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CRITICAL REVIEW

Hybrid and biohybrid silicate based materials: molecular *vs.* block-assembling bottom–up processes†

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This *critical review* introduces a discussion on the influence of preparative procedures (nanofabrication) of nanostructured hybrids and biohybrids, comparing their structural and textural characteristics that determine the properties of the resulting materials. Selected examples of silicate-based hybrids of analogous compositions prepared by both molecular and blocks-assembly bottom–up strategies are discussed to show advantages and inconveniences of each methodology (341 references).

1. Introduction

Nanostructured hybrid and biohybrid compounds are considered as one of the main research areas in materials science and technology for developing functional and structural advanced materials.[1–10] The design and preparation procedures[11] are critical to obtain nanomaterials provided of suitable properties.

Nanomaterials fabrication habitually applies bottom–up and top–down concepts. Bottom–up implies the construction and growth using precursors that became organized from the nanometric level mainly through chemical processes such as sol–gel, chemical vapour deposition (CVD), template synthesis or spray pyrolysis.[5] In the opposite way, top–down approaches essentially consist in the controlled nanostructuration of a bulk material by breaking it into smaller pieces or patterning it using diverse physical and/or chemical tools. In addition to molecular precursors, bottom–up strategies can also make use of already formed entities or nano-objects as small building units, which are hierarchically combined to fabricate the targeted nanomaterial in a procedure that could be named as *blocks-assembly* or *building blocks approach*.[4] In addition to naturally occurring entities that are used as nanobuilding blocks, other nano-objects can be designed and synthesized with well-defined molecular or nanosized structure

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† Part of the themed issue on hybrid materials.

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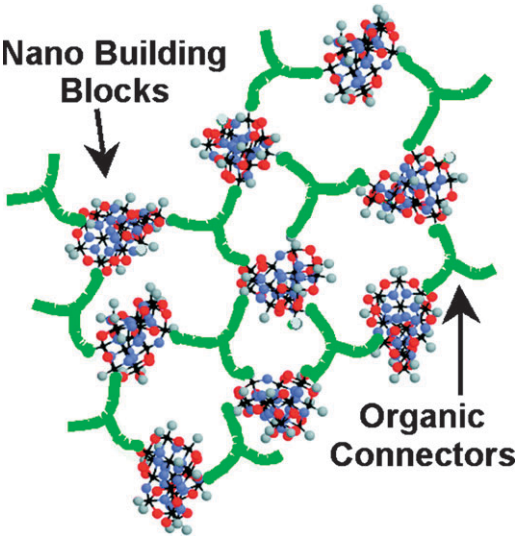

Fig. 1 Nanoparticulate-based hybrid composed by inorganic nanobuilding blocks (*e.g.* polyoxometalate clusters connected by organic linkers. (Reprinted with permission from ref. 12. Copyright 2001 American Chemical Society.)

and well-defined size and shape, and provided with interesting chemical or physical properties, which is a key factor for the fabrication of functional materials. Usually the construction of complex materials from nanobuilding blocks involves their assembly at the nanometric scale with a second component, including diverse entities from molecular and polymeric species to nanoparticles.[12,13] The concept of LEGO™-like chemistry regarding the assembling of nanobuilding blocks (Fig. 1), can be included within the blocks-assembly methodology together with others than imply the assembly between molecular and polymeric species, nanosized particles, and even biological fragments or entities.

Organic–inorganic hybrid materials result from the combination between the two organic and inorganic integrating parts at the molecular level, *i.e.* at the nanometer range.[14] The synthesis of this type of materials requires soft conditions, being commonly carried out by certain bottom–up procedures including molecular approaches (*e.g.* sol–gel processes) and blocks assembly (*e.g.* intercalation processes). Hybrids composed of alike organic and inorganic components may have chemical similitude but different structural arrangements and textural features, and therefore they can exhibit different properties. Examples include hybrids composed of silica and surfactant agents that are prepared by assembling of a layered silica solid, such as sodium octosilicate, and long-chain alkylammonium species, giving rise to an organo-silica *via* intercalation processes. However, the template syntheses starting from molecular silica precursors (*e.g.* TEOS) in the presence of the alkylammonium surfactants can result in diverse mesophases that show different structures and topologies (lamellar, cubic, hexagonal, ...).

Table 1 shows some examples of the preparation of organic–inorganic hybrid and biohybrid materials containing silica and silicate as inorganic counterpart following different approaches of nanofabrication.

The aim of this review is to introduce and to discuss nanostructured hybrids and biohybrids prepared by using two bottom–up strategies, molecular approach and blocks-assembly (Fig. 2), which yield materials of analogous composition but provided with different functionalities, properties and applications. In this context, we intend to select illustrative examples, derived mainly from our own experience rather than make an exhaustive report on materials, methods and applications appeared amongst the scientific literature.

2. Hybrids from discrete organic molecules assembled to silica and silicate matrices

2.1 Surfactants assembling to silica and silicates

Surfactants form structured molecular assemblies in concentrated solutions and their structures depend on the conditions, including concentration, temperature, additives and so on.[15,16]

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Table 1 Schematic classification of most common nanofabrication methods of hybrid and biohybrid silica and silicate based materials

Nano-fabrication method	Synthesis approaches	Examples	Refs.
Molecular strategy	Sol–gel process	Entrapment of dyes in a silica matrix generated from TEOS	Levy & Avnir, 1991 (ref. 89)
	Template synthesis	Silica–surfactant mesophases	Beck *et al.*, 1992 (ref. 22)
Blocks assembly	Intercalation	Crown-ethers intercalation in clay minerals	Ruiz-Hitzky & Casal, 1978 (ref. 62)
	Layer-by-layer	Protein–silicate films	Lvov *et al.*, 1996 (ref. 340)
	Grafting	Organosilicic compounds by reaction of organosilanes on silicates surface	Ruiz-Hitzky, 2004 (ref. 14)

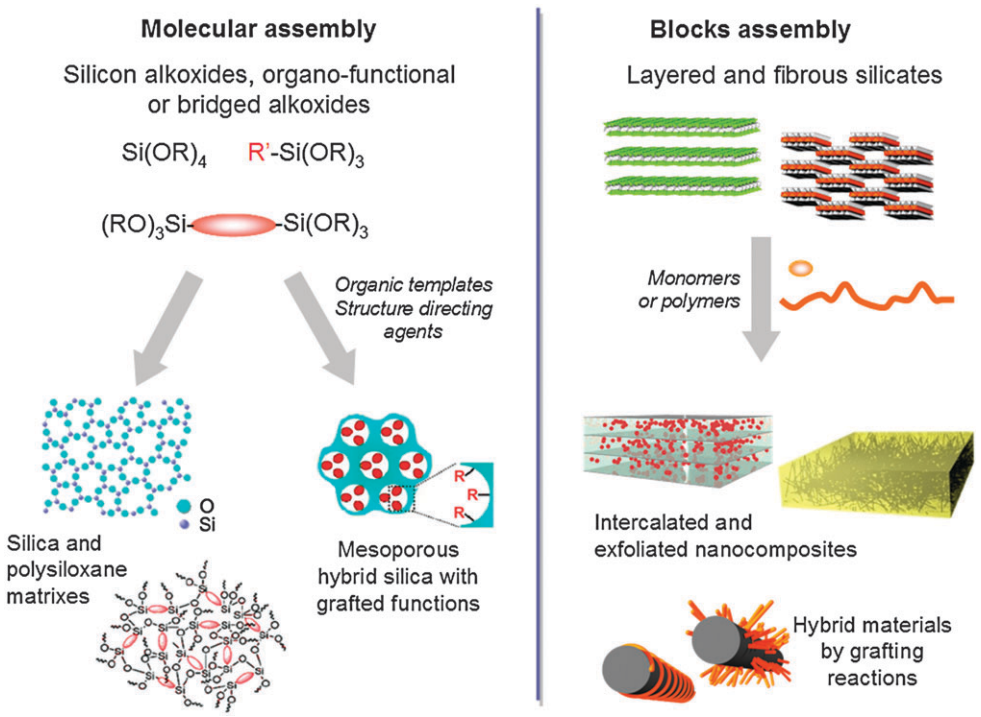

Fig. 2 Schematic representation of bottom–up strategies involving molecular-assembly or blocks-assembly.

Surfactant aggregates formed at interfaces[17] have attracted interest for constructing molecular devices and thin functional coatings.

It is known that surfactants can solubilize various molecular species with retention of ordered structures. Surfactant aggregates have also been used, not only simply to incorporate molecular species into the ordered structure to form host–guest systems, but also as structure directing agent for various organic[18] and inorganic polymers.[19–21] Lamellar phases of surfactant aggregates have been used to prepare lamellar inorganic polymers such as silica.[19–21] One beautiful example of this kind of inorganic–surfactant mesophases is the precursor (silica–surfactant mesostructured compounds) of mesoporous materials such as MCM-41.[22] Originally, it was thought that soluble silica species are immobilized on the hydrophilic part of surfactant mesophases (hexagonal mesophase for MCM-41 (Fig. 3) and cubic and lamellar for MCM-48 and MCM-50, respectively) to form organic–inorganic hybrid mesostructures.[22–24] Later on, a silicatropic mechanism was proposed for the formation of silica–surfactant mesostructured materials, when surfactant aggregation occurred by the interactions between soluble silica and the hydrophilic head group of the surfactant. This idea is supported by the fact that the silica–surfactant mesostructured materials are formed in diluted surfactant solutions, where the surfactant itself does not form mesophases.

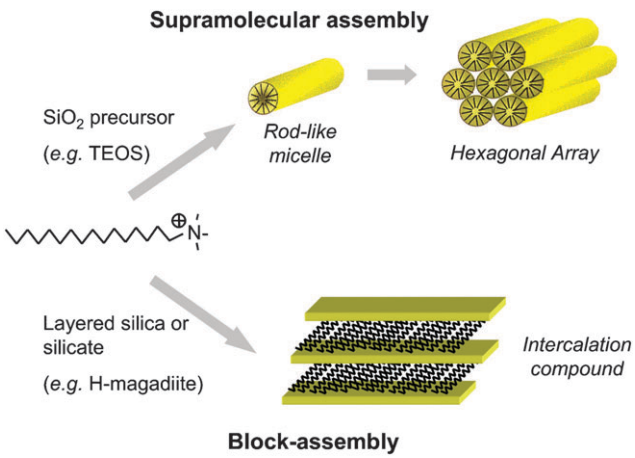

Fig. 3 Schematic representation of the formation of silica-based hybrids containing cationic surfactants. Different arrangements are possible depending on the adopted bottom–up strategy.

Inorganic–surfactant hybrid mesophases are also formed when homogeneous solutions containing soluble silica species and surfactant are dried by casting, spin and dip-coating.[25–27] Depending on the adopted experimental conditions such as silica : surfactant ratio, various surfactant mesophases have been immobilized by assembling with silica.[28] These cooperative assembly processes are very important to give highly ordered mesostructures. Depending on the synthetic conditions, such as solvent evaporation rate and pH of the precursor, physical mixtures or composites without regular periodic structures are often formed.

Being similar to those of aqueous surfactant mesophases, silica–surfactant mesostructured materials can "dissolve" organic molecular species during the hybrid formation. The incorporation can be done to control the pore size of MCM-41[22] as well as imparting functions such as optical properties into the mesostructured materials.[29–31]

Organosilanes containing a surfactant-chain can be spontaneously self-organized as micellar systems showing the capacity of being hydrolysed and condensed through the alkoxy groups allowing the preparation of organo-silica materials.[32] In this way, surfactant-silanes, such as *n*-octadecyldimethyl(3-trimetoxysilylpropyl)ammonium chloride, are able to give hybrid micelles of lamellar or hexagonal symmetries. The condensation of the hydrolysed alkoxysilane head with itself or with other silanes (*e.g.* TEOS) gives rise to lamellar or hexagonal mesophases of MCM-41 like materials (Fig. 4). These mesophases can be thermally treated to obtain the corresponding self-organized silica mesoporous materials but, more interestingly, they themselves show selective molecular swelling properties.[32] This behaviour is explained by the presence of the lipophilic charged-chains that allows the uptake of ions and molecules of different nature, being of interest in the development of different functional materials for optics, magnetics and other applications.

Hybrids resulting from the assembly of alkylammonium-based surfactants on various solid surfaces have been investigated so far. Various forms of silica (silica gel, colloidal silica, quartz, *etc.*) are known to adsorb surfactants on their surface from aqueous solutions.[33] The adsorption of surfactants on layered silicates is a unique example where surfactant is confined in a two-dimensional nanospace, the molecular arrangement being controlled by the host–guest interactions (Fig. 3).[34–38] In this intercalation system, the arrangement of surfactant is simply determined by the layer charge density of the surface, which is a self-organization process (block assembly, where the nanostructures were determined by the surface characteristics of the silicate layers) apparently different from previously mentioned silica-surfactant mesostructures, where cooperative assembly occurs (from molecular precursors). The arrangement is discussed on the basis of changes in the basal spacing values deduced from X-ray diffraction patterns. The packing and orientation of the alkyl-chains in the interlayer spaces depends on the surface layer charge density.[34] Recent studies and model calculations reveal more detailed description on the alkyl-chains organization in the interlayer space[39,40] though Lagaly's conceptual model is still useful to explain the interactions and spatial arrangements and distances measured.[41] Electrostatic interactions between the silicate surface and the cationic head group are the driving force for the molecular intercalation, while the intercalated surfactant can interact with adjacent surfactant (intermolecular interactions) to form a unique assembly under the effects of the cooperative van der Waals forces.[37] Therefore, host–guest interactions and guest–guest interactions play a dominant role for the nanostructure formation in this type of silicate based hybrids.

Smectite clays are the most common layered silicate materials and organo-ammonium ions surfactants are the most extensively studied guest species in the intercalation chemistry of smectites, giving the so-called organoclays. The assembly of organo-ammonium ions in the interlayer space of layered silicates can be regarded as a novel state of aggregates confined in a two-dimensional nanospace immobilized by ultra-thin inorganic layers. Organoclays have found numerous applications because the presence of surfactants renders the hydrophilic interlayer space of phyllosilicates as an organophilic environment.[42] The combination of the hydrophobic nature of the surfactant and the stable layered structures of the silicate sheets lead to unique physicochemical properties. Thus, organoclays based on smectites have been extensively studied for industrial and environmental applications, such as

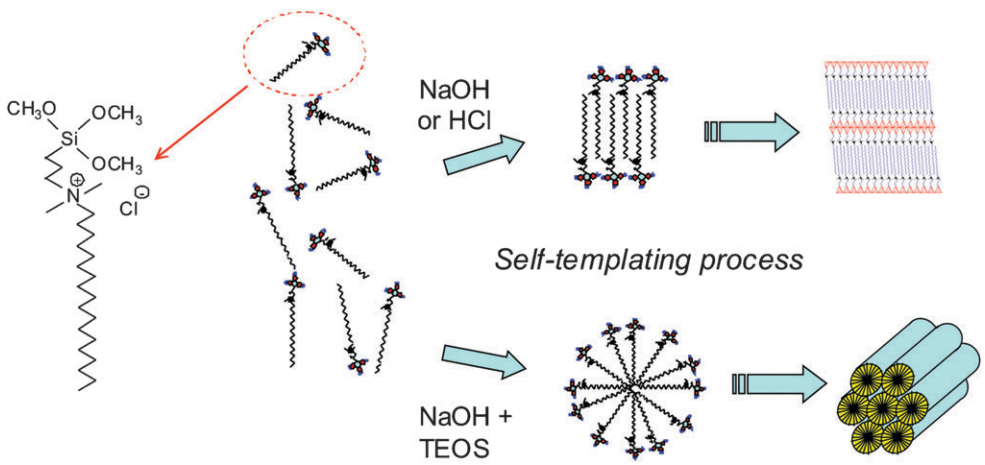

Fig. 4 Use of a surfactant-silane for self-templating assembly to give hybrid micelles of lamellar or hexagonal symmetries (based on ref. 32).

rheology controlling agents in paints, greases and cosmetics, nanofillers in the preparation of clay–polymer nanocomposites, adsorbents for poorly water soluble species, hosts for electrochemical reactions, as matrices for photofunctional species and catalytically active species, as well as in the so-called environmentally-oriented pesticide formulations that avoid or reduce the loss of bioactivity due to volatility or photodegradation of insecticides and herbicides.[41] The surfactant in the interlayer space can be regarded as an aggregate, since phase transition of the dioctadecyldimethylammonium ion intercalated in smectites has been reported and the phase transition between the gel and liquid-crystalline phases affected the diffusion and reaction of solute molecules.[43,44] However, new tendencies in organoclays preparation focus on the use of non-toxic modifiers of biological origin such as lecithin based tensioactives[45] or diverse biopolymers[46] instead of the conventional surfactant quaternary ammonium based agents because their "bio-friendly" character may enlarge their applications to the food, pharmaceutical and biomedical fields.[41] Some examples of these materials are discussed in sections below.

