text{ cm}^{-1}$ and Si–OH bond stretching at 882 cm^{-1} , as well as typical absorption bands for Si–O–Si network vibrations at $1,130$ and 823 cm^{-1} . The characteristic absorption band of Si–O–Si asymmetric stretching ($1,130\text{ cm}^{-1}$) became stronger and moved to higher wave number ($1,180\text{ cm}^{-1}$) with the addition of the coupling agent, indicating a more “condensed” silica network. FTIR spectra can also supply evidence of the existence of hydrogen bonding or covalent bonding between organic and inorganic phases. The examples of hydrogen bonds between the polymer and the residual silanol of silica in the hybrids investigated by FTIR spectroscopy can be found in many references [37, 198–202].

FTIR results show the formation of Si–O–Si via a sol–gel reaction, ²⁹Si solid-state NMR gives further information on the structure of silica and the degree of Si–OH condensation reaction. In principle high-resolution solid-state NMR spectra can provide the same type of information that is available from corresponding solution NMR spectra, but special techniques/equipment are required, including magic-angle spinning (MAS), cross polarization (CP), etc. [203]. In the ²⁹Si solid-state NMR spectra, peaks are generally denoted by the symbol Q_n to show un-, mono-, di-, tri-, and tetra-substituted siloxanes [(RO)_{4-n}Si(OSi)_n, R) H or an alkyl group]. For instance, a sample exhibiting a 100% Q₄ environment would possess a full condensed silica phase (i.e., corresponding to stoichiometric SiO₂). Such a deconvolution method displays only semiquantitative results but enables comparison of samples with each other in terms of the condensation state of their silicate phases. The degree of condensation within the SiO₂ particles can be evaluated from the Q₄ percent [37, 204]. The strong Q₄ indicated that the degree of silicon condensation was very high. A weak peak at -92 ppm , which was assigned to Q₂, is also observed in the spectrum. The existence of Q₃ and Q₂ reflected the incomplete condensation of the TEOS. Moreover, ²⁹Si CP MAS NMR proved to be useful for the characterization of the grafted structures formed at the silica surface.

5.2 Characterization based on microstructure and morphology

The crystallization behavior of Polypropylene/silica nanocomposites prepared in situ via solid-state modification and sol–gel reaction was also investigated with DSC [205]. Results showed that silica nanoparticles formed in situ acted as nucleating agents. The non isothermal crystallization kinetics of the nanocomposites was studied using a combined Avrami-Ozawa approach and showed a two-stage crystallization process: the primary stage was characterized by nucleation and spherulitic growth, and the secondary stage was characteristic of the perfecting of crystals. Silica increased the rate of the primary stage, resulting in a more narrow lamellar thickness distribution.

The microscopic structure of polymers is often studied by X-ray techniques (including WAXD/XRD, WAXS, and SAXS) and neutron scattering. The XRD technique is based on the elastic scattering of X-rays from structures that have long-range order, and it is an efficient analytical technique used to identify and characterize crystalline materials. For the nonlayered silica nanoparticle composites, WAXD was commonly performed to analyze the degree of crystallinity of the nanocomposites. The WAXD of nanocomposites of PU/silica showed a lower angle peak, at about $2\theta\ 6^\circ$, and most showed a distinct shoulder at 2θ

20° [206]. The crystallization behavior of Polypropylene/silica nanocomposites prepared via solid-state modification and sol–gel reaction was investigated [205].

Scattering is a powerful tool to access the bulk structure in a nondestructive way. X-ray scattering is well-suited for many polymer/inorganic composites. WAXS, a technique that involves measuring scattering intensity at scattering angles 2θ larger than 5° , has been used to investigate the changes in crystalline structure.

Neutron scattering is preferred sometimes due to the extended q -range (with respect to standard X-ray laboratory sources), giving access to length scales between several and several thousand angstroms. Also, cold neutrons penetrate macroscopically thick samples more easily, and they offer the potential to extract the conformation of polymer chains inside the composite. SANS is therefore a method to unveil the structure of nanocomposites [207].

Oberdisse et al. [208] have analyzed the structure of the resulting filled latex films by means of this method. The scattered intensity varied enormously with the physico-chemical parameters, indicating considerable structural modifications.