Materials based in the interaction of alkylammonium ions with layered polysilicates, such as kanemite ($NaHSi_2O_5$) and magadiite ($Na_2Si_{14}O_{29}{\cdot}nH_2O$), have been also reported.[47] The interaction of kanemite with such cations was initially investigated by Beneke and Lagaly who reported the formation of intercalation compounds of kanemite with several organo-ammonium ions.[48] These silicate–organic complexes show three-dimensional silica network formation with characteristics that depend on the degree of ion-exchange, expansion of interlayer spacing, and silanol condensation between the layers. In fact, after thermal treatment of the intercalated phases three-dimensional silica networks with high specific surface areas (about 900 $m^2\ g^{-1}$) are retained and, more importantly, the pore size varies with the chain length of the ions used.[49] For instance, when kanemite is allowed to react with alkyl-trimethylammonium ions, the silicate structure of the product (silicate–organic complexes) leads after calcination to mesoporous silica with narrow pore size distributions and a very large surface area (*ca.* 1000 $m^2\ g^{-1}$). A folded-sheet mechanism of silicate layers of kanemite has been proposed with regard to the formation mechanism of the three-dimensional silicate–organic complexes.[50] The proposed mechanism involves the intercalation of ions into the interlayer space of kanemite *via* an ion-exchange process of interlayer sodium ions and subsequent folding and condensation of thin silicate layers.

Organoammonium-exchanged layered silicates of the smectite family can be used as intermediates to template mesoporous silica, *e.g.* M41S, that remains as pillars separating the phyllosilicate layers giving rise to the so-called porous clay heterostructures (PCHs).[51] The organoclay which incorporates long-chain alkylammonium ions is further solvated with an amine (*e.g.*, decylamine) to organize micelles in the interlayer space of the clay to which the silica precursor (tetraethoxysilane, TEOS) can enter. The silica formed is templated by the surfactant–amine micelle and after calcination a PCH is obtained with a typical basal spacing in the order of 3 nm and BET surface areas up to 800 $m^2\ g^{-1}$.[51] This is a kind of bottom–up process in a nanoscopic environment (interlayer space) and the approach has been applied to other types of layered silicates as well as to other layered materials such as transition-metal oxides.[52,53] For instance, pillaring of magadiite, kenyaite ($Na_2Si_{21}O_{43}{\cdot}nH_2O$) and ilerite ($Na_2Si_{14}O_{29}{\cdot}nH_2O$) has been carried out by the intercalation and polymerization of TEOS into octylammonium-intercalated silicates swollen with octylamine. Silica pillared ilerite showed a BET surface area as great as 1100 $m^2\ g^{-1}$ upon calcination at 873 K and *ca.* 600 $m^2\ g^{-1}$ even at 1173 K where conventional zeolites tend to collapse when heated at these temperatures.[54,55] The above-mentioned case is another beautiful example of molecular intercalation and subsequent self-assembly of the intercalated surfactant following a bottom–up process that occurs within the interlayer space of silica-based solids of 2D structural arrangement.

When organoclays based on layered silicates are expanded in the presence of an alcohol of relatively low polarity (*e.g.*, *n*-butanol), which allows the incorporation of a silicon alkoxide (*e.g.*, tetramethoxysilane, TMOS) that is further hydrolysed in a controlled manner, the subsequent polycondensation provokes a sol–gel transition of the system. In contrast to the abovementioned PCHs, the resulting materials consist of a silica network between the phyllosilicate layers, that under well determined experimental conditions can lead to the delamination of the layered silicate (smectites and vermiculite).[56,57] After removal of the organic material the resulting materials also show high surface areas and porosity, providing the possibility of their functionalization *via* grafting reactions with organoalkoxysilanes.[57]

2.2 Macrocyclic ligands assembly to silica and silicate

The assembling of macrocyclic compounds such as crown-ethers, azacrowns, silacrowns and cryptands to silica based matrices has been carried out following three different methods (Fig. 5): (i) intercalation in layered host solids, (ii) entrapping into inorganic matrices generated by sol–gel, and (iii) grafting of macrocycles on inorganic surfaces (Table 2).[58]

The complexing ability of crown ethers and cryptand macrocycles towards alkaline and alkaline-earth cations in solution was an unusual property that opened the way to supramolecular chemistry.[59–61] The availability of this type of cations located in the intracrystalline region of certain inorganic solids, was the basis for their assembling with those macrocyclic compounds that acted as ligands, giving very stable organic–inorganic hybrids. In this way, the great affinity of the macrocycles towards the above-mentioned cations was utilized to obtain very stable intercalation compounds in which the macrocycles acted as ligands of intracrystalline cations of layered solids such as 2 : 1 charged phyllosilicates.[62–64] This type of layered silicates belongs to the clay minerals group (smectites and vermiculites) containing negatively charged layers, that are compensated by cations (exchangeable cations) as extra-framework ions located in the interlayer space, which usually are present in their hydrated form.

The intercalation processes are topotactic reactions involving the replacement of the solvation shell of the interlayer cations by the macrocyclic compounds as schematised

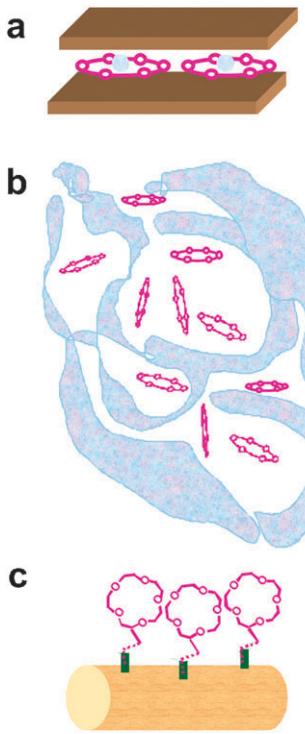

Fig. 5 Immobilization of macrocycles (*e.g.*, crown-ethers) by intercalation in 2D solids, (b) entrapping into an silica matrix generated by sol–gel processing, and (c) grafting on a silica surface.

in Fig. 5a. Diverse analytical techniques including ^{23}Na-NMR spectroscopy and laser microprobe mass spectrometry (LMMS) analysis inform about the formation of true intracrystalline complexes.[64,65] This occurs through exothermic processes, with enthalpy values greater than in solution, as corresponds to the overall intercalation process.[66] An important behaviour of macrocyclic-clay hybrids is that the ion-exchange capacity of the pristine silicate is maintained without appreciable desorption of the intercalated macrocycles. This feature is of interest concerning the control of the ion-mobility which is useful for solid-state electrolytes[67] and ion-membrane[68] applications. These macrocycles can be also assembled to silica-based matrices generated by sol–gel methods (Fig. 5b).[58,69–74] The use of precursors such as TEOS or TMOS incorporating crown-ethers such as 12C4, 15C5 and 18C6 generates organosiloxane matrices with low flexibility and high fragility, that prevent their use for film preparations, contrarily to the hybrids formed by intercalation of the macrocyles into layered silicates. It is crucial to use precursors containing alkyl- or alkenyl-chains, such as ETEOS and MAPTMS, to give organopolysiloxane matrices with improved physical properties that allow their processing as continuous films.[72] Interestingly, the sol–gel procedure allows formation on diverse substrates such as borosilicate or polyacrylonitrile porous supports and conducting solids (graphite, noble metals, ...), which are useful for development of membranes and modified electrodes, respectively. The nature of the macrocyclic compounds strongly influences the topochemistry of the silica framework as it directly affects the assembly of silica monomers. In this way, macrocycles exhibiting a basic character, such as cryptands, determine the formation of opened silica networks with low degree of reticulation, which could drive the release of the entrapped ligands. This is just the opposite behaviour to that observed in cryptand–silicate intercalation materials that are practically irreversibly entrapped. A significant feature that must be taken into account in the hybrids formed by the sol–gel procedures is the possibility to have the macrocycle available for entrapment of ionic species, or the capacity to create a network in the presence of salts with large anions that allows the incorporation of ion-exchange properties, as occurs in the intercalation compounds.[75]

An alternative method for immobilizing macrocycles in silica-based matrices is their assembly through covalent bonding by grafting of macrocycles on silica gel (Fig. 5c), which can be achieved following different types of coupling reactions with the surface silanol groups.[76–79] As in the hybrids formed by the sol–gel route, the macrocycles preserve their capacity to act as selective ligands of cationic species, for molecular recognition and other properties. In fact, the possibility to use the so-called ''spacer'' groups of different length allows the tuning of distance between the macrocycle and the silica surface, with the aim to have better ion-binding interactions between immobilized crown-ethers and cations in solution.[80] Moreover, the opportunity for immobilizing

Table 2 Routes to assemble macrocyclic compounds to silica-based matrices and the influence on features and properties

Hybrid system	Nanofabrication method	Structural & textural features	Properties & applications	Refs.
Entrapment of crown-ethers in silica matrices	Sol–gel	Great influence of silica precursors. *e.g.*, TEOS: monolithic blocks without porosity	Complexing ability of salts. Ion-sensor devices	Aranda *et al.*, 1995 (ref. 70); Ruiz-Hitzky *et al.*, 1995 (ref. 71); Jiménez-Morales *et al.*, 1998 & 2003 (ref. 72 and 75); Colilla *et al.*, 2010 (ref. 74)
Interlayer complexes in clays	Intercalation	Mono- or bi-layer coverage depending on the macrocycle cavity size and nature of interlayer cations	Ion-exchange capacity of clay is maintained. Solid electrolytes and iono-selective membranes	Ruiz-Hitzky & Casal 1978 (ref. 62); Aranda *et al.*, 1992 (ref. 67); Aranda *et al.*, 1994 (ref. 68)
Anchorage on silica substrates	Grafting	Macrocycles located at the external surface of silica with great stability towards desorption	Complexing ability of salts. Ionic chromatography	Ruiz-Hitzky *et al.*, 2001 (ref. 58)

macrocycles on external non-constrained surfaces facilitates the grafting of chiral ligands on silica, preserving their stereochemical characteristics, being able for instance, to resolve racemic mixtures.[81] All the above hybrid materials have similar chemical compositions but the way in which the building blocks (silica/silicate and macrocycles) are assembled, leads to supramolecular organizations with variable structural arrangements and topochemical behaviour. This is crucial in determining the final properties and therefore the applications of each type of hybrid. In this way, macrocycles grafted to silica can be applied in chromatography either for separation of cations (*e.g.*, alkaline and alkaline earth, heavy and noble metals), separation of anions (*e.g.*, halides, pseudohalides, isopolyacids, heteropolyacids), or separation of non-charged compounds.[77,78,82–84] For instance, benzo-crowns linked in different ways on silica exhibit variable separation ability towards alkaline ions. Thus, benzo-18C6/silica columns show excellent discrimination of cations with retention time increasing in the sequence:

$$Li^+ < Na^+ < Rb^+ < Cs^+ < K^+$$

that could be directly correlated with the stability of the corresponding crown-ether/cation complexes.[79] Steric hindrance and charge effects in the hybrids control the ion-complexing ability of the same type of macrocycle assembled to silica-based matrices in different environments. In this way, using data published by Aranda and co-workers[70] of the resistance of cations to the passage through membranes based on 18C6 assembled to a silica matrix generated by sol–gel from ethyltriethoxysilane (ETEOS), it can be determined the sequence for the passage is:

$$Li^+ < Na^+ \sim Rb^+ < Cs^+ \sim K^+$$

showing in general lower discrimination than similar hybrids prepared by grafting on silica. This behaviour is quite similar to that found for membranes based on 18C6 intercalated into montmorillonite, in which ion-exchange processes are operative.[68]

The capacity to complex cations can be used to modulate the cation-mobility especially by incorporating salts in which the counter ion are large negatively charged species, such as for instance tetraphenylborate anions. Membranes based on the hybrids resulting from the assembly of macrocycles and silica matrices that incorporate those species act as potentiometric electrodes for ion-recognition.[73–75] However, these systems are unable to work as solid electrolytes due to ion-pair recombination effects inside these dense silica matrices. In the macrocycle-layered silicates intercalation materials the host silicate acts as an immobile anion while the cations are able to move under an electrical field and therefore these systems can behave as solid electrolytes.[67,71] The affinity of macrocycles towards interlayer cations modulates their ion-mobility, and therefore by choosing the appropriate macrocycle ligand, inorganic–organic electrolyte materials with predetermined properties can be designed.[14,58]

2.3 Photoactive molecules-silica based hybrids

A variety of hybrid materials based on the assembly of chromophores and dyes and silica matrices (porous silica and minerals such as zeolites and clays) have been prepared following diverse bottom–up approaches. Soft procedures such as the sol–gel technique and deposition in solution in combination with the Langmuir–Blodgett technique are mild preparation methods that protect sensitive dye molecules from chemical degradation.[85] The arrangement and photophysical properties of the resulting hybrids may be influenced by the chemical properties of the mineral hosts, *e.g.*, polarity and acidity, as well as their spatial constraints on the guest molecules in the material.

As a molecular strategy, there is a very old and exciting example of dye–silica hybrids, where the dye (alkyl orange) was used as a template to enable molecular recognition ability

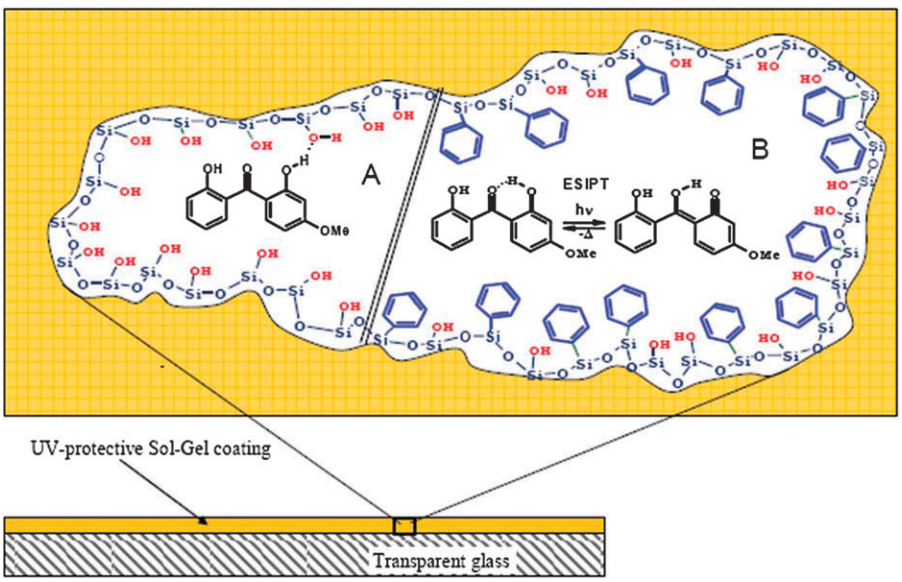

Fig. 6 Schematic representation of a UV-absorber molecule entrapped in a silica matrix prepared by sol–gel to give an UV-protective coating. (Ref. 95: reproduced by permission of The Royal Society of Chemistry.)

(molecular imprinting).[86] Selective separation technologies are very important for the purification, concentration and quantitative analyses of solutes such as toxins, drugs, and chemicals, where the molecular imprinting technique is very useful. The molecular imprinting idea was extended to make various inorganic and organic polymers for molecular recognition.[87] and not only for small molecules but also for proteins and crystals.[88] Dye-containing silica has also been prepared by the sol–gel approach, where both ionic and nonionic dyes were used,[89] for gaining insight into the nanoscale properties of sol–gel derived materials,[90] as well as for constructing possible practical uses such as optical recording materials.[91] Alkoxysilane containing chromophores were also used as starting materials[92,93] for the formation of hybrids, this strategy being especially useful for sensor and adsorbent applications, because the elimination and leaching of chromophore is less probable if compared with those obtained by the interactions by non-covalent bonding.