Berriot et al. [209] found by SANS that there were two opposite effects that control the final dispersion state of the filled elastomers that composed cross-linked polyethylacrylate chains reinforced with grafted silica nanoparticles during the polymerization. The first one was a depletion mechanism favoring the formation of aggregates. The second one was a repulsive steric interaction due to the growth of polymer chains from the particle surfaces avoiding contacts between the silica inclusions. Using these results, they could prepare sets of samples having the same particle/matrix interface but different dispersion states.

El Harrak et al. [210] described ATRP from silica nanoparticles and the dispersion of particles was checked using SANS at every stage of the functionalization. SANS measurements made on the polymer-grafted particles led to an understanding of the system behavior during the polymerization procedure. These observations permitted improvement of the synthetic conditions to get a better dispersion of the particles and a better control of the polymerization process. The SANS technique was well suited for the size range of interest, and due to the unique possibility of contrast variation, it was able to highlight independently the contributions of the polymer layer and of the silica beads or aggregates.

Positron annihilation lifetime spectroscopy (PALS) is a technique that probes the free volume cavities by measuring the lifetime of *ortho*-positronium (*o*-Ps) before annihilation in the free volume regions of the polymer. The lifetime of *o*-Ps (normally 2–5 ns) is a direct measure of the free volume size. The free volume sizes and interstitial

mesopore sizes in PTMSP/silica nanocomposites and the correlation between nitrogen permeability and cavity sizes were studied by PALS at filler concentrations between 0 and 50 wt% [211]. A bimodal free volume distribution was observed for PTMSP, and the size of the larger free volume cavities was significantly increased upon addition of hydrophobic fumed silica. Nanometer-sized interstitial cavities in filler agglomerates were observed in all PTMSP/fumed silica nanocomposites and in neat hydrophobic fumed silica.

TEM, SEM, and AFM are three powerful microscopy techniques to observe the morphology of nanocomposites. TEM is a microscopy technique whereby a beam of electrons is transmitted through an ultrathin specimen and carries information about the inner structure of the specimen. It is difficult to receive details of some samples due to low contrast resulting from weak interaction with the electrons; this can partially be overcome by the use of stains such as phosphotungstic acid and RuO₄. Sometimes the organic components of the sample would be decomposed by the electron beam; this can be avoided using cryogenic microscopy (cryo-TEM), where the specimen is measured at liquid nitrogen or liquid helium temperatures in a frozen state. High resolution TEM (HRTEM) can afford a much closer look at the samples [203]. Images from SEM, TEM, and AFM can be used to study membranes of two dimensional structure with pore size of subnano-scale [212].

The recent application of electron energy loss spectroscopy imaging techniques to TEM (ESI-TEM) can provide information on the composition of polymer surfaces. This is a powerful technique for the characterization of colloidal nanocomposite particles. The internal nanomorphologies of two types of vinyl polymer/silica (P4VP/silica and PS/silica) colloidal nanocomposites were assessed using ESI [213].

SAXS in combination TEM is a useful method to characterize the morphology of hybrid organic–inorganic materials. Combined TEM and SAXS investigations on thermoplastic nanocomposites poly(MMA-*co*-HEMA) copolymer filled with 10 nm SiO₂ particles with different particle surface coatings have been shown to be important tools in gaining complete information about the morphology of the materials [214]. TEM analysis gave visible information on the extent of particle separation in the nanocomposites depending on the surface modification over a broad scale range including especially large sized aggregates. On the other hand, SAXS analysis enabled acquisition of more detailed information about size distributions of primary particles and “mean” size aggregates in the real nanosize range below 20 nm.

The scanning electron microscope (SEM) is a type of electron microscope that creates images by the electrons

emitted when the primary electrons coming from the source strike the surface and are inelastically scattered by atoms in the sample. SEM images have a characteristic 3-D appearance and are therefore useful for judging the surface structure of the sample [203].

Besides the emitted electrons, X-rays are also produced by the interaction of electrons with the sample. These can be detected in a SEM equipped for energy-dispersive X-ray (EDX) spectroscopy [203].

AFM is an effective tool to characterize nanocomposites by providing the morphological information. The AFM consists of a sharp tip (10–20 nm diameter) attached to a stiff cantilever. The tip is brought close to the surface, and the sample is scanned beneath the tip. The tip moves in response to tip-surface interactions, and this movement is measured by focusing a laser beam onto the back of the cantilever and detecting the position of the reflected beam with a photodiode. Different modes of operation can be used [203]. A detailed investigation on the modified nanoparticles in the absence and presence of a PP(polypropylene) matrix was carried out by AFM [215]. The results indicated that the loosened agglomerates of the untreated SiO₂ became more compact due to the linkage between the nanoparticles offered by the grafting polymer.