Dyes and pigments have been incorporated in silica through sol–gel processes for applications such as optical recording (photochromism and photochemical hole burning), light manipulation (luminescence, lasing and nonlinear optical properties),[94] and UV-absorbing coating[95] (Fig. 6). In order to maintain the advantages of the sol–gel processes including possible morphosyntheses for high optical quality products, the compositional tuning, mixing, and processing have been carefully examined.

Blocks-assembly is a promising strategy applied to prepare hybrids with high concentration of dyes with a low degree of aggregation. These dye-containing hybrids are built by the adsorption of dyes onto structured silica/silicate particles producing photofunctional materials.[96–98]

The introduction of dyes into blocks (porous materials) has been done by both post-synthetic approaches as well as direct synthesis as follows: (i) solubilizing guest species into the surfactant mesophase (molecular approach); (ii) complexation of functional surfactants with silica (molecular approach); and (iii) introduction of functional units into porous silicas (block-assembly).

For the introduction of functional units into silica by approach (iii), several options can be followed: adsorption on silica by the interaction with silanol groups, covalent attachment of dye–silane coupling agent on the pore surface, or adsorption of ionic dyes into surface modified silica. The interactions between the pore surface and the chromophore affects the excited-state properties. Taking advantage of the molecular approach, hierarchical structuration was achieved in nanometer scale dye arrangements as well as in (sub)-micrometer scale fabrication as thin films, fibers and well-defined particles. Combining the selective adsorption (molecular recognition) due to the possible structuration by templating as well as surface modification, and a variety of optical functions due to the possible surface modification as well as transparency of silica/silicate materials, the applications of silica/silicate based hybrid materials for recognition and sensing have actively been investigated.[99] Both colorimetric and fluorimetric systems have been developed[100] to detect various cations and anions in solution at very low concentrations and, in some cases, detection can be done by naked-eye observations (Fig. 7). The merits of silica to immobilize a receptor (or chromophore) for detection purposes are its large surface area and pore size for a wide variety of receptors. The resulting hybrids have been fabricated as powders and thin films.

When adsorption of dyes occurs in the interlayer space of layered silicates, especially in smectites, the dye orientation and location can be manipulated by host–guest interactions for controlled photochemical processes. An example of this is the aggregation of cyanine dyes which are well known compounds used as photosensitizers in silver halide photographic systems.[101] A cyanine dye (pseudoisocyanine: PIC) cation was adsorbed on smectites in aqueous suspension to form J-aggregates when a clay with a higher layer charge density was used.[102] Aggregation of rhodamines have been investigated for aqueous smectite suspension as well as for oriented films.[103] Organic laser dyes have found an increasing variety of applications in spectroscopy, optics and lasers. One of the key problems in their investigation and application is their fixation into matrices, because the spectral characteristics are largely affected by the nature of matrices. The fluorescent properties of the resulting intercalation compounds have been discussed on the basis of the dye arrangements in the interlayer space. The aggregation of a rhodamine depends on the amount of loaded dye in the clay dye films. The possible role of mesopore surface and the surface modification were shown in the aggregation of anionic cyanine dye in mesoporous SBA-15 modified with aminopropyl functionality.[104]

Surface modification by surfactants[105] and pillaring with alumina[106] are shown to be effective ways to incorporate cationic dyes such as tetrakis(1-methyl-4-pyridyl)porphyrin and 7-diethylamino-4-methylcoumarin. The luminescence intensity of the coumarin-pillared clay composite was reported to be six times greater than that of coumarin-clay composite. More recently, a luminescence quantum yield of as high as 80% was achieved for surfactant clay films containing small amounts of rhodamine dye.[107]

One of the most attracting goals of this kind of research is the construction of artificial photosynthetic systems from molecular building-block processes. Accordingly, possible electron/energy transfer by photoexcitation has been investigated. Tris(2,2′-bipyridine)ruthenium(II) (abbreviated as $[Ru(bpy)_3]^{2+}$) has been incorporated in various forms of silicas and silicates for this purpose to control the spatial distribution of the dyes for optimum photoinduced events.[108–111] In this case, not only the use of blocks (scaffolds) for the dye organization is necessary, but surface modification has to be performed to manipulate dye arrangement on silica/silicate.[112,113]

Recently, more complex systems are under study in order to develop biomimetic or bioinspired devices for solar energy (sunlight) conversion to chemical energy. In this case, the photo-active molecules, such as chlorophyll, are of biological origin as discussed below.

2.4 Functional organosilanes assembly to silica and silicates

Alkoxy- and halogen-organosilanes containing different types of functional groups, such as alkenyl, phenyl, thiol, amino, *etc*.,

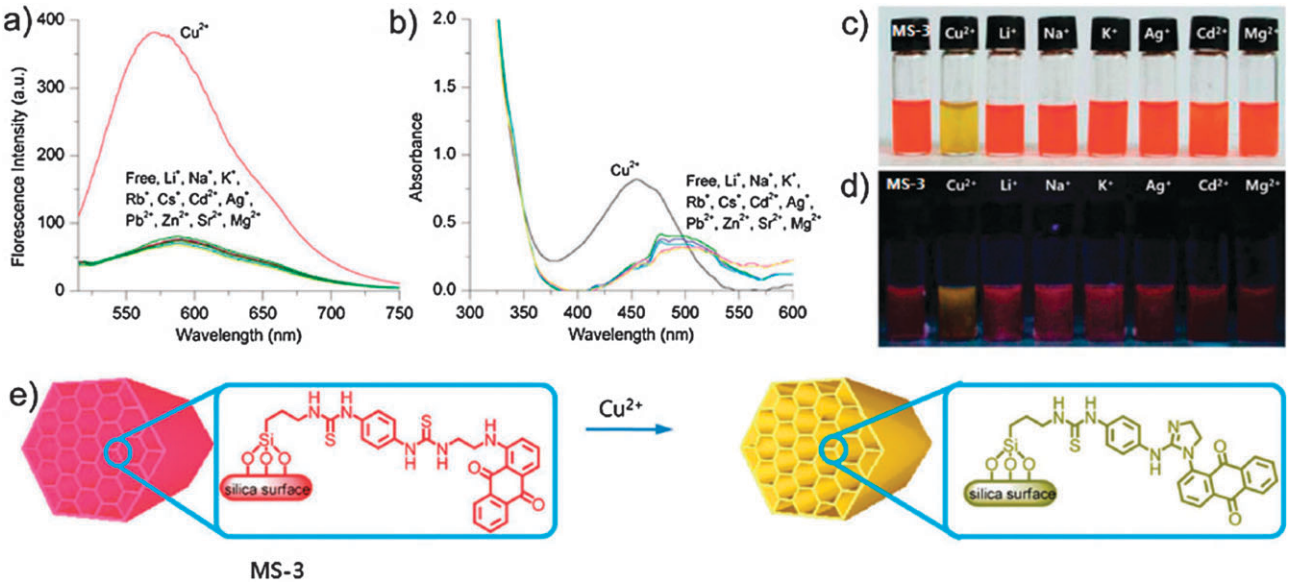

Fig. 7 Dye-mesoporous silica for colorimetric and fluorimetric detection of cations and anions in solution. (Reproduced from ref. 100 by permission of Wiley-VCH.)

can be incorporated into silica networks as one of the building blocks in sol–gel processes, or assembled by grafting to silanol groups on the silica and silicate surfaces. This is a frequent way to introduce (multi)-functionality to the resulting hybrids. Despite similar chemical compositions, these materials may show significant differences in their characteristics depending on the nature of the building blocks precursors as well as the experimental procedures (one-pot, multi-step or post-synthesis treatments) and the presence of additional species (additives) present in the synthesis medium.

Consider as an illustrative example, hybrids containing sulfonic acid groups, that can be introduced on silica and silicate matrices by several chemical routes including sol–gel and grafting reactions. For instance, one-pot sol–gel processes involving phenylchlorosilanes mixed with alkoxysilane precursors results in hybrids with randomly distributed phenyl functions that can be further sulfonated by treatment with chlorosulfonic acid.[114] Similar reactions using mercapto- or unsaturated-silanes in the presence of templates give rise also to randomly distributed functions, that can be further transformed to sulfonic groups, but located in this case in mesoporous silica solids with periodic order (MCM-41, SBA-15, *etc*).[110,115–117] Grafting reactions on preformed mesoporous silica allows to prepare randomly distributed sulfonic groups using diverse organosilanes.[118] Following the procedure reported by de Juan and Ruiz-Hitzky[119] it is possible to selectively introduce those functions inside the silica mesopores or at the external surface, and eventually, incorporate additional functionalities in a topochemical way. The basis of this method consists of gradual functionalization in three steps (Fig. 8): (i) grafting on the external surface of silica containing the template; (ii) extraction of the template; and (iii) grafting of new different groups in the interior of pores by reaction with a second functional silane.[119] The introduced chemical anisotropy makes the resulting materials unique for applications such as highly selective molecular adsorbents and catalysts, with preferred accessibility for organic cations, either on the interior or at the external silica surface.

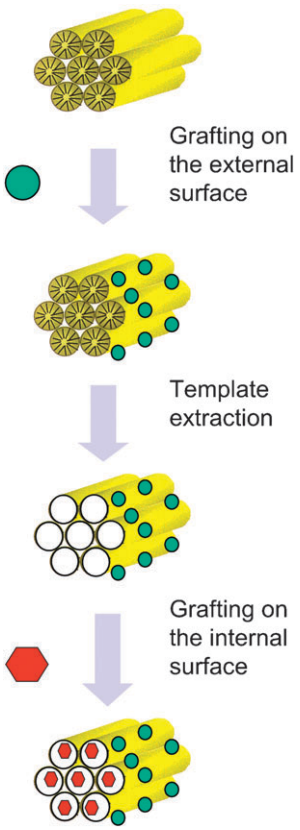

Fig. 8 Schematic representation of the selective functionalization of mesoporous silica by grafting of different active groups on the external and on the internal surfaces (nanopores) of the silica (based on ref. 119).

Table 3 Assembly of PEO to silica-based solids

Hybrid compositions	Assembling mechanisms	Properties/applications	Authors/refs.
PEO/layered silicates	Intercalation	Anisotropic ion-conductivity; Cationic transport number ~1; Electrochemical devices; Organization of pillaring agents in pillared clay preparation	Ruiz-Hitzky & Aranda, 1990 (ref. 130); Aranda & Ruiz-Hitzky, 1992 (ref. 131); Vaia *et al.*, 1995 (ref. 136); Michot *et al.*, 1993 (ref. 139)
PEO/silica or silicate nanoparticles	Hydrogen bonding	Isotropic ion-conductivity (when alkaline salts are incorporated); Cationic transport number ~0.6; Rheological and biocompatibility control	McFarlane *et al.*, 2010 (ref. 141); Zaman *et al.*, 2000 (ref. 142); Lafuma *et al.*, (ref. 143); Ruiz-Hitzky, 2001 (ref. 341); Aranda *et al.*, 2006 (ref. 137)
PEO/silica or polysiloxane networks	Sol–gel	Intermediates in the synthesis of mesoporous silica (SBA type); Conformation as powders, films or monoliths	Zhao *et al.*, 1998 (ref. 147); Kohjiya *et al.*, 1990 (ref. 149); Bronstein *et al.*, 2007 (ref. 148)

Crystalline solids containing available ordered silanol groups allows controlled topochemical functionalization by assembling building blocks with reactive sites pre-localized on the solids. Continuing with the example of sulfonic groups, the external surface of silicates such as sepiolite can be functionalized directly by coupling reactions with organosilanes (*e.g.* phenylsilanes),[114,120,121] whereas in layered silica materials (*e.g.* octosilicate), it is the internal surface that is modified by reaction with organosilanes (3-mercaptopropyltrimethoxysilane).[122] In a second step, the phenyl- and mercapto-groups are further treated for their transformation to the corresponding grafted sulfonic species.

Obviously, amorphous silica-gel can be functionalized in a similar way although in this case the surface modification affects all the surface, including meso- and micro-pores, with the only restriction imposed by the access of organosilanes of appropriated size.[123,124]

The sulfonic silica-based hybrids discussed above exhibit similar chemical functionality but the sulfonic active groups are organized and topologically distributed on the solids in a diverse manner, which is crucial with a view to their applications (selective/non-selective adsorption and catalysis, active phase of sensor devices, confinement of dyes and other photoactive species, *etc.*).

Here we have illustrated the functionalization of silica and silicates using organosilanes, in this case, providing sulfonic groups. Many other examples introducing a very diverse range of organic functionalities are known with the procedure being in general based on the building-blocks assembly strategy.[1,119,125,126] In some cases, this general strategy corresponds to processes based on so-called *click chemistry* procedures concerning joining small units together,[127] applied to silica-based clicked hybrid materials.[128]

3. Hybrids and bio-hybrids from macromolecules and biomacromolecules in silica and silicate matrices

3.1 Synthetic polymers

Many synthetic polymers have been assembled to silica-based solids with different purposes although the most studied and applied are the well known polymer–clay nanocomposites.[6,129] Related to these materials, poly(ethylene oxide), PEO, acts similarly to crown-ethers complexing interlayer cations in layered silicates (*e.g.* smectite clays), giving rise to hybrid polymer electrolytes showing relatively good ion-conductivity at moderate temperatures.[67,129–133] As occurs in PEO-salt solid electrolytes the polymer in the hybrids facilitates ion-mobility, avoiding PEO crystallization and ion-pair formation, which are the major drawback of these ion-conductors.[134,135] The polymer intercalated in the silicate acts as pillars separating the layers and procures an adequate environment facilitating the mobility of the interlayer cations in the plane defined by the silicate layers, *i.e.* the (*a*,*b*) plane. The incorporation of salts increases the total conductivity, that can become isotropic, but in the resulting hybrids both cations and anions participate in the electrical conductivity (ion-pair contribution). Since the first report in 1990 by Ruiz-Hitzky and Aranda,[130] different approaches (adsorption from solution, melt intercalation, microwave assisted assembling, *etc*) have been published, with the aim to obtain hybrid materials with enhanced ionic conductivity for applications as solid electrolytes for batteries and other electrochemical devices.[134–138] PEO and other alkyl polyethers can also interact with swollen layered silicates organising the system in the presence of pillaring solutions, *e.g.* $([Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+})$ polycations, that drives to the formation of pillared clays with enhanced crystallographic ordering compared to conventional procedures by ion-exchange reactions (Table 3).[139,140]

In other building-block processes, silica and silicate particles can be also assembled to PEO of different molecular weight.[137,141–143] It is assumed in those cases that surface silanol groups are in hydrogen bonding interactions with the oxygen atoms of the polyether chains. Mesoporous silica solids (*e.g.* SBA-15) containing liquid plasticizers in the nano-sized pores strongly enhance the ionic conductivity of the (PEO)-$LiClO_4$ matrix.[144] PEO and SiO_2 particles can be also assembled by *in situ* reactions that involve the simultaneous formation of the polymer network and inorganic nanoparticles by ultraviolet irradiation of a PEO macromer and silica produced *in situ* by sol–gel.[145] The incorporation of $LiBF_4$ to the PEO–SiO_2 composite leads to a lithium-ion conducting solid electrolyte with a significant increase in the Li^+ transference number, up to 0.56, together with a slight decrease in the ionic conductivity.[145] These results have been explained in terms of interactions between the surface OH

groups of the inorganic particles, the cations, the anions, and the ether oxygen atoms on the PEO backbone, as occurred in PEO-smectite systems, although this latter system showed a Li^+ transference number close to 1.[134]

The use of sol–gel approaches to prepare PEO–silica hybrid materials may drive to mesophases of nanoporous silica-based matrices as occurs when using amphiphilic triblock copolymers, for instance Pluronic block copolymers.[146,147] The systems based on PEO-block copolymers, silica precursors and Li-salts give hybrids exhibiting enhanced conductivity (up to 5×10^{-5} S cm^{-1}) with improved mechanical properties when compared to equivalent pure PEO-Li salts polymer electrolytes.[148] The use of the sol–gel approach to prepare silica matrices in the presence of polyethers (*e.g.* poly(oxypropylene) glycol, poly(oxytetramethylene) glycol) was proposed by Kohjiya and co-workers in 1990[149] and applied for developing organic–inorganic hybrids for optical applications. However, this first study revealed that those hydroxyl terminated organic polyethers were not reactive enough to be incorporated into the silica networks. In recent years this approach is being increasingly explored with different purposes including the formation of Li^+ [150] and H^+ [151] solid electrolytes. Laridjani *et al.*[152] demonstrated by NMR and other techniques that the structural features of a silica–poly(ethylene glycol) hybrid prepared by sol–gel were strongly influenced by the catalyst used to generate the silica network. The use of mixtures of alkoxysilanes and organo-alkoxysilanes (*e.g.*, (3-glycidylopropyl)trimethoxysilane, GLYMO) directly introduces ether groups in the silica matrix and in the presence of Li-salts allows the development of electrolytes with relatively good conductivity and able to be processed as thin films.[153,154] Click-chemistry concepts can be also used to create more complex systems such as polymersome–silica capsules by assembling of PEO-block co-polymers with a silica precursor (TEOS).[155]

3.2 Assembly of phospholipids to silica and silicates

Phospholipids are amphiphilic molecules which can self-assemble to give different structural arrangements (planar, cylindrical, spherical, *etc*). As biological materials they have an enormous importance because lipid planar bilayers constitute the basic building-blocks of cellular walls. Phospholipids have been supported on silica-based substrates in order to study their structural arrangement and cell-interaction mechanisms, as well as for developing chemical sensors, bioreactors, immobilizing proteins arrays, *etc*.[156]

As occurs with other hybrid entities already discussed in previous sections, the assembling of phospholipids to silica-based matrices may take place from molecular precursors in the presence of this type of entity or from building-blocks assembly. In this case the amphiphilic character of phospholipids allows electrostatic interactions with silica and silicate surfaces.