The particle size distributions of the colloidal nanocomposites can be assessed using two techniques: dynamic light scattering (DLS) and disk centrifuge photosedimentometry (DCP). The former technique reports an intensity-average diameter (based on the Stokes–Einstein equation), and the latter reports a weight-average diameter. Given the different biases of these two techniques, it is expected that the DLS diameters would always exceed the DCP diameters [216].

X-ray photoelectron spectroscopy (XPS, also called electron spectroscopy for chemical analysis, ESCA) is a surface analytical technique for assessing surface compositions. The sample is placed under high vacuum and is bombarded with X-rays, which penetrate into the top layer of the sample (approximately nanometers) and excite electrons (referred to as photoelectrons). Some of these electrons from the upper layer are emitted from the sample and can be detected. The electron binding energy is dependent on the chemical environment of the atom, making XPS useful to identify the elemental composition of the surface region [201].

XPS is especially suitable to assess the surface compositions of colloidal particles since its typical sampling depth is only 2–5 nm. The XPS data combined with TEM studies of the ultramicrotomed particles can shed further light on the particle morphology. Armes et al. [217] reported a detailed XPS study of the surface compositions of selected vinyl polymer/silica nanocomposites.

5.3 Characterization based on thermal properties

Thermal properties are the properties of materials that change with temperature. They are studied by thermal analysis techniques, which include DSC, TGA, DTA, TMA, DMA/DMTA, dielectric thermal analysis, etc. As is well known, TGA/DTA and DSC are the two most widely used methods to determine the thermal properties of polymer nanocomposites. TGA can demonstrate the thermal stability, the onset of degradation, and the percent silica incorporated in the polymer matrix. DSC can be efficiently used to determine the thermal transition behavior of polymer/silica nanocomposites. TGA characterization of the thermal stability of silica/PMMA nanocomposites made by in situ radical polymerization showed that the addition of nanosilica particles slightly reduced the thermal stability of the nanocomposite sample at low temperatures and slightly delayed random initiation along the polymer backbone [218]. Similar behavior was also observed with PMMA/silica nanocomposite films prepared by copolymerizing MMA with AGE-functionalized silica nanoparticles [219].

6 Literature survey on biopolymer/silica composite materials

Biopolymer incorporation in silica gels is of great interest in the context of biotechnological devices. Many biopolymers have been utilized as templates towards the synthesis of silica nanocomposites of importance.

Natural polymers such as protein, cellulose, starch, rubber and polysaccharides are building materials for all animals and plants tissues. Polysaccharides are most abundant, biodegradable and renewable biopolymeric materials and their properties can be suitably tailored by chemical modification. In general the properties of the natural polysaccharides are altered to a remarkable degree by the introduction of very small amounts of substituent groups of either neutral or ionic types.

Use of polysaccharides as biopolymeric materials in the templated nanocomposite synthesis for designing multi-component biologically-active materials is the recent area of interest. A brief survey of literature on the polysaccharide templated organic–inorganic silica composite materials is summarized as under:

6.1 Gum acacia

Synthesis of electrically active biopolymer-SiO₂ nanocomposite aerogel has been reported [220], where the composition of silica/Acacia gum was tailored to optimize the material's electronic properties.

6.2 Chitosan

Using polycondensation of tetraethoxysilane in presence of chitosan, synthesis of nanocompositional sorbent material for high-performance liquid chromatography [221] is reported. Hybrid xerogels of chitosan and silica were produced using the sol–gel technique [222], which were transformed into porous silica by elimination of the organic phase.

Composite material using chitosan [223] with tetraethoxysilane was developed for the bovine serum albumin (BSA)-encapsulated monolithic column for capillary electrochromatography.

The hydrolytic polycondensation of tetraethoxysilane in the presence of chitosan as templates resulted nanohybrid composite sorbents-nanofractals [224].

A new type of material was prepared [225] from natural chitosan and a completely water-soluble precursor, tetrakis (2-hydroxyethyl) orthosilicate (THEOS) by sol–gel process without using organic solvents and catalysts.

A novel sol–gel nanocomposite material [226] was produced by silica sol–gel process in micro emulsion organogels prepared by a percolating droplet network containing chitosan. The structural features of the obtained chitosan-silica composites have been described and compared with silica-gelatin nanocomposites.

In the prepared matrix, covalently bonded coating and morphology manipulation on silica gel using one-pot sol–gel process starting from γ -glycidoxypropyltrimethoxysiloxane (GPTMS) and chitosan in the atmosphere of imprinting polyethylene glycol (PEG) have been reported [227, 228]. Self-hydrolysis of GPTMS, self-condensation, and co-condensation of silanol groups (Si–OH) from siloxane and silica gel surface, and in situ covalent cross-linking of chitosan are reported to create an orderly coating on silica gel surface. PEG extraction using hot ammonium hydroxide solution gave a chemically and mechanically stabilized pore structure and deactivated residual epoxy groups.

Ion-imprinting concept and polysaccharide incorporated sol–gel process were applied to the preparation of a new silica-supported organic–inorganic hybrid sorbent [228] for selective separation of Cd (II) from aqueous solution. In the prepared shell/core composite sorbent, covalently surface coating on the supporting silica gel was achieved by using a Cd (II)-imprinting sol–gel process starting from an inorganic precursor, γ -glycidoxypropyltrimethoxysiloxane and chitosan (CS).

An amperometric glucose biosensor based on glucose oxidase immobilized in sol–gel chitosan/silica hybrid composite film [35] prepared from chitosan and methyltrimethoxysilane (MTOS), on the surface of Prussian blue (PB)-modified glass carbon electrode has been also

reported. A new strategy [229] based on multi-walled carbon nanotubes (CNT), Pt nanoparticles and sol–gel derived chitosan (CS)/silica hybrid composite for fabricating a sensitivity-enhanced glucose biosensor is reported. Silica sol–gel chitosan composite film [230] was also used for an amperometric H_2O_2 biosensor. The film was used to immobilize horseradish peroxidase on a carbon paste electrode.

Suitable for tissue engineering 3D hybrid scaffolds based on silica and chitosan in various compositions are reported [231]. A one-step way to prepare organosilica/chitosan crosslinked nanospheres [232] was developed through self-assembly of amphiphilic copolymers synthesized by concurrent grafting polymerization and sol–gel reaction. The core ‘organosilica’ was formed by hydrolysis and condensation of an alkyloxosilane-3-(trimethoxysilyl) propyl methacrylate that was simultaneously polymerized using chitosan/tert-butyl hydroperoxide as redox-pair initiator.

Various unique shapes of silica/chitosan hybrid particles [233] were obtained by biomimetic synthesis of silica with chitosan (CS) where the chitosan solution was first incubated for different periods of time, leading to different aggregation states and then some amount of prehydrolyzed tetraethylorthosilicate (TEOS) was added and reacted.

New organic–inorganic hybrids SiGCX ($X = 1–3$) were prepared from the biopolymer chitosan with a degree of the deacetylation of 86% and three distinct silylating agents of the type $(\text{CH}_3\text{O})_3\text{Si-R-NH}_2$ [$R = -(\text{CH}_2)_3-$, $-(\text{CH}_2)_3\text{NH}(\text{CH}_2)_2-$ and $-(\text{CH}_2)_3\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2-$] [234]. Both chitosan and silylating agents had the amine groups crosslinking through linear glutaraldehyde units.

Homogeneous polymer hybrids of silica gel and carbamated chitosan [235] are reported and the silica/chitosan composite film has been used to immobilize horseradish peroxidase on a carbon paste electrode.

Silica-butyrylchitosan hybrid films with potential good blood compatibility [236] were produced by a sol–gel technique, using butyrylchitosan as the organic species incorporated into the silicon alkoxide based network. 3-acryloxypropyl trimethoxysilane was used effectively to combine the organic and inorganic species to form uniform hybrid biomaterials.

The nanocomposite composed of carboxymethyl chitosan and gold nanoparticles [237] is reported and horseradish peroxidase, as a model enzyme, was immobilized on it to construct a novel H_2O_2 biosensor.

6.2.1 Cross-linking in micro-/nanogels

The cross-linking in micro-/nanogels is accomplished either by non-covalent physical associations, covalent chemical cross-linkages, or their combinations [238–243].