Phosphatidylcholine (PC) and related phospholipids are able to form micelles in water, which can be used as templates for silica assembling from molecular alkoxysilanes (*e.g.* TEOS). These resulting systems were used to generate nanocapsules of *ca.* 100 nm, able to entrap molecular species with different type

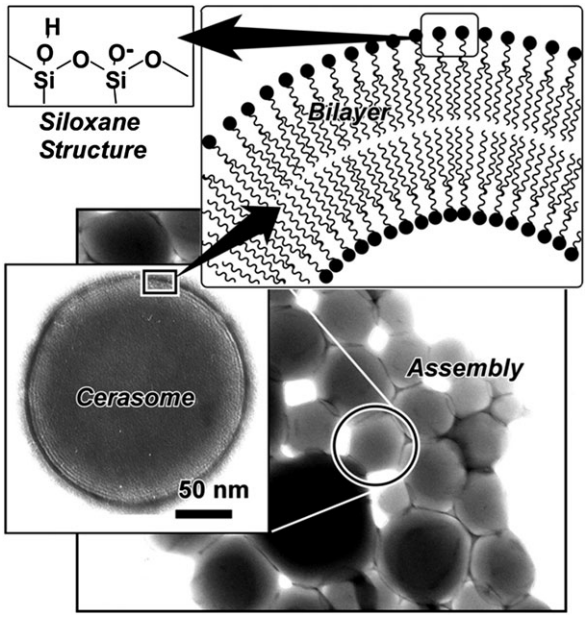

Fig. 9 TEM image and schematic representation of a cerasome structure. (Reproduced from ref. 10 by permission of Wiley-VCH.)

of functions, such as for instance anionic dyes.[157] The nature of the PC tail as well as the silica precursor determine the textural properties of lipid–silica mesophases. In this way, Dunphy *et al.*, have demonstrated the possibility to control the formation of silica and hybrid thin films with 1D, 2D or 3D phases of the phospholipid templates following the so-called evaporation-induced-self-assembly processes.[158] Mixed-micelles, as for instance those formed from PC-dodecylamine, can act as a template of sponge-like mesoporous silica using TEOS as molecular precursor.[159] The resulting mesoporous silica shows a 3D pore structure similar to SBA-16 with a specific surface area of up to 800 m^2 g^{-1}, and able to encapsulate enzymes and other biomolecules for use as biocatalysts and biosensor devices.[159]

In fact, PC-liposomes can be used either for growth of a siliceous shell or to entrap silica particles. Ariga's group have developed an innovative strategy using organo-alkoxysilanes with a lipid-like structure that leads to the formation of the so-called "cerasomes".[160–163] These hybrids are vesicles in which a siloxane network is covalently attached to the bilayer membrane surface as shown in Fig. 9. Interestingly, cerasomes can be functionalized by using diverse type of biomolecules, such as enzymes and antibodies, through covalent linkages for creating various kinds of biomimetic silica nanohybrids including cell-like inorganic structures.[10]

Phospholipid layers can be assembled onto silica nanoparticles giving rise to hybrids, with an organization similar to a living cell with a PC membrane, but where the core is in this case the inorganic silica particle.[164] Using spherical nanoparticles of different size (from 5 to 100 nm diameter), Ahmed and Wunder used these model hybrid membranes to study the basic interactions of the lipidic chains and free volume in these systems, which is important to understand molecular passage through cellular membranes.[164]

PC vesicles can be also adsorbed on the external surface of microparticulate phyllosilicates such as montmorillonite. In aqueous media swollen silicate particles are present as dispersed platelets, which can assemble with PC, rendering hybrid micelles. These systems are of interest because they can incorporate lipophilic molecular species, as for instance, in herbicides to procure environmentally friendly formulations for slow release of pesticides.[165–167]

Recently, another building-block strategy in the preparation of clay–PC hybrids has been reported. In this method, PC is dispersed in methanol or ethanol avoiding micelle formation and allowing the surface adsorption of discrete PC molecules. In layered silicates (*e.g.* montmorillonite) PC molecules can be intercalated between the silicate layers following a cation-exchange mechanism, whereas in fibrous clay silicates (*e.g.* sepiolite) the molecules are adsorbed on the external surface with interactions between the zwitterionic headgroup and the silanol groups.[45] The resulting materials can be considered as bio-inorganic composites with either mono- or bi-layer phospholipid species arranged on the silicate core particles, acting as agents for micotoxin sequestration, as recently reported by Wicklein and co-workers.[45,168]

3.3 Polysaccharide-based silica and silicate biohybrids

Polysaccharides are polymeric carbohydrate structures formed of repeating units joined together by glycosidic bonds and represent some of the most widespread natural polymers on Earth (starch, cellulose, chitin). Their use in the development of nanostructured hybrid materials, mainly in the so-called bionanocomposites, is experiencing a remarkable growth in recent years since natural polysaccharides are envisaged as promising substitutes of non-degradable polymers due to their properties of biodegradability, biocompatibility, low cost and availability.[8,10,169,170] In a similar way to conventional nanocomposites, the inorganic counterpart assembled to the biopolymer in most of polysaccharide-based bionanocomposites belongs to the clay minerals family. These biopolymers can be also assembled to silica derived from different sources (silicic acid, sodium silicate or silicon alkoxides), in order to develop new hybrid materials.[171] Several polysaccharides have been proven to promote silica precipitation yielding amorphous silica assembled to the polysaccharide template, mimicking the biomineralization processes that occur in nature.[172–174] Both types of materials, based on the assembly of polysaccharides and silica or silicates, have applications in many different areas such as protective coating, food packaging, or structural composites, as revealed by some selected examples in Table 4.

The mechanisms controlling the polysaccharide–silicate interactions depend on the nature of both components and involve ionic interactions, van der Waals forces, hydrogen bonds and water bridges. Polysaccharide chains can penetrate into the clay interlayer space through an intercalation mechanism or be adsorbed on the external surface of silicates.[175] In the case of silica-based materials, the main interactions of the silica phase with the polysaccharide are due to hydrogen bonds between the silanol groups and groups of the biopolymer chains.[176] In the case of positively charged polymers such as chitosan, electrostatic interactions can also take place, and even covalent bonds could be established from transesterification of chitosan hydroxy-groups by silanol.[177]

As mentioned above, polysaccharide–silicate nanocomposites together with analogous polyester-based materials are envisaged as eco-friendly materials, being promising substitutes for conventional plastics derived from petroleum. One of the main applications of 'green nanocomposites' or biodegradable plastics is food packaging, and starch is one of the most employed polysaccharides for this purpose.[178] This application requires materials provided with good mechanical and thermal characteristics, as well as improved gas and water vapour barrier properties.[178–180] The incorporation of natural or synthetic clay minerals, including montmorillonite[181] as well as kaolinite or hectorite,[182] produces a reinforcing effect in the biopolymer matrix. At the same time, the clay particles enhance the water vapour barrier property, overcoming the inconvenient hydrophilicity of polysaccharides. The excellent barrier properties in nanocomposites are due to the ability of clay layers to delay molecular transport with the introduction of tortuous diffusion pathways.[180] Profiting from this type of properties, some polysaccharide-silicate hybrids have been also applied as composite membranes in pervaporation processes. Recent examples report the use of hydrophilic pervaporation membranes based on alginate–montmorillonite materials,[183] as well as biohybrids involving mesoporous silica (MCM-41)[184] or sulfonate-modified silica nanoparticles acting

Table 4 Biohybrids based on the assembly of polysaccharides to silica or silicates for diverse applications

Approach	Molecular precursor or building block	Polysaccharide	Properties	Application	Ref.
Molecular assembly	Tetraethoxysilane (TEOS)	Vinyl-modified guar gum	Adsorption properties, mechanical stability	Removal of pollutants	Singh *et al.*, 2008 (ref. 186)
	Sodium silicate	Alginate	Nanometre size, non-cytotoxicity	Drug delivery	Boissière *et al.*, 2006 (ref. 189)
	Tetramethoxysilane (TMOS)	Chitosan	Non-cytotoxicity, cell proliferation	Bone regeneration	Lee *et al.*, 2009 (ref. 201)
Blocks assembly	Montmorillonite, cloisite, kaolinite, hectorite	Starch and derivates	Mechanical stability, gas and water vapour barrier properties	Food packaging	Sorrentino *et al.*, 2007 (ref. 180)
	Montmorillonite	Chitosan	Adsorption properties, anion exchange sites	Removal of anionic pollutants	An & Dultz, 2007 (ref. 188)
	Sepiolite	Chitosan	Anion exchange properties, mechanical stability	Potentiometric sensors	Darder *et al.*, 2006 (ref. 204)

as crosslinkers of chitosan,[185] for dehydration of organics with high separation performances.

The performance of silica–polysaccharide materials for the removal of pollutants has been successfully evaluated. Thus, nanocomposites derived from the polycondensation of tetraethoxysilane (TEOS) in presence of vinyl modified guar gum showed a high binding ability of Zn(II) ions, most likely through a complexation mechanism.[186] Similarly, nanocomposites derived from the assembly of polysaccharides and silicates can be also used for this application. For instance, protonated amino groups in a chitosan-montmorillonite nanocomposite acted as anion-adsorption sites, showing preferential adsorption of the inorganic anions Cr(VI) and As(V)[187] or organic pollutants such as tannic acid.[188] The influence of pH in this material was very strong and the adsorption ability was reduced at extreme pH values.

Within the biomedical field, interesting applications of silica– or silicate–polysaccharide hybrids can be found in the area of drug and gene delivery, as well as for tissue engineering purposes. Concerning drug delivery systems, chitosan and alginate seem to be the preferred polysaccharides for the development of silica-based biohybrids, making use of spray-drying techniques for processing these materials as nanoparticles.[189] In this way, silica/poly-L-lysine/alginate composites were processed in a one-pot synthesis as nanobeads (Fig. 10) and *in vitro* experiments proved the non-cytotoxicity and the easy internalization of these biohybrid nanoparticles by endocytosis.[189] Chitosan crosslinked with glycidoxypropyltrimethoxysilane (GPTMS) was also processed as nanoparticles and applied as pH-responsive drug delivery materials, profiting from the strong influence of pH on this polysaccharide.[190] Following a blocks-assembly approach, biohybrids based on mesoporous silica accommodating drug molecules in the pores and combined to chitosan were evaluated as a drug delivery system for the ultrasound-triggered smart release of ibuprofen.[191]

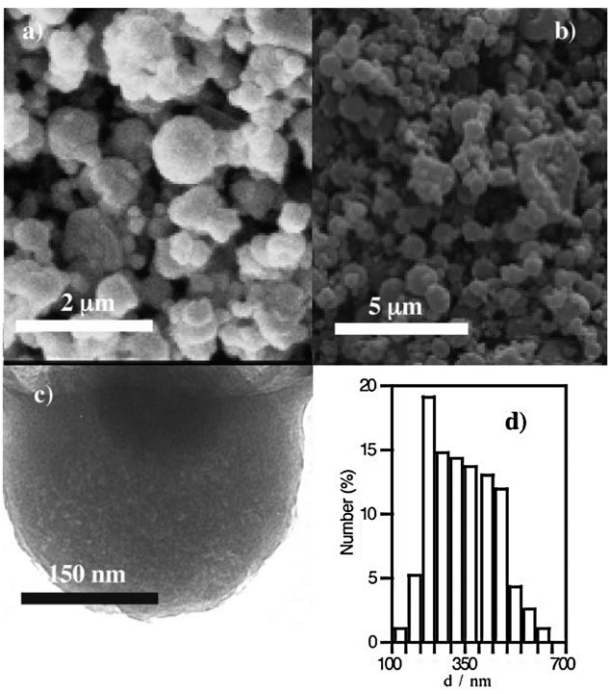

Fig. 10 SEM images of spray-dried nanospheres of (a) poly-lysine/alginate and (b) silica/poly-lysine/alginate. (c) TME image of spray-dried silica/poly-lysine/alginate nanospheres and (d) measurement of nanoparticle size by dynamic light scattering. (From ref. 189: reproduced by permission of The Royal Society of Chemistry.)

Although pristine silicates have been widely used as carriers of several drugs, polysaccharide–clay hybrids offer more advantages related to the enhanced stability of drug-loaded hybrid suspensions, higher drug encapsulation efficiency, modulation of ion exchange behaviour, swelling capacity or improved cellular uptake.[192] The non-cytotoxicity of polysaccharide–silicate nanoparticles has been also confirmed, as in the case of quaternized chitosan/clay nanocomposites, which were successfully applied for delivery of proteins[193] and also as a novel non-viral gene carrier, affording good transfection efficiency in both *in vitro* and *in vivo* experiments.[194]

Clay minerals assembled to polysaccharides afford suitable materials for application in regenerative medicine, being provided with good mechanical properties and biocompatibility, and are an alternative to commonly employed hydroxyapatite (HAP) and other calcium phosphates. For bone repair and other tissue engineering purposes, biohybrids are usually processed as macroporous materials by means of diverse techniques including freeze-drying,[8,195,196] since the presence of interconnected pores facilitates the transportation of nutrients and the removal of metabolic wastes, and allows the attachment and proliferation of cells.[197] Chitosan–montmorillonite–HAP biohybrids were evaluated as implants, in which the presence of the silicate was proven beneficial to enhance the mechanical properties as well as the cell proliferation rate.[198] This can be attributed to London/van der Waals forces and hydrogen bonding interactions between the growing cells and the silicate.[199]

Similarly to silicate-based materials, there is some work on the development of implants based on silica–polysaccharide hybrids. Among them, scaffolds composed of agarose and a glass powder derived from TEOS have been prepared with a designed architecture.[200] These materials are bioactive, promoting the formation of HAP after soaking in a simulated body fluid (SBF), and seem promising materials for bone repair applications. Good *in vivo* results were obtained with chitosan–silica xerogel hybrid membranes, which were evaluated in a rat calvarial model, demonstrating enhanced bone regeneration in comparison to pristine polysaccharide membranes.[201]

A few functionalized polysaccharide–silicate nanocomposites with suitable properties has been applied for sensing purposes. The assembly of chitosan to smectites or sepiolite can convert the cation exchange capacity (CEC) of the pristine clays into an anionic exchange capacity (AEC) due to the presence of available protonated amino groups. This resulted in functional nanocomposite materials with enhanced mechanical properties that were applied as the active phase in potentiometric sensors for the determination of anions.[202–204] To the best of our knowledge, no application of polysaccharide–silica materials without further functionalization has been reported for sensing purposes. However, the incorporation of functional compounds by grafting to both the organic or

inorganic counterparts may be an appropriate way to obtain biohybrids with interesting properties. Thus, $[Ru(bpy)_3]^{2+}$-doped silica nanoparticles assembled to chitosan allowed the preparation of composite films acting as the active phase of chemiluminescence sensors.[205]

Silica-polysaccharide hybrids also offer a suitable environment for immobilization of enzymes with long-term preservation of the catalytic activity. Additional advantages are the enhanced stability, mechanical resistance and easy processability in the desired configuration (surface coating, bulk) for the development of enzymatic biosensors,[206] bioreactors[207,208] or stationary phase in monolithic chromatographic columns.[209]

Polysaccharides assembled to clay minerals may also offer a stable and biocompatible support for enzymes, but until now very few applications have been reported in this area. For instance, different chitosan–clay hybrids were proven as a favourable microenvironment for glucose oxidase[210] and horseradish peroxidase,[211] which retained their native conformation, allowing the application of the enzyme-loaded biohybrids in electrochemical biosensors. Only one attempt of applying enzyme-loaded polysaccharide–silicate materials as bioreactors can be found in the literature, but the tested chitosan-clay-protease beads did not show the best results,[212] indicating that optimization is required in this area.