The cross-links in the physically cross-linked gels arise from non-covalent attractive forces such as hydrophobic interactions, hydrogen bonding, and ionic interactions between the polymers or blending and interpenetrating networks of two dissimilar polymers. For example, chitosan chains form physical interactions with PMAA chains, which results in formation of nanogels [244]. The nanogels presented negative surface charge at $\text{pH} \approx 5.0$. The zeta potential tended to be neutral as the molar ratio of MAA-to-glucosamine decreased. This result is consistent with the complexation mechanism based on electrostatic interactions between the carboxyl groups of MAA and amino groups of chitosan. The interplay of other interactions, such as hydrophobic association of methyl groups of PMAA chains, may also contribute to the stability of the nanogels. Recently, the first direct observation of the pH-induced expulsion of PMAA chains from the physically associated chitosan-PMAA-CdSe QD hybrid nanogels during a time period of 32 h (Fig. 11) [244], which is longer than the time period (20 h) required for macromolecular colloids to accumulate in solid tumors through the blood stream [245]. The mechanism of chain expulsion of the weak polyelectrolyte nanogels in response to a pH variation may involve pH-induced accumulation of excess charge within the nanogels [246–249]. The constructed physically associated hybrid nanogels would not be an ideal candidate for optical sensing. In contrast, the chemically cross-linked hybrid nanogels are very stable. Chemically cross-linked gel networks were formed by polymerizing MAA monomers in the presence of chitosan chains and cross-linking agents. The gel networks formed by such cross-links, also called semi-interpenetrating (semi-IPN), can exhibit a reversible structural change in response to a pH change, leading to a reversible optical response of the constructed hybrid nanogels. These results provided fundamental guidance for the construction of feasible and reliable hybrid micro-/nanogel-based optical probes. Chemically cross-linked micro-/nanogels can also be formed by cross-linking of the functional groups presented on the polymer backbone.

6.3 Chitin

Cuttlebone β -chitin was used as a highly organized organic template with macroscopic porosity to prepare silica-polysaccharide composites having 3-D interconnected box structures.

A silica-chitin-based sponge skeleton with respect to chemical composition and structure may prove to be a novel model for the biomimetic synthesis also of N-acetyl glucosamine (NAG) and poly-NAG-based composites analogous to well established chitosan-silica hybrid materials [250, 251] with very attractive bioactive properties for applications in biomedicine. It was reported [252] that silicon was found to be a constituent of certain glycosaminoglycans. It was concluded that Si is present as silanolate, that is, ether (or ester-like) derivative of orthosilicic acid and that $\text{R}_1\text{-O-Si-O-R}_2$ bridges play a role in the structural organization of glycosaminoglycans. Thus Si may function as a biological cross-linking agent and contribute to architecture and resilience of connective tissue [252]. Figure 12 is showing the Silica-NAG-based materials in the form of rods or spheres using TMOS and sol-gel techniques in vitro. The diameter of these spheres could be varied between 2 and 10 nm. SEM investigations on micro and nanostructural organization of silica-NAG composites revealed strong evidence that oriented nanocrystals of NAG (Fig. 12a) could be also observed in form of nanocrystals compactly embedded within amorphous silica matrix (Fig. 12b, d). Probably this kind of NAG nanodistribution is responsible for observed high mechanical stability and resistance of these composite materials to swelling and following dissolution in water containing solutions (Fig. 12c) [253]. These properties could be probably of interest for technical purposes similar to intercalated chitosan/layered silicate nanocomposites prepared to develop robust and stable sensors useful for anionic detection in aqueous media as reported on [254, 255]. This suggest that silica-chitin and silica-NAG (-poly NAG) composites could be highly optimized bio-compatible structures that would support and organize

Fig. 11 Schematic diagrams showing the difference between a physically and chemically cross-linked chitosan-PMAA-CdSe hybrid nanogel (Adapted from Ref. [233]. Reprinted with permission from Elsevier Publishing Group, Copyright (2011))

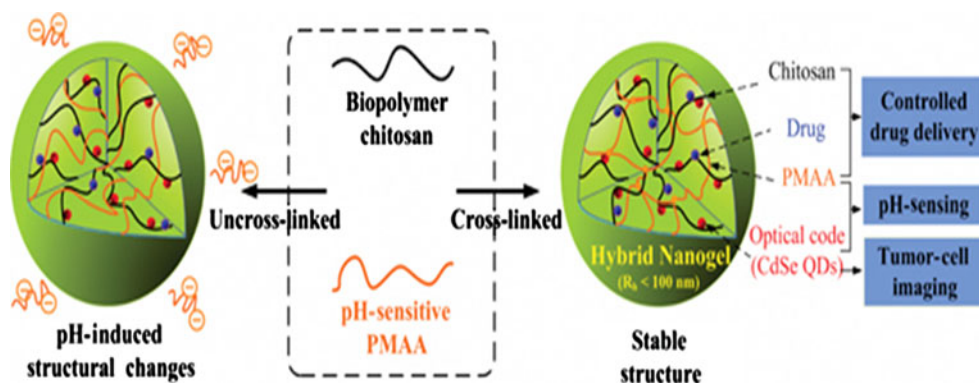
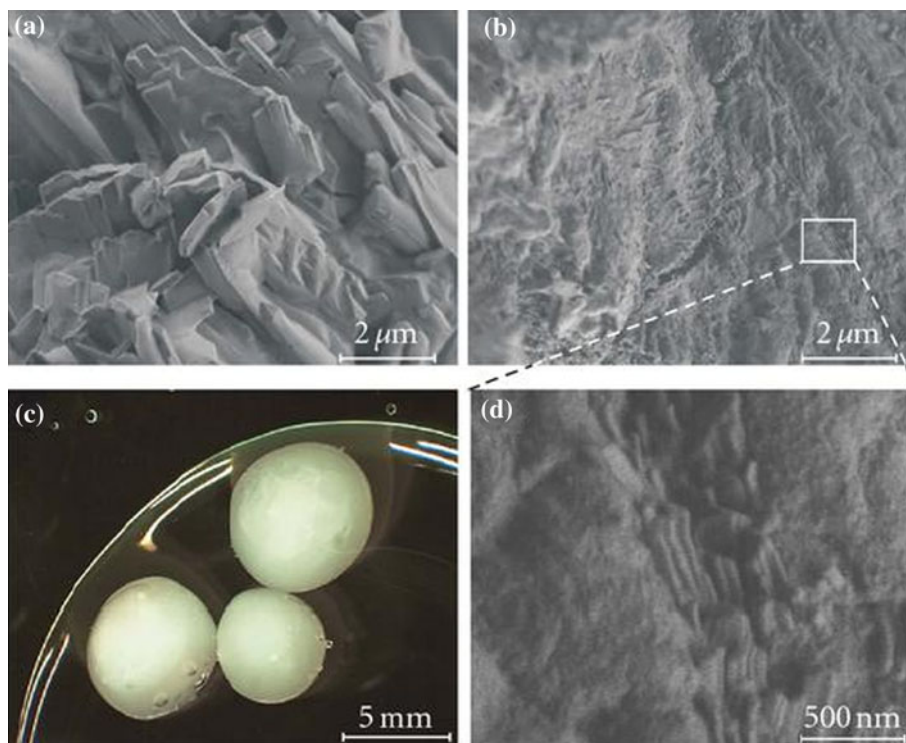


Fig. 12 Crystals of N-acetyl glucosamine obtained from solution (a) could be also visualized using SEM even if being included into amorphous silica matrix (b). SEM image (d) revealed strong evidence that oriented crystals of NAG are observed in form of nanocrystals compactly embedded within this matrix. Light micrograph (c) of the silica-NAG spherical composites, which are highly stable in water-containing solutions (Adapted from Ref. [242])



functional tissues if applied in tissue engineering of bone and cartilage replacements similar to silica-chitosan-based biomaterials [256].

6.4 Carageenan

Sol gel synthesis and structure of silica nanocomposites, containing carageenan are also reported [257] where the synthesized biocatalysts were used in an enzyme degradation process of the toxic, carcinogenic and mutagenic substances.

Tetrakis(2-hydroxyethyl)orthosilicate (TEOS) was used to synthesize monolithic hybrid biomaterials on the basis of silica and three main types of carrageenans, κ -, ι -, and λ -carrageenans [258] where κ - and ι -carrageenans experienced a thermo reversible phase transition in the hybrid materials owing to the helix-coil transition.

Pillaring effects in macroporous carrageenan-silica composite microspheres [259] have been studied where the hybrid was prepared by the impregnation of a carrageenan gel by a silica sol.