3.4 Structural proteins-based silica and silicate biohybrids

Structural proteins or polypeptides are a group of biological macromolecules that confer stiffness and rigidity to otherwise-fluid biological components. One of the best known proteins with structural and mechanical functions is collagen, found in connective tissue such as cartilage and in hard structures such as bones or ivory, in which it is assembled to a type of calcium phosphate known as hydroxyapatite (HAP) constituting naturally occurring biohybrids. The aim of developing biomimetic materials based on collagen or its denatured derivative gelatin is mainly addressed to the production of scaffolds for bone repair purposes,[213–215] but protein–silicate biohybrids can also find application in many other different areas including drug delivery systems, protective coatings, packaging materials, adsorbents, stationary phase for chromatographic applications and even electrode materials in electrochemical devices (Table 5). The different applications are related to the properties of the biohybrids, which can be tailored in some cases by the preparation procedure.

Silica–protein nanostructured hybrids can be produced in a molecular assembly approach from different precursors: sodium silicate, silicon alkoxides and organoalkoxysilanes.[215,216] In nature, silaffin proteins involved in biomineralization processes induce the precipitation of amorphous hydrated SiO_2 and control the assembly of the silica nanospheres.[217] These biosilicification processes may serve as an inspiration for the development of new silica-based hybrids with a variety of desired structural and functional properties, in which structural proteins used as template have the ability to control silica precipitation, as well as its morphological and textural characteristics.[216,218–220] Silica–protein interactions are driven by hydrogen bonding between silanol groups of silica and C═O and N–H groups of the polypeptides as well as by electrostatic interactions at high pH values.[221]

When the blocks-assembly approach is followed using silicates of the clay minerals family, the mechanisms controlling the assembly of structural polypeptide molecules to layered silicates are mainly driven by electrostatic interactions between the clay lamellae and the protein chains, together with strong van der Waals' attraction. As proposed in the 1950s to explain the intercalation of gelatin in montmorillonite, these interactions would cause the protein molecule to uncoil, facilitating its penetration into the clay interlayer space where it replaces the interlayer cation.[222] In the case of fibrous silicates, the contribution of electrostatic interactions may be lower due to the low cationic exchange capacity of this type of clays, and most likely hydrogen bonds are established between the protein and the silanol groups located at the clay surface. From observations of the enhancement of gelatin crystallinity by addition of sepiolite, it has been recently suggested that the characteristic textural features of channels and tunnels in this clay mineral might provide a suitable environment for the crystallization (triple helix formation) of gelatin, displacing the helix coil equilibrium towards the helix conformation.[215,223]

Within the scope of bone regeneration, silica-based biohybrid materials involving structural proteins are promising materials for application as implants, according to the good properties of biocompatibility and non-cytotoxicity.[224] An additional advantage of these biohybrids is their bioactivity, a property related to the ability to induce the formation of HAP after soaking in a simulated body fluid (SBF), which is beneficial for the further attachment and proliferation of cells constituting the new tissue. This property has been achieved in

Table 5 Biohybrids involving structural proteins assembled to silica or silicates for diverse applications

Approach	Molecular precursor or building block	Structural protein	Properties	Application	Ref.
Molecular assembly	Sodium silicate	Collagen	Bioactivity, non-cytotoxicity	Tissue engineering	Desimone *et al.*, 2010 (ref. 224)
	3-Glycidoxypropyl-trimethoxysilane	Gelatin	Non-cytotoxicity, functionalization	Gene transfection	Wang *et al.*, 2008 (ref. 239)
	Colloidal silica, methyltrimethoxy-silane, vinyltrimethoxysilane	Gelatin	Hydrophobicity, biocompatibility, transparency	Anti-wetting coatings	Smitha *et al.*, 2007 (ref. 236)
Blocks assembly	Wollastonite (calcium silicate)	Silk fibroin	Bioactivity, non-cytotoxicity, enhanced mechanical properties	Tissue engineering	H. Zhu *et al.*, 2010 (ref. 226)
	Cloisite-Na®	Gelatin	Gas and water vapour barrier properties	Food packaging	Bae *et al.*, 2009 (ref. 235)

different silica–protein hybrids and points out to a possible synergistic effect of silica and collagen on the material bioactivity, since those components alone were not able to promote the formation of apatite.[225] A similar behaviour was found in silicate-based hybrids, for instance in the assembly of silk fibroin to wollastonite, a calcium silicate mineral, resulting in a biohybrid material with higher bioactivity than the pristine protein scaffold.[226]

Following a blocks-assembly approach, layered silicates of the smectite family[227–229] or fibrous clays such as sepiolite[215,223,230] have been explored as the inorganic reinforcing component of biohybrids, in an attempt to develop new materials mimicking natural bone or similar tissues. Recent examples reveal different roles of the silicate platelets or fibres in the resulting biohybrids. On the one hand, the montmorillonite layers in a bio-nanocomposite based on gelatin help to diminish the biodegradation rate, since they protect the involved biopolymers against the action of lysozyme that naturally exists in body fluids.[228] Fibrous silicates such as sepiolite assembled to collagen were also proven to be effective for the protection of the biopolymer against the action of collagenase enzyme activity, showing biocompatibility for the adhesion and proliferation of human skin fibroblasts.[230] On the other hand, a second role of the silicate platelets is to act as physical crosslinking sites, enhancing the mechanical stability of the material. This effect is favoured as the interactions between the charged residues in the protein backbone and the silicate are stronger, it being possible to achieve an increase of 50% in modulus in the case of a recombinant protein involving a repeated sequence of elastin and silk fibroin amino acid motifs, that improves the compatibility with the silicate platelets.[231]

In order to prepare macroporous scaffolds, lyophilization and similar techniques can be applied to hybrids prepared from both molecular or blocks-assembly approaches. The resulting scaffolds need to be mechanically strong to resist *in vivo* stresses and, thus, the reinforcing effect of silicate platelets assembled to the structural proteins is beneficial to procure foams with an enhanced mechanical resistance in spite of their low density, with Young's modulus values up to *ca.* 10 MPa.[226,227,229] Gelatin–silica biohybrids were also processed as porous scaffolds, showing a bimodal distribution of pores (Fig. 11), and successfully tested for *in vitro* cell culture,[232,233] but none of these studies report on the mechanical properties of these materials.

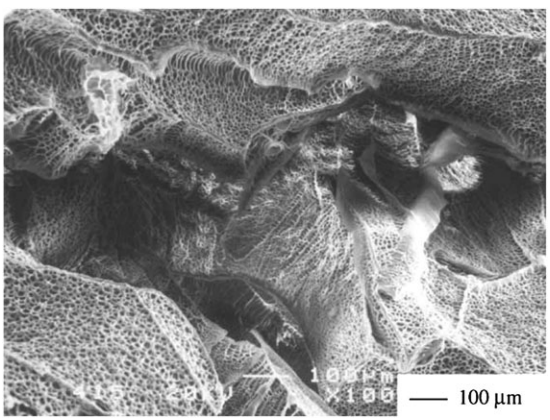

Fig. 11 Gelatin–silica hybrid processed as a porous scaffold showing a bimodal-pore distribution, with bigger pores 300–500 µm in diameter and smaller pores 5–10 µm in diameter. (Reproduced from ref. 232 with permission from Elsevier.)

The nanodispersion of clay sheets in the protein matrix confers new properties to the biohybrid materials: enhancement of thermal and mechanical stability of the composite, reduced swelling behaviour of the protein due to the dispersed silicate sheets,[234] as well as improved gas and water vapour barrier properties. This properties are important for the development of sustainable packaging materials, since protein–clay composites can be processed as relatively transparent and homogeneous ecological films that show a significant decrease in oxygen permeability as well as a considerable enhancement in the water vapour barrier properties.[235] The assembly of silica nanoparticles to structural proteins does not enhance gas or water vapour barrier properties as shown in silicate-based biohybrids, but the presence of silanol groups makes it possible to tailor the properties of the hybrid material by covalent grafting of appropriate groups to the silica counterpart. Thus, recent examples reported the increase of hydrophobicity in silica/gelatin hybrids functionalized with organoalkoxysilanes bearing methyl or vinyl groups, allowing their application as anti-wetting and transparent biocompatible coatings.[236,237]

Drug delivery applications can also make use of biohybrid nanoparticles due to their size in the nanometre range, lack of toxicity, and possibility of functionalization. Hybrid core–shell gelatin/silica nanoparticles prepared by a nano-emulsion route were easily internalized and intracellularly degraded by fibroblast cells, being promising materials for drug transport.[238] The possibility of functionalization of gelatin/siloxane nanoparticles with a peptide that exhibits high affinity towards DNA through electrostatic interaction allows their application as a non-viral vector in gene transfection.[239]

3.5 Functional proteins and enzymes assembled to silica and silicates

The aim of assembling biological species with silica and silicate matrices is addressed to provide them with a protective support, yielding easy-to-handle biohybrid materials in which the functionality of the entrapped biologicals is retained due to prevention of denaturation. The main advantages are the increased stability of these systems allowing a long-time performance and the easy recovery and reuse of the resulting materials, which are key factors for their application in biosensors, enzyme reactors and affinity separations (Table 6).

The mild conditions of the sol–gel process make it a very common procedure to encapsulate a wide variety of biological entities including proteins and enzymes, with the aim to develop functional biomaterials for biotechnological and analytical applications.[10,240–244] Following a sol–gel process, silica matrices prepared from sodium silicate or different types of alkoxysilanes have been widely employed over several decades for the immobilization of enzymes,[245,246] in the search for more robust and stable devices, mainly focused on the development of biosensors.[247]

Table 6 Biohybrids involving globular proteins or enzymes assembled to silica or silicates for diverse applications

Approach	Molecular precursor or building block	Enzyme	Properties	Application	Ref.
Molecular assembly	Sodium silicate	Horseradish peroxidase and glucose-6-phosphate dehydrogenase	Good catalytic activity, Michaelis–Menten kinetics, no enzyme leaching	Promising materials for biosensors, affinity supports and enzyme reactors	Bathia & Brinker, 2000 (ref. 250)
	Silicon alkoxide and organoalkoxysilane precursors	Horseradish peroxidase	Patterning of the modified sol–gel by soft-lithography, high stability, reusability	Optical waveguide biosensor	Llobera *et al.*, 2008 (ref. 256)
	Silicon alkoxide and organoalkoxysilane precursors	Bovine serum albumin	High stability, enantiomeric separation of D- and L-tryptophan (Trp)	Monolithic columns in chromatography	Kato *et al.*, 2002 (ref. 255)
Blocks assembly	MCM-41 mesoporous silica	Cytochrome c	Non-cytotoxicity, easy internalization by living human cells	Transmembrane protein delivery	Slowing *et al.*, 2007 (ref. 266)
	Laponite	Polyphenol oxidase	Sensitivity towards a citrus flavonoid, long-term catalytic activity	Amperometric biosensor	Mousty *et al.*, 2007 (ref. 278)
	Sepiolite	Lipase	High stability, facile recyclability	Enzyme reactor for biodiesel production	V. Caballero *et al.*, 2009 (ref. 285)

The encapsulation of proteins proceeds with the growth of the silica matrix around the enzyme biomolecules, creating pores of similar size to the protein in which the biological element can keep its native conformation and is protected even under harsh conditions.[248] This procedure is advantageous for immobilization of large size globular proteins, which may be restricted when using layered silicates with narrow galleries. The entrapped proteins need to undergo conformational changes when binding the analyte and, thus, some free space between the outer surface of the protein and the silica surface of the cage, including some water molecule layers, is beneficial to preserve the protein activity.[248] However, silica matrices derived from TEOS and similar alkoxysilanes are not able to preserve the catalytic activity for a long time as the silica matrix causes conformational changes, and slow denaturation of the protein takes place upon aging.[249] Thus, new sol–gel processing methods using organically modified silane precursors or incorporating additives are more appropriate methods for functional stabilization of biomolecules, contributing as well to overcome the brittleness of pure silica matrices.[247] Different approaches are addressed for this purpose: use of alcohol- and catalyst-free routes,[250] removal of the alcohol produced in the hydrolysis step before the addition of biologicals,[251] use of polyol-containing precursors that generate biocompatible alcohols,[252,253] or incorporation of glycerol to the silica matrix.[254] The stability of entrapped enzymes may be also improved by using silica–biopolymer materials as the immobilization support, as mentioned in section 3.3. For instance, the brittleness of BSA–silica systems as a stationary phase in monolithic columns for capillary electrochromatography[255] can be overcome by incorporation of chitosan or gelatin to the silica system.[255]

A remarkable characteristic of the sol–gel method is the possibility to process the enzyme-containing biohybrid materials with the desired conformation, from thin films to monoliths and, in some cases, making use of soft-lithography techniques that allow the microstructuration of the biohybrid as the replica of a given pattern.[256] With a suitable composition of organoalkoxysilanes, the mechanical properties of the enzyme-modified silica matrix may be good enough to build stable structures of high aspect ratio for application as waveguides in full-field photonic biosensors.[256] Another important advantage is the optical transparency of the silica matrix in comparison to matrices based on silicates. This allows carrying out direct measurements of the entrapped proteins through spectroscopic techniques[257] and can be utilized for biosensing applications based on the optical transduction of the enzymatic response.[244,258]

The accessibility of analytes to the entrapped protein is also an important factor in view of the possible applications of biohybrids. In comparison to the open frameworks of silicates, silica matrices prepared from alkoxysilanes in a sol–gel process show very low porosity, which may hamper the accessibility of analytes. A strong interaction of silica with the protein residues constituting its active site may also contribute to impede the recognition of analytes, thus reducing the catalytic activity.[247]

In order to overcome the problems due to by-products generated during the sol–gel process and to the lack of porosity of silica matrices derived from alkoxysilanes, silica–enzyme materials can be also prepared in a blocks-assembly approach, using previously formed mesoporous silica materials. The compatibility of the pore diameter with the size of some proteins and enzymes controls their inclusion in the pores.[259,260] Thus, small size enzymes may penetrate into the nanometre size pores, while large enzymes are most likely immobilized in the large interparticle voids.[261] Adsorption of proteins inside the pores may be influenced by pH and ionic strength[262,263] or by the presence of heteroatoms in the silica framework.[264] Immobilization can also proceed *via* a pressure-driven method, carried out by cycling the enzyme stock solution through a pre-packed silica chromatographic column under high pressure,[265] which leads to a high enzyme loading and reduced enzyme leaching in comparison to conventional adsorption procedures. Covalent immobilization may also enhance the stability of the enzyme biohybrids rather than simple adsorption, increasing their resistance towards different solvents, high temperatures and extreme pH conditions.[261] Although most of the former examples report the use of enzyme biohybrids in biosensing or enzyme reactors, other

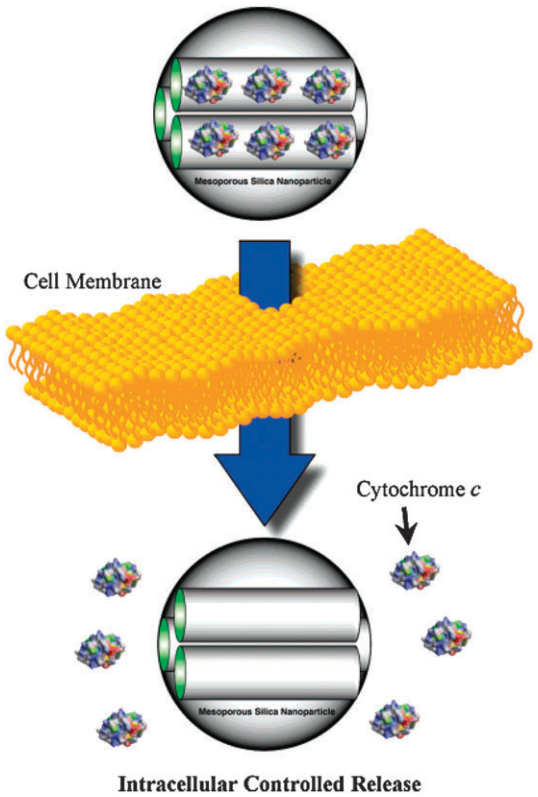

Fig. 12 Schematic representation of the application of MCM-41 mesoporous silica nanoparticles entrapping cytochrome c as a transmembrane delivery vehicle. The cytochrome c passes through the cell membrane due to the shielding effect of the mesoporous silica support and is released into the cytoplasm. (Reprinted with permission from ref. 266. Copyright 2007 American Chemical Society.)

advanced applications are also proposed such as controlled release of proteins in living cells. Thus, MCM-41 mesoporous silica nanoparticles entrapping cytochrome c have been successfully tested as a transmembrane delivery vehicle, being easily internalized by cells due to the shielding effect of the mesoporous silica support (Fig. 12).[266]

In a similar way to mesoporous silica, zeolites are suitable solid supports for enzyme immobilization. These microporous aluminosilicate minerals, usually prepared by synthetic procedures with a wide variety of Si/Al compositions and conformations[267] are assembled to enzymes by an adsorption process. Zeolites present a highly heterogeneous surface with multiple adsorption sites, such as framework oxygen, silanol groups and some compensating cations, that may afford strong interactions between the enzyme and the zeolite surface. Both the structure and composition of the zeolite have a marked influence on adsorption and, in consequence, on the catalytic activity.[268] As recently reported, the immobilization is mainly driven by electrostatic interaction, but the Brønsted acidity of diverse zeolite structures may originate different adsorption performances in each of them.[269] Structures with little acidity and with lower Si : Al ratio seem to procure the best catalytic performance.[268] The resulting biohybrids show enhanced stability and may be easily recovered after use. Also, the adsorbed enzyme could be removed by calcination and the zeolite support reused for immobilization of new enzyme.[270] Thus, due to these properties, the enzyme–zeolite hybrids are usually applied as bioreactors, for instance in fluidized beds[271] or constituting new microreactor devices in which the biohybrids are immobilized within a microfluidic channel as a stationary phase.[272]

Also in a blocks-assembly approach, clay minerals have been proven as suitable host matrices for the stable immobilization of enzymes, mainly those belonging to the group of layered silicates. As recently reviewed, most enzyme–silicate biohybrids developed for biosensing applications make use of natural and synthetic silicates such as montmorillonite and laponite, respectively.[273] The interlayer space of these natural and synthetic silicates can accommodate a large variety of biomolecules within the constrained interlayer regions. The entrapment of proteins in montmorillonite was reported for the first time in 1939 by Ensmiger and Gieseking[274] and, later, McLaren's group continued in the 1950s with an extensive work on this subject, including a curious application in which montmorillonite was used as a caliper to estimate the diameter of the intercalated enzymes.[275] The inorganic layers have the advantage of high chemical inertness and biocompatibility, and offer a protective environment for the enzymes, avoiding microbial degradation. For instance, the availability of horseradish peroxidase assembled to montmorillonite for microorganisms can be reduced by 90% in comparison with the free enzyme.[276] At the same time, the accessibility of substrates to the active sites of immobilized enzymes is guaranteed by the open frameworks of the layered silicates, which is essential for diverse applications of biohybrid materials.[277] In electrochemical biosensors the access of electroactive ions or redox mediators to the immobilized enzyme is also required. For this purpose, an additional advantage is the possibility of incorporating these redox mediators between the silicate layers by an ion-exchange process.[273,278,279] In some cases, the clay platelets not only contribute to the long term stability but also may improve the analytical performance. For instance, a biosensor based on laponite/polyphenol oxidase (PPO) biohybrid was able to detect rutin, a citrus flavonoid, which could not be detected with a biosensor prepared simply by chemical cross-linking of PPO onto the electrode surface,[278] this improvement being ascribed to the biocompatibility of the clay material and the high permeability of the laponite-enzyme coating.[280]

The immobilization of very large size proteins in the clay interlayer space may be restricted due to the narrow interlayer distance of *ca.* 0.2 nm, and the protein molecules may be then adsorbed on the external surface of clay platelets.[281] The intercalation can be achieved by previous intercalation of an appropriate compound that produces a spatial enlargement of the clay galleries. Organic tetraalkylammonium species are commonly used to enlarge the interlayer space, facilitating the further intercalation of large size enzymes such as myoglobin or haemoglobin (Fig. 13),[277] but recently polymeric species such as α,ω-diaminopoly(oxypropylene) were also successfully employed for this purpose.[282]

A new route for the intercalation of enzymes proposed the use of a synthetic aminopropyl-modified magnesium silicate following an exfoliation/restacking mechanism.[283,284] The initial exfoliation was produced by protonation of the amino

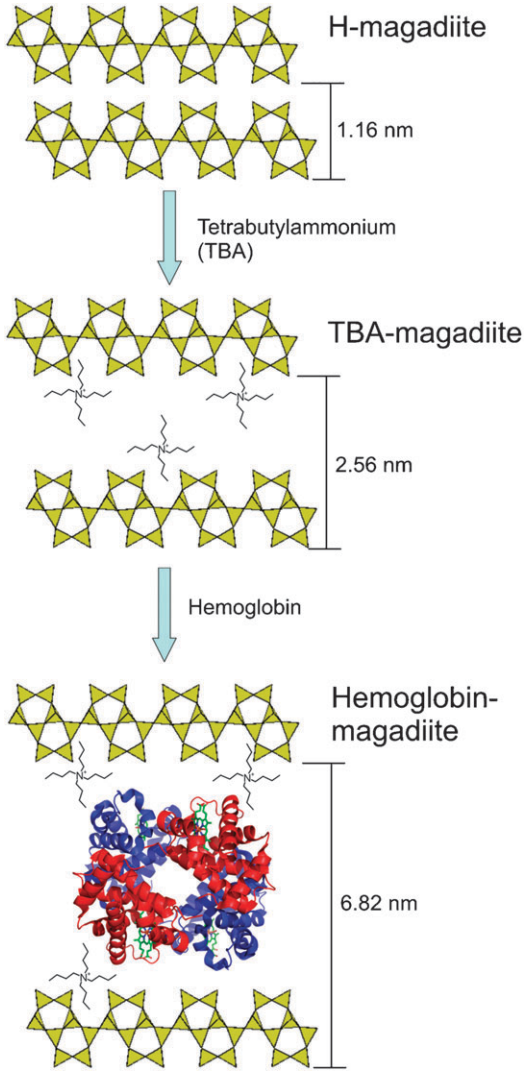

Fig. 13 Haemoglobin intercalated in organically modified magadiite. The previous intercalation of tetrabutylammonium species enlarges the clay galleries, facilitating the access of voluminous proteins. Based on data from ref. 277.

groups in aqueous solution and the layered silicate was spontaneously reassembled incorporating negatively charged small size biomolecules between the layers, leading to intercalation compounds in a process driven by electrostatic interactions. Higher size proteins, such as haemoglobin, gave rise to exfoliated materials after reassembly of the protonated layers.[284]

The stability of intercalated enzymes is usually high and they remain between the silicate layers even after treatment of the biohybrid with other biomolecules, which could be attributed to the strong adsorption of enzymes to the silicate layers.[282] In few cases, such a strong adsorption has been reported as a negative factor leading to reduction of the catalytic activity.[279] This has been also observed after adsorption of enzymes onto fibrous clay minerals such as sepiolite and palygorskite,[285,286] and may be attributed to a variety of factors, including blocking interaction of the amino acids essential for catalysis with the surface of the clay mineral, disruption of the three-dimensional structure of the protein, as well as steric hindrance for the substrate or diffusional limitations. However, fibrous clays are suitable supports for enzyme adsorption due to their biocompatibility as well as high specific surface area and porous morphology, yielding biohybrid materials of high stability that are usually applied as bioreactors, for instance in the production of biodiesel from sunflower oil.[285]

In other cases the stability of the biohybrid may be enhanced by crosslinking the enzymes with different compounds including glutaraldehyde (GA), poly(methyl methacrylate) (PMMA), or poly(*o*-phenylenediamine) (PPD)[273] or using GA to covalently bind the enzyme to the silicate layer previously modified with 3-aminopropyltriethoxysilane.[287] In this last case, the high stability of the biohybrid guarantees its continuous use in a packed bed reactor for 96 h with only a 15% loss in activity.

3.6 Nucleic acids assembling to silica and silicates

Nucleic acids are macromolecules composed of chains of monomeric nucleotides that have the function to carry genetic information or form structures within cells, with deoxyribonucleic acid (DNA) and ribonucleic acid (RNA) being the most common nucleic acids. These biomacromolecules can interact with silica or silicates following molecular- or blocks-assembly strategies, originating biohybrid materials with applications mainly related to bioanalysis or to the biomedical field.

Typical examples of silica–nucleic acid materials concern the conjugation of silica nanoparticles with biological entities such as DNA, by physisorption or by covalent attachment on the silica surface. This assembling results in biohybrid materials which are very useful in bioanalysis and gene transfection, which take advantage of the properties of nano-sized silica particles: inherent low cytotoxicity, high transfection efficiency, versatility, unrestricted plasmid size or better shelf-life, as recently reviewed.[288] The nucleic acids may be also entrapped within a porous matrix following a molecular-assembly approach, but very few examples of encapsulation in silica networks derived from silicon alkoxides in sol–gel process have been reported until now. Tests carried out by encapsulation of guanine and adenine proved that both DNA purines preserved their structural integrity within the silica network.[289] However, they interact with the silanol groups of the matrix by hydrogen bonding, contributing to create macropores in the silica matrix.[289] Pierre and co-workers found that DNA molecules were stably retained within a silica network, which was attributed to possible complexation between phosphate groups of DNA and the surface of the silica cage, as well as to the microporous pore size in the silica gel network that impedes the removal of entrapped molecules.[290] The DNA–silica biohybrids showed mechanical and chemical stability in both aqueous and organic solvents. The entrapped DNA molecules were proven to retain their specific functions, being able to adsorb typical DNA-interactive chemicals. This adsorption property together with the possibility to recycle and reuse this biohybrid, make it a promising material for separation of harmful

DNA-interactive chemicals and in environmental clean-up applications.[291,292] An additional advantage in this type of DNA–silica material is the protection of the entrapped DNA molecules against hydrolysis by nuclease enzymes.[293]

Following a blocks-assembly approach, diverse inorganic solids conjugated with nucleic acids were also able to protect the adsorbed molecules from enzymatic degradation. This was observed in the case of mesoporous silica nanoparticles with large pores, which were effective in the adsorption of plasmid DNA, leading to stable materials that resist the attack of nucleases.[294] Silicates belonging to the clay minerals family have been also tested for protection of DNA. Adsorption of nucleic acids on smectites resulted in formation of micro-composites, as these biomacromolecules are not able to penetrate into the clay interlayer space and adsorb on the external surface of the silicate, fitting to a Langmuir isotherm in the case of montmorillonite.[295] Montmorillonite and kaolinite were also proven to provide protection for DNA against nuclease degradation, this being higher in the case of montmorillonite although it shows a lower binding affinity of DNA.[296] These results suggested that the DNA degradation does not depend on the degree of DNA binding on the silicates or on changes in the DNA structure due to adsorption, but on the efficient retention of nucleases that bind to clay minerals.[296] Strong interaction with the silicate surface may cause structural changes in the DNA backbone due to a reorientation of the phosphate groups, as observed in the wrapping of DNA on halloysite, a nanotubular aluminosilicate clay mineral.[297] As mentioned above, the retention of nucleic acids on clay minerals may be enhanced by previous modification of the inorganic solid support with appropriate compounds, as shown in the cases of biohybrid materials involving the polysaccharide chitosan intercalated in rectorite[194] or the gelatin/siloxane hybrid nanoparticles functionalized with appropriate peptides.[239]

Other modifications of silicates with organic compounds are addressed to achieve intercalation compounds, in which the DNA molecules could be accommodated between the inorganic host layers. This is the case of a synthetic amino-propyl-modified magnesium silicate that can be exfoliated by protonation of the amino groups in aqueous solution and spontaneously reassembled incorporating the negatively charged DNA molecules between the layers through electrostatic interactions (Fig. 14).[283,298]

Conventional organoclays derived from intercalation of alkylammonium compounds in smectites can be also conjugated with nucleic acids. As recently reported, the expansion of the interlayer space of montmorillonite could allow the accommodation of DNA molecules within the galleries of the organoclay, which provides protection against nuclease degradation, and was successfully tested for transfection of DNA to the nucleus of cells.[299] *In vivo* experiments carried out with a montmorillonite–plasmid DNA material confirmed the suitability of this type of silicate-DNA biohybrids for application as a non-viral vector for gene-delivery.[300] Oral administration of the montmorillonite–plasmid DNA material in mice showed the successful transfection of the plasmid into the cells of the small intestine. Given that transfection was not observed for the naked plasmid, this result suggests the protective effect of inorganic support on the plasmid from the acidic environment in the stomach and DNA-degrading enzymes in the intestine.[300] In addition to gene delivery, another application of this type of materials is related to bioanalysis. A recent example reported the use of DNA assembled to aluminium-modified smectites in the building of carbon paste electrodes (CPE), which were applied as sensors to study the different binding strength of low molecular weight compounds with ssDNA and dsDNA.[301]

4. Bio-hybrids from biological entities in silica and silicate matrices

4.1 Fragments of biological entities assembled to silica and silicates

Silica and silicate matrices are appropriate supports for the entrapment of biological species, resulting in biohybrid materials in which the functionality of the entrapped biologicals is retained due to the protective effect of the inorganic host. Some examples of biohybrid materials including cell fragments or complex protein systems assembled to silica and silicates are found in literature, prepared either by a molecular approach, the sol–gel process, or through a blocks-assembly approach using appropriate silicates and mesoporous silica.

In addition to the suitable conditions of the sol–gel process to avoid harm of the entrapped biologicals, an additional advantage is that the gel network grows around the biological entity, which acts as a structural template during the process, without any restriction due to the biomolecule size. Thus, the molecular assembly from sol–gel precursors seems to be the best procedure to encapsulate large size biologicals such as complex protein systems[302] or cell fragments,[303] which could not be accommodated in the interlayer space of clays due to its narrow size or in preformed mesoporous silicas. An interesting application of silica-encapsulated biological fragments is related to the successful entrapment of "protein synthesis machinery" from *E. coli* within a silica matrix derived from a mixture of alkoxysilanes.[304] This biological machinery involves ribosomes, which are particulate sub-cellular components made from complexes of RNAs and proteins, as well as other enzymes and nucleic acids required in the synthesis of proteins (Fig. 15). The functionality of immobilized biological compounds was preserved within the silica sol–gel matrix, allowing the reproduction of complicated biological process within an inorganic matrix, in a similar way as they occur in living cells.