Biosilica-coated κ -carrageenan microspheres for yeast alcohol dehydrogenase encapsulation are also reported [260].

6.5 Alginate

Preparation and catalytic properties of novel alginate-silica-dehydrogenase hybrid biocomposite beads are

reported [261] Alginate-silica hybrid gel [262, 263] was prepared through in situ growth of the silica precursor within an alginate solution, which was followed by Ca^{2+} cross-linking. The gel was used for the conversion of carbon dioxide to methanol using three dehydrogenases which were encapsulated in the gel. Silica-gel was also obtained by sol-gel route using aqueous precursors in presence of alginates [264], whose gelation could be consequently done on addition of a divalent metal cation.

6.6 Cellulose

SiO_2 /cellulose nanocomposites [265] were prepared using two distinct methodologies: deposition of morphological well-defined SiO_2 nanoparticles at the fiber's surface via polyelectrolytes assembly and the synthesis of SiO_2 nanoparticles via tetraethoxysilane (TEOS) hydrolysis in the presence of cellulose fibers.

The nano- SiO_2 /cellulose composites [266] were successfully synthesized by a sol-gel method using tetraethylorthosilicate (TEOS) and cellulose in heterogeneous ethanol solution. The hydrophobicity, thermal stability and mechanical properties of nano- SiO_2 /cellulose composites in the heterogeneous system were higher than those of the cellulosic materials.

Cellulose/silica hybrids were also prepared using tetramethoxysilane (TMOS) in $\text{CF}_3\text{CO}_2\text{H}$ [267]. As a result; translucent and heterogeneous composites were obtained because of high crystallinity of cellulose. To improve the

affinity between them, ionic liquid modified alkoxy silane and cubic silsesquioxane were synthesized as inorganic species. Consequently, transparent polymer hybrid could be prepared by utilizing these inorganic species.

Organic–inorganic hybrid based on cellulose fibers from eucalyptus globulus kraft pulp [268] was prepared at room temperature by a sol–gel method using TEOS as the silica precursor and $\text{H}_3\text{PW}_{12}\text{O}_{40}$ as the catalyst.

Bacterial cellulose/silica hybrid was prepared by mimicking biocomposites by nature [269]. Bacterial cellulose–silica hybrid [270] was also prepared from bacterial cellulose membranes and tetraethoxysilane (TEOS) at neutral pH conditions at room temperature.

6.7 Hydroxypropyl cellulose

Hydroxypropyl cellulose (HPC) was incorporated in situ with silica by the sol–gel process involving various amounts of added tetraethoxysilane, and hybrids [271] with nanometre-sized silica particles were prepared. Mesomorphic behaviour of (2-hydroxypropyl) cellulose in organic–inorganic hybrid materials was investigated [272]. Hydroxypropyl cellulose (HPC)/silica micro-hybrids [273] with various amounts of nanometer-size silica particles were produced with a sol–gel process, by incorporating HPC with tetraethoxysilane-derived silica.

6.8 Acetylcellulose

Acetylcellulose (AC)/silica composite were prepared [274] by sol–gel method in an attempt to realize materials with Young's moduli and bending strengths similar to those of cortical bones. $\text{Si}(\text{OCH}_3)_4\text{-AC-H}_2\text{O-HNO}_3\text{-tetrahydrofuran-CH}_3\text{OC}_2\text{H}_4\text{OH}$ solutions were allowed to be gelled, where AC/TMOS mole ratios were defined for AC monomers, and the gels were dried at 30–70 °C to obtain composites.

A series of organic/inorganic hybrid films [275] were prepared using cellulose acetate (CA) as the organic component and tetraethyl orthosilicates (TEOS) as the inorganic component. Hybrid composites based on cellulose acetate (CA) and SiO_2 are also reported [276] by hydrolysis of tetraethoxysilane. The thermal stability of the hybrids was similar to pure CA. Composite membranes were prepared by casting of CA/TEOS mixtures onto a poly (vinylidene fluoride) support. The presence of the inorganic phase did not inhibit the growth of *Thricoderma harzianum* fungi.

6.9 Xanthan gum/locust bean gum

Tetrakis (2-hydroxyethyl) orthosilicates (THEOS) was used to prepare hybrid nanocomposites containing various

Xanthan gum, hydroxyethylcellulose and uncharged locust bean gum and the materials were evaluated for the enzyme immobilization [155].