When photofunctional elements are immobilized, another important advantage of using the molecular assembly of silica precursors is the optical transparency of the resulting silica matrix. This fact allows direct measurements of the photochemical activity of entrapped systems, for instance the spinach Photosystem I (PSI) complex involved in the conversion of solar energy into chemical energy.[302] PSI was able to retain its structural and photocatalytic integrity after encapsulation within silica, resulting in a promising biohybrid material for building biobased optoelectronic devices as well as novel artificial photosynthesis systems.[302] In a similar

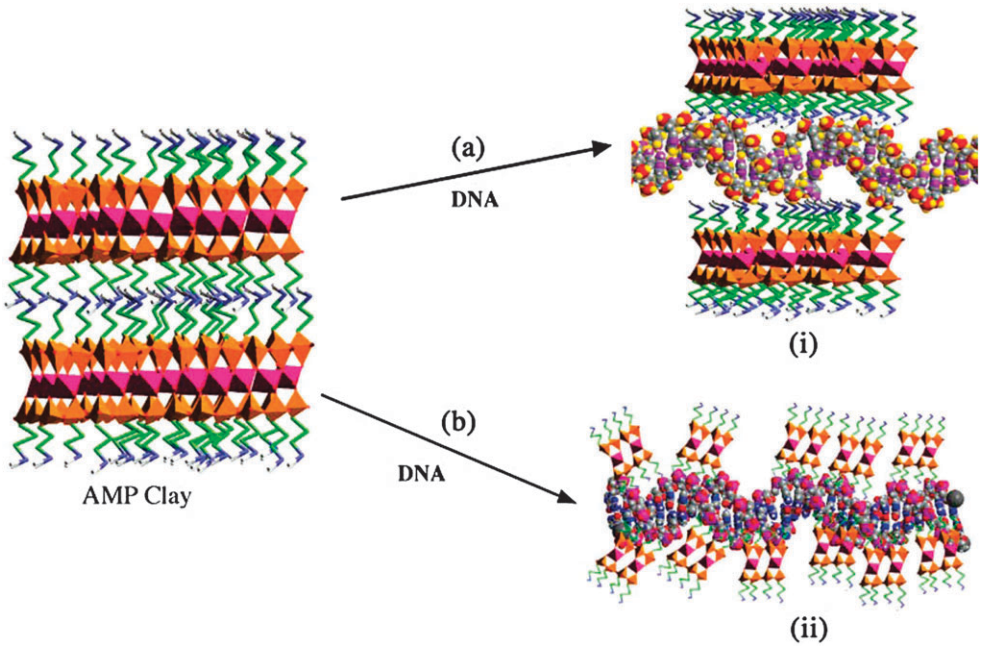

Fig. 14 Aminopropyl-modified magnesium silicate (AMP) may be exfoliated in water due to protonation of amino groups forming dispersed nanosheets. Electrostatically induced reassembly of these organoclay layers by association with DNA may lead to: (a) an ordered mesolamellar nanocomposite, or (b) to an ultrathin organoclay covering on individual DNA molecules when the exfoliated AMP is fractionated by gel chromatography, leading to molecular-scale isolation of the double-helical strands. (Reprinted with permission from ref. 298. Copyright 2007 American Chemical Society.)

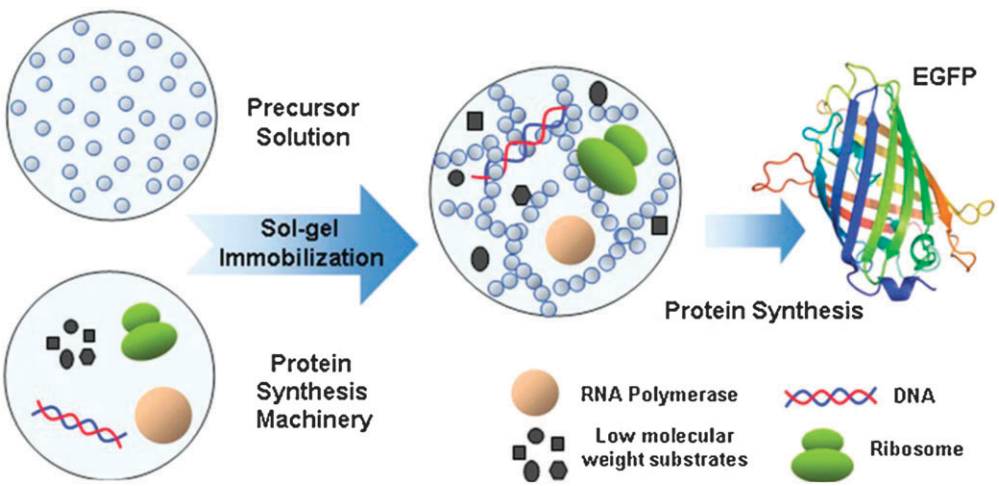

Fig. 15 Schematic representation of the encapsulation of "protein synthesis machinery" by sol–gel within a silica matrix and performance of the biohybrid system in the synthesis of proteins. (Reproduced from ref. 304 by permission of Wiley-VCH.)

approach, sub-cellular plant structures called thylakoids have been entrapped within a silica matrix formed in a sol–gel process from TEOS precursor.[305] Thylakoids are photosynthetic membranes enclosed within a double membrane that forms a structure known as the chloroplast, the centre for photosynthetic reactions, and are not stable when isolated. The encapsulation of these entities requires optimization of the sol–gel procedure, such as removing the by-product ethanol and controlling the pH before addition of thylakoids. The amount of silica and the subsequent degree of condensation of the silica framework formed around the thylakoids need also to be optimized to avoid a large amount of shrinkage of the matrix, which could destroy the entrapped biologicals due to an excessive pressure. The resulting biohybrids show the enhanced stability of thylakoids, which preserve their bioactivity up to one month. Thus, these biohybrids could be envisaged as new "living materials" for application as photocatalytic reactors capable of biomimicking photosynthetic processes, such as harvesting solar energy and splitting water molecules.[305]

In natural photosynthetic systems, the sunlight conversion processes to chemical energy are carried out by specific proteins containing chlorophyll. Chlorophyll *a* has been incorporated in silica–surfactant mesostructured materials[306]

Table 7 Applications of biohybrids involving biomass and living cells and microorganisms assembled to silica or silicates

Approach	Molecular precursor or building block	Cells or microorganisms	Properties	Application	Ref.
Molecular assembly	Organoalkoxysilanes	Microalga *Chlorella vulgaris*	High long-term stability, affinity towards heavy metal ions	Amperometric sensors in electroanalysis	Darder *et al.*, 2010 (ref. 318)
	Silicon alkoxide precursor	Pancreatic islets of Langerhans	High long-term stability, immunoisolation of transplanted tissue with minimal rejection and fibrosis	Bioartificial organs	Pope *et al.*, 1997 (ref. 322)
	Sodium silicate and colloidal silica	Cyanobacteria	Long-term stability, preservation of photoactivity	Photobioreactors	Rooke *et al.*, 2008, (ref. 333)
Blocks assembly	Bentonite	*Alga ulva* sp.	High biomass loading, easy recovery, possibility of reuse	Biosorbent for recovery of hexavalent uranium from water	Donat & Aytas, 2005 (ref. 337)
	Zeolite	Xylanolytic bacteria	Stable storage and easy application	Biogas production	Weiß *et al.*, 2010 (ref. 339)
	Sepiolite	Influenza virus	Preservation of antigenic activity, enhancement of immunogenic effect	Intranasal or intramuscular vaccines	E. Ruiz-Hitzky *et al.*, 2009 (ref. 324)

as well as in mesoporous silica modified with 1,4-butanediol.[307] Energy transfer in the hybrid has been investigated by photocurrent generation,[306] photoluminescence and photoreduction.[308,309] The arrangement of chlorophylls and the distance between adjacent molecules are crucial factors to determine the absorption/fluorescence, energy transfer efficiency, and charge separation probability as a result of molecular interactions. In the mesoporous host–guest systems, they are regulated by the pore size and different types of interactions which occur among chlorophyll aggregates in the mesopores.

In addition to create a nanospace mimicking protein environment for pigment immobilization, mesopores have been used to immobilize enzymes. One current research trend consists in the development of nanostructured materials biomimicking photosynthesis stabilizing the protein into nanoporous silica hybrids.[310,311] A photosynthetic reaction center (RC) pigment–protein complex was effectively adsorbed to mesoporous silica with a pore size of 7.9 nm.[312]

Although to a lesser extent than silica and mesoporous silica, clays can be also employed as supports for complex protein systems. An interesting example reports the intercalation of rhodopsin in an organoclay. Rhodopsin is a pigment of the retina that is responsible for both the formation of the photoreceptor cells and the first events in the perception of light. Humans have four photoreceptive proteins; one for twilight vision, and three others for color vision. The first is present in rod-cells, and its photoreceptive protein is called "rhodopsin" ($\lambda_{max} \sim 500$ nm). The latter are present in cone-cells, and called by their absorbing colors, such as "human blue" ($\lambda_{max} \sim 425$ nm), "human green" ($\lambda_{max} \sim 530$ nm), and "human red" ($\lambda_{max} \sim 560$ nm). In all cases, the chromophore is the protonated retinal Schiff base in the 11-*cis* isomeric state (RSB-11) that is bound to a lysine residue at the 7-th helix of the opsin. Protein structures composed of 7-transmembrane helices are common not only for the visual proteins but also for thousands of G-protein coupled receptors. Colour originates from the energy gap of the protonated RSB-11 between its electronically excited and ground states. Although artificial construction of wide colour tuning of the rhodopsin chromophore in other materials had been unsuccessful for a long time, Sasaki and Fukuhara[313] reported that the λ_{max} of all-*trans* RSB at 530 nm was achieved when mixed with a montmorillonite (Kunipia-F) modified with dimethyloctadecylamine (DOA) in benzene solution. Exchange of interlayer cations with DOA presumably leads to a great affinity for organic molecules, and hence all-*trans* RSB was intercalated and a proton was supplied from DOA. While the colour tuning mechanism is yet to be understood, the clay thereby became a potential protein-like model matrix. Thus, the assembly of protein and clay, completely different matrices, works similarly to RSB, the chromophore molecule of our vision.

4.2 Silica and silicate biohybrids incorporating whole cells and microorganisms

The preparation of biohybrid materials by combination of microorganisms and silica or silicates may follow molecular- and blocks-assembling processes, but the literature on this subject reflects a preferential use of sol–gel technology for the entrapment of biological entities such as living cells, yeasts, algae, lichens, virus and bacteria.[314] The interest in maintaining the viability of the immobilized entities depends on the type of application, and this aim appears to be a real challenge. Non-living biomass associated to silica or silicates is employed as biosorbent for removal of pollutants[315,316] or for electroanalytical purposes.[317,318] However, many other applications require biohybrids with encapsulated living cells and microorganisms, for use as bioreactors profiting from their metabolic activity for production of beneficial compounds,[319–321] as well as in other interesting applications within the biomedical field.[322–324] Selected examples of the possible applications of these materials are summarized in Table 7.

As occurs in the case of protein encapsulation, the soft conditions of the sol–gel procedure and the inertness of the formed silica are suitable for entrapment of living cells and microorganisms, but this process requires optimization in order to guarantee their viability.[325] One of the first actions taken for this purpose was the removal of harmful by-products such as alcohol released during the process prior to the incorporation of microorganisms.[326] An alternative procedure is the so-called Biosil process, consisting in the use of common

silicon alkoxide precursors in the vapour phase (chemical vapour deposition) which can react with surface-adsorbed H_2O and exposed –OH.[323] The addition of glycerol[327,328] or phospholipids[329] may also help to maintain the viability of entrapped cells within the silica cage, as it contributes to the formation of a protective layer surrounding them that avoids excessive drying of water. Organopolysiloxane precursors bearing biocompatible groups such as gluconolactone seem also helpful for this purpose, producing a biocompatible matrix.[330] The aim of all these approaches is to produce robust biohybrid materials in which the viability of cells is guaranteed, showing a long-term stability. These properties are of major importance for the diverse areas of application. The encapsulation of yeasts and algae is mainly addressed to application as bioreactors, profiting from the metabolic products of the encapsulated microorganisms, such as dyes for application in food and cosmetic industries[320] or with potential therapeutic uses.[328] These approaches also afford biohybrids for interesting biomedical applications in the field of tissue engineering and development of bioartificial organs, whose activity was proven after *in vivo* implantation.[322,323] Again, the transparency of the silica matrices can be utilized for monitoring the activity of the entrapped cells by means of spectroscopic techniques, in order to assess their long-term activity.[331] The brittleness of silica matrixes can be overcome by using organoalkoxysilanes, that produce flexible and resistant networks, free of fractures, in which non-living biomass can be entrapped (Fig. 16A and B). The biohybrids may be easily processed as thin coatings on electrode surfaces and applied in the electroanalytical determination of heavy metal ions in aqueous solution.[317,318] The algae could be also removed from the polysiloxane network leaving only a trace of the algal cells (Fig. 16C–E), resulting in imprinted materials prepared by a soft lithographic approach that could be potentially used as artificial receptors for electrochemical sensing of algae target species.[318]

Aqueous silicates may be more suitable silica precursors for encapsulation of living biological entities due to their biocompatibility and the low ecological impact of silicate chemistry, but they show several disadvantages such as the lack of diversity, flexibility, and processability.[332] Thus, silicon alkoxides are preferred for processing the biohybrids as thin films, for instance in biosensing applications, while the aqueous silicates and colloidal silica lead to bulk gel materials with potential application as bioreactors, for instance photobioreactors based on the immobilization of photosynthetic cyanobacterial strains.[333]

Porous materials processed by freeze-cast techniques from silica nanosols, resulting in the so-called biocers,[334] or by freeze-drying of silicate-based nanocomposites[335] may be a novel alternative to sol–gel technologies for entrapment of microorganisms such as yeasts, bacteria and algal cells. These open structures facilitate the accessibility of nutrients, and in the case of macroporous nanocomposites, the growth and proliferation of cells inside the pores was confirmed,[335] which has not been reported in the case of cells encapsulated in silica-based matrices.

Although to a lesser extent than silica, different types of natural and synthetic silicates have been also tested as

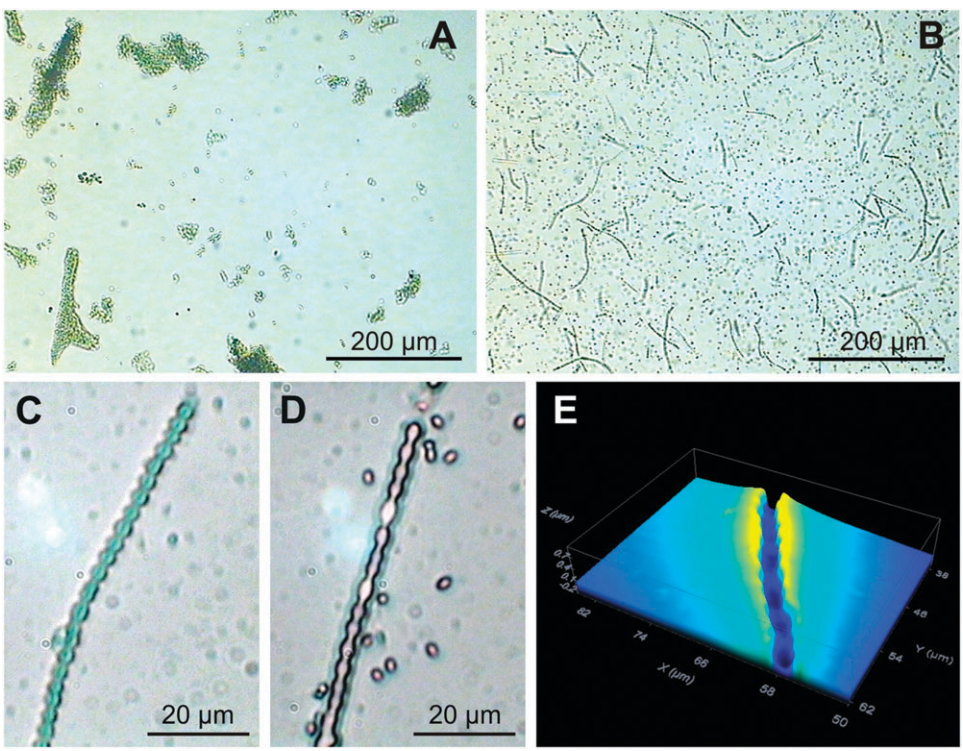

Fig. 16 (A) *Chlorella vulgaris* and (B) *Anabaena sp. PCC7120* algal cells entrapped in polysiloxane networks. (C) Imprinting of the polysiloxane by soft-lithography technique with the chain of Anabaena cells acting as template during polycondensation and aging of the xerogel film, and (D, E) trace on the dry xerogel after removal of algal cells. Images A–D taken on an optical microscope and image E with a confocal microscope. (More information in ref. 318.)

supports for immobilization of living cells and microorganisms. In contrast to encapsulation by sol–gel processes, the association of biological entities to silicates proceeds through adsorption on the surface of the inorganic solids. The huge size of this type of organisms, ranging from 50 nm in the case of viruses up to 10 μm in most cells, also impede the access to the galleries of layered silicates, so that these entities are associated to the external surface of silicates. Recent studies confirmed that silicates such as montmorillonite and kaolinite, used as biocompatible supports of several types of bacteria, have positive effects in the growth of assembled microorganisms,[336] which may be partially attributed to the removal of metabolic inhibitors or to the buffering of pH by the clay minerals. Thus, these silicates may create a beneficial environment that enhances the biodegradation activity of the supported bacteria.

Non-living biomass associated to silicates may be employed as biosorbent for removal of pollutants. Thus, a biosorbent of radioactive species was prepared by assembly of low-cost and available components, *Alga ulva* sp. and sodium bentonite, and successfully applied to the recovery of hexavalent uranium ions from water.[337] Similar biosorbents for removal of heavy-metal ions were based on yeast cells assembled to the fibrous silicate sepiolite.[338] The use of supported biomass is advantageous, since it allows higher biomass loadings, easy recovery from the reaction mixture and possibility of reusing the biomass. In addition to batch experiments, the supported biomass can also constitute the stationary phase of columns. Other interesting applications of biohybrids based on silicates and living microorganisms are related to the areas of energy production and biomedicine. An example of the former is the production of biogas, a valuable source of renewable energy, using a enriched hemicellulolytic bacteria immobilised on an activated zeolite, loaded with trace metal elements, which is able to enhance the microbial activity.[339] A recent work has reported the preparation of vaccines against influenza, based on the assembly of viral particles to sepiolite fibres previously modified with the polysaccharide xanthan to increase the retention of virus.[324] The silicate in this biohybrid acts not only as a carrier, but also as an adjuvant that contributes to enhance the immune response. Another important result of this work is that the assembly to the silicate surface does not reduce the antigenic properties of the supported virus.[324]

5. Conclusion

From a simplistic point of view, bottom–up strategies for development of hybrids and biohybrids involving silica and silicates, consist basically in the two following approaches.

(i) The direct assembly of silica-based blocks already prepared and organic species mainly with the aim to introduce functionality to the inorganic counterpart. This is for instance the case of intercalation processes, grafting reactions or direct adsorptions on silica/silicate surfaces.

(ii) The assembly of organic and inorganic species from molecular precursors that drive to the building of hybrid materials using the components to be joined together. This is the case of sol–gel processes resulting in a silica matrix entrapping organic and biological species.

Discussion about hybrids and biohybrids of very similar composition but prepared by these two approaches has been introduced during this review trying to illustrate the different characteristics that can be exhibited by the designed materials depending on the used synthesis strategy. More complex preparative methods that combine both type of strategies are increasingly applied with a view to develop new sophisticated multifunctional nanostructured materials. Of particular relevance is the preparation of biomimetic and bioinspired hybrid systems, using the above-discussed principles and strategies, with the aim to provide a multifunctionality on a level to that found in Nature.

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References

1 *Functional Hybrid Materials*, ed. P. Gómez-Romero and C. Sánchez, Wiley-VCH, Weinheim, Germany, 2004.
2 G. Ozin and A. Arsenault, *Nanochemistry: A Chemical Approach to Nanomaterials*, Royal Society of Chemistry, Cambridge, UK, 2005, ch. 10.
3 *Colloids and Colloid Assemblies: Synthesis, Modification, Organization and Utilization of Colloid Particles*, ed. F. Caruso, Wiley-VCH, Weinheim, 2003.
4 *Hybrid Materials: Synthesis, Characterization, and Applications*, ed. G. Kickelbick, Wiley-VCH, Weinheim, Germany, 2007.
5 *Bottom–up Nanofabrication: Supramolecules, Self-Assemblies, and Organized Films*, ed. K. Ariga and H. S. Nalwa, American Sci. Pub., Stevenson Ranch, CA, USA, 2009.
6 *Polymer-Clay Nanocomposites*, ed. T. J. Pinnavaia and G. W. Beall, John Wiley and Sons, West Sussex, UK, 2000.
7 E. Ruiz-Hitzky, *Chem. Rec.*, 2003, **3**, 88–100.
8 M. Darder, P. Aranda and E. Ruiz-Hitzky, *Adv. Mater.*, 2007, **19**, 1309–1319.
9 E. Ruiz-Hitzky, P. Aranda and M. Darder, in *Bottom-Up Nanofabrication: Supramolecules, Self-Assemblies, and Organized Films*, ed. K. Ariga and H. S. Nalwa, American Sci. Pub., Stevenson Ranch, CA, 2009, vol. 3, ch. 2, pp. 39–76.
10 E. Ruiz-Hitzky, M. Darder, P. Aranda and K. Ariga, *Adv. Mater.*, 2010, **22**, 323–336.
11 E. Ruiz-Hitzky, *Mol. Cryst. Liq. Cryst. Inc. Nonlinear Opt.*, 1988, **161**, 433–452.
12 C. Sanchez, G. J. A. A. Soler-Illia, F. Ribot, T. Lalot, C. R. Mayer and V. Cabuil, *Chem. Mater.*, 2001, **13**, 3061–3083; C. Sanchez, B. Julián, P. Belleville and M. Popall, *J. Mater. Chem.*, 2005, **15**, 3559–3592.
13 K. Ariga, J. P. Hill, M. V. Lee, A. Vinu, R. Charvet and S. Acharya, *Sci. Technol. Adv. Mater.*, 2008, **9**, art.#014109 (96pp); K. Ariga, A. Vinu, J. P. Hill and T. Mori, *Coord. Chem. Rev.*, 2007, **251**, 2562–2591.
14 E. Ruiz-Hitzky, in *Functional Hybrid Materials*, ed. P. Gómez-Romero and C. Sánchez, Wiley-VCH, Weinheim, 2004, ch. 2, pp. 15–49.
15 C. Tanford, *The Hydrophobic Effect: Formation of Micelles and Biological Membranes*, Krieger, Malabar, FL, USA, 1991.
16 J. H. Clint, *Surfactant Aggregation*, Blackie, New York, NY, USA, 1992.
17 A. Ulman, *An Introduction to Ultrathin Organic Films*, Academic Press, San Diego, CA, USA, 1991.
18 *Interactions of Surfactants with Polymers and Proteins*, ed. E. D. Goddard and K. P. Anathapadmanabhan, CRC Press Inc., Boca Raton, FL, USA, 1993.

19 K. Sakata and T. Kunitake, *J. Chem. Soc., Chem. Commun.*, 1990, 504–506.
20 K. Sakata and T. Kunitake, *Chem. Lett.*, 1989, 2159–2162.
21 M. Dubois, Th. Guik-Krzywicki and B. Cabane, *Langmuir*, 1993, **9**, 673–680.
22 J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowitcz, C. T. Kresge, K. D. Schmitt, C. T. W. Chu, D. H. Olson, E. W. Sheppard and S. B. McMullen, *J. Am. Chem. Soc.*, 1992, **114**, 10834–10843.
23 A. Monnier, F. Schüth, Q. Huo, D. Kumar, D. Margolese, R. S. Maxwell, G. D Stucky, M. Krishnamurty, P. Petroff, A. Firouzi, M. Janicke and B. F. Chmelka, *Science*, 1993, **261**, 1299–1303.
24 C. T. Kresge, M. E. Leonowitcz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710–712.
25 M. Ogawa, *J. Am. Chem. Soc.*, 1994, **116**, 7941–7942.
26 M. Ogawa, *Chem. Commun.*, 1996, 1149–1150.
27 Y. Lu, R. Gangull, C. A. Drewien, M. T. Anderson, C. J. Brinker, W. Gong, Y. Guo, H. Soyez, B. Dunn, M. H. Huang and J. I. Zink, *Nature*, 1997, **389**, 364–368.
28 M. Ogawa and N. Masukawa, *Microporous Mesoporous Mater.*, 2000, **38**, 35–41.
29 M. Ogawa, *Langmuir*, 1995, **11**, 4639–4641.
30 M. Ogawa, T. Igarashi and K. Kuroda, *Chem. Mater.*, 1998, **10**, 1382–1385.
31 M. H. Huang, B. S. Dunn, H. Soyez and J. I. Zink, *Langmuir*, 1998, **14**, 7331–7333.
32 E. Ruiz-Hitzky, V. Prévot and S. Letaïef, *Adv. Mater.*, 2002, **14**, 439–443.
33 R. K. Iler, *The Chemistry of Silica*, John Wiley & Sons, Inc., New York, 1979.
34 G. Lagaly, *Solid State Ionics*, 1986, **22**, 43–51.
35 G. Lagaly and K. Beneke, *Colloid Polym. Sci.*, 1991, **269**, 1198–1385.
36 M. Ogawa and K. Kuroda, *Bull. Chem. Soc. Jpn.*, 1997, **70**, 2593–2618.
37 E. Ruiz-Hitzky, P. Aranda and J. M. Serratosa, in *Handbook of Layered Materials*, ed. S. M. Auerbach, K. A. Carrado and P. K. Dutta, Marcel Dekker, New York, USA, 2004, ch. 3, pp. 91–154.
38 G. Lagaly, M. Ogawa and I. Dékány, in *Handbook of Clay Science*, ed. F. Bergaya, B. K. G. Theng and G. Lagaly, Elsevier, Amsterdam, 2006, vol. 1, ch. 7.3, pp. 309–377.
39 H. Heinz, H. Koerner, K. L. Anderson, R. A. Vaia and B. L. Farmer, *Chem. Mater.*, 2005, **17**, 5658–5669.
40 H. Heinz, R. A. Vaia, R. Krishnamoorti and B. L. Farmer, *Chem. Mater.*, 2007, **19**, 59–68.
41 E. Ruiz-Hitzky, P. Aranda, M. Darder and G. Rytwo, *J. Mater. Chem.*, 2010, **20**, 9306–9321.
42 J. W. Jordan, *J. Phys. Colloid Chem.*, 1950, **54**, 294–307.
43 T. Seki and K. Ichimura, *Macromolecules*, 1990, **23**, 31–35.
44 Y. Okahata and A. Shimizu, *Langmuir*, 1989, **5**, 954–959.
45 B. Wicklein, M. Darder, P. Aranda and E. Ruiz-Hitzky, *Langmuir*, 2010, **26**, 5217–5225.
46 F. Chivrac, E. Pollet, M. Schmutz and L. Avérous, *Biomacromolecules*, 2008, **9**, 896–900.
47 G. Lagaly, K. Beneke and A. Weiss, *Am. Miner.*, 1975, **60**, 642–649.
48 K. Beneke and G. Lagaly, *Am. Miner.*, 1977, **62**, 763–771.
49 T. Yanagisawa, T. Shimizu, K. Kuroda and C. Kato, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 988–992.
50 S. Inagaki, Y. Fukushima and K. Kuroda, *J. Chem. Soc., Chem. Commun.*, 1993, 680–681.
51 A. Galarneau, A. Barodawalla and T. J. Pinnavaia, *Nature*, 1995, **374**, 529–531.
52 M. E. Landis, B. A. Aufdembrink, P. Chu, I. D. Johnson, G. W. Kirker and M. K. Rubin, *J. Am. Chem. Soc.*, 1991, **113**, 3189–3191.
53 P. Aranda, C. Belver and E. Ruiz-Hitzky, in *Clays and Materials*, ed. L. F. Drummy, M. Ogawa and P. Aranda, CMS Workshop Lectures, vol. 17, The Clay Minerals Society, (e-Workshop Lectures), in press.
54 K. Kosuge and A. Tsunashima, *J. Chem. Soc., Chem. Commun.*, 1995, 2427–2428.
55 S. T. Wong and S. Cheng, *Chem. Mater.*, 1993, **5**, 770–777.
56 S. Letaïef and E. Ruiz-Hitzky, *Chem. Commun.*, 2003, 2996–2997.
57 S. Letaief, M. A. Martin-Luengo, P. Aranda and E. Ruiz-Hitzky, *Adv. Funct. Mater.*, 2006, **16**, 401–409.
58 E. Ruiz-Hitzky, B. Casal, P. Aranda and J. C. Galván, *Rev. Inorg. Chem.*, 2001, **21**, 125–159.
59 C. J. Pedersen, *J. Am. Chem. Soc.*, 1967, **89**, 7017–7036.
60 J. M. Lehn and J. P. Sauvage, *J. Chem. Soc. D*, 1971, 440–441.
61 *Progress in Macrocyclic Chemistry*, ed. R. M. Izatt and J. J. Christensen, John Wiley and Sons, New York, NY, USA, 1979 and 1981, vol. 1 and 2.
62 E. Ruiz-Hitzky and B. Casal, *Nature*, 1978, **276**, 596–597.
63 E. Ruiz-Hitzky and B. Casal, in *Chemical Reactions: in Organic and Inorganic Constrained Systems*, ed. R. Setton, NATO-ASI Series C Vol 165, D. Reidel, Pub. Comp., Dordrecht, 1986, pp. 179–189.
64 B. Casal, P. Aranda, J. Sanz and E. Ruiz-Hitzky, *Clay Miner.*, 1994, **29**, 191–203.
65 B. Casal, E. Ruiz-Hitzky, L. Van Vaeck and F. C. Adams, *J. Inclusion Phenom.*, 1988, **6**, 107–118 (1988).
66 P. Aranda, B. Casal, J. J. Fripiat and E. Ruiz-Hitzky, *Langmuir*, 1994, **10**, 1207–1212.
67 P. Aranda, J. C. Galván, B. Casal and E. Ruiz-Hitzky, *Electrochim. Acta*, 1992, **37**, 1573–1577.
68 P. Aranda, J. C. Galván, B. Casal and E. Ruiz-Hitzky, *Colloid Polym. Sci.*, 1994, **272**, 712–720.
69 J. C. Galván, P. Aranda, J. M. Amarilla, B. Casal and E. Ruiz-Hitzky, *J. Mater. Chem.*, 1993, **3**, 687–688.
70 P. Aranda, A. Jiménez-Morales, J. C. Galván, B. Casal and E. Ruiz-Hitzky, *J. Mater. Chem.*, 1995, **5**, 817–825.
71 E. Ruiz-Hitzky, P. Aranda, B. Casal and J. C. Galván, *Adv. Mater.*, 1995, **7**, 180–184.
72 A. Jiménez-Morales, P. Aranda, J. C. Galván and E. Ruiz-Hitzky, in *Organic/Inorganic Hybrid Materials*, ed. R. M. Laine, C. Sanchez, C. J. Brinker and E. Giannelis, Warrendale, 1998, MRS Symposium Proceedings, vol. 519, pp. 211–216.
73 E. Ruiz-Hitzky, J. C. Galván, P. Aranda and A. Jiménez-Morales, *Spanish Pat.*, 2160052, 2001.
74 M. Colilla, P. Aranda, M. Darder and E. Ruiz-Hitzky, *C. R. Chim.*, 2010, **13**, 227–236.
75 A. Jiménez-Morales, P. Aranda and J. C. Galván, *J. Mater. Process. Technol.*, 2003, **143–144**, 5–10.
76 T. G. Waddell and D. E. Leyden, *J. Org. Chem.*, 1981, **46**, 2406–2407.
77 J. S. Bradshaw, R. L. Bruening, K. E. Krakowiak, B. J. Tarbet, M. L. Bruening, R. M. Izatt and J. J. Christensen, *J. Chem. Soc., Chem. Commun.*, 1988, 812–814.
78 M. Nakajima, K. Kimura and T. Shono, *Anal. Chem.*, 1983, **55**, 463–467.
79 T. Iwachido, H. Naito, F. Samukawa, K. Ishimaru and K. Tôe, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 1475–1480.
80 L. F. Lindoy, *The Chemistry of Macrocyclic Ligand Complexes*, Cambridge University Press, Cambridge, UK, 1989.
81 K. Kimura and T. Shono, *J. Liq. Chromatogr.*, 1982, **5**, 223–255.
82 E. Blasius, K. P. Janzen, W. Klein, H. Klotz, V. B. Nguyen, T. Nguyen-Tien, R. Pfeiffer, G. Scholten, H. Simon, H. Tockemer and A. Toussaint, *J. Chromatogr., A*, 1980, **201**, 147–166.
83 E. Blasius and K. P. Janzen, *Isr. J. Chem.*, 1985, **26**, 25–34.
84 R. M. Izatt, R. L. Bruening, M. L. Bruening, B. J. Tarbet, K. E. Krakowiak, J. S. Bradshaw and J. J. Christensen, *Anal. Chem.*, 1988, **60**, 1825–1826.
85 G. Schulz-Ekloff, D. Wöhrle, B. van Duffel and R. A. Schoonheydt, *Microporous Mesoporous Mater.*, 2002, **51**, 91–138.
86 F. H. Dickey, *Proc. Natl. Acad. Sci. U. S. A.*, 1949, **35**, 227–229.
87 G. Wulff, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1812–1832.
88 B. Sellergren, *Angew. Chem., Int. Ed.*, 2000, **39**, 1031–1037.
89 D. Levy and D. Avnir, *J. Photochem. Photobiol., A*, 1991, **57**, 41–63.
90 D. Higgins and M. Collinson, *Langmuir