6.10 Glucomannan

Glucomannan/silica hybrid and acetylated glucomannan (GM-Ac) membranes [277] were prepared and their mechanical properties and gas permeability were examined. It was demonstrated that the carbohydrate macromolecules located on the hydrophobic surface did promote silica precipitation, serving as a template [278].

α -Galactosidase enzyme was successfully encapsulated into sol–gel derived hybrid polysaccharide/silica nanocomposites and the main properties of the immobilized enzyme were studied [279]. Endo-1,3- β -d-glucanases (laminarinases) separated from marine *bivalvia Spisula sacchalinensis* and *Chlamys albidus* were immobilized into hybrid polysaccharide–silica nanocomposite materials by means of the sol–gel processing [280].

New monolithic nanocomposite silica biomaterials [281] were synthesized on the basis of various natural polysaccharides and tetrakis (2-hydroxyethyl) orthosilicates. The density of network, thickness of fibers, and properties of synthesized biomaterials depended on the polysaccharide type, charged degree of their macromolecule, and concentration. By varying these parameters, it was possible to manipulate the structural organization of hybrid polysaccharide–silica nanocomposites. Recent data on novel types of hybrid polysaccharide–silica nanocomposite materials fabricated with the help of THEOS has been summarized by Shchipunov et al. [282].

7 Polysaccharide and protein dual templating

The proteins also provide a unique opportunity to regulate the silica morphology and properties by means of a change of their secondary and tertiary structure through pH and temperature [283]. Biomimetic dual templating of silica by polysaccharide/protein assemblies is also reported [284], where gelatin and alginic acid were added to silicate solutions to allow the formation of complex structures resulting from the combined templating effect of both components at different scales.

Literature revealed that no attempt till now has been made to utilize abundantly available commercial guar gum in making silica hybrids. Guar gum (GG) is an edible carbohydrate polymer [285] found in the seeds of *Cyanopsis tetragonolobus*. It is cold water swelling polymer [286] and is reported to be one of the most highly efficient water thickeners. It is routinely used as a dispersion agent, as a viscosity builder, and water binder in many industries

such as mining, textiles, explosives, paper, and petroleum. Although an advantageous property, this viscosity is difficult to control because of its quick biodegradation [287], that is why it is rarely used in its natural form. Modification by grafting of water-soluble vinyl monomers onto GG results in the retention of desirable properties and incorporation of favorable properties [288–290].

But author has already exploited this commercial guar gum for the synthesis of silica composite materials using vinyl modified guar gum. The vinyl modified guar gum was preferred for making the composites as they are reported to have better shelf life besides having additional functionalities as vinyl grafts. Poly (acrylonitrile) and poly (acrylamide) modified guar gum templates were used with TEOS as silica precursor for the composite synthesis [291–294]. The synthesized composite materials were evaluated as adsorbents in the removal of Zn (II) and Cd (II) from aqueous solutions.

8 Conclusion

The area of organic/inorganic hybrid network materials prepared by the sol–gel approach has rapidly become a fascinating new field of research in materials science. The explosion of research in the past decade in this field has promoted considerable progress in both the fundamental understanding of the sol–gel process in general and its use in the development and applications of new organic/inorganic hybrid materials. It has been discussed within this review, a very wide range of hybrid material and nanocomposites of different properties can be generated by combining the appropriate features of a given inorganic metal moiety with those of appropriately selected organic species.

Different synthetic strategies have been discussed. Composite material derived by combining the sol–gel approach and organic polymers and template directed synthesis of hybrid material were also the focus area of review. It has also been demonstrated in this review that a more complete understanding of their structure–property behavior can be gained by employing many of the standard tools that are utilized for developing similar structure–property relationships of organic polymers.

Specifically, use of FTIR, NMR, electron microscopy, SEM, TEM, AFM, XRD, Thermal analysis and many important techniques were discussed for characterization of novel nanomaterials. Literature surveys on biopolymer/silica composite materials were also part of review. Biomimetic dual templating of silica by polysaccharide/protein assemblies will be the research area of the future. Although the number of commercial hybrid sol–gel products is still relatively small, the promise of their use in new

technological applications remains high. It is expected that over the next decade, numerous such materials will enter into the marketplace and serve an important function in the ever growing field of materials science.

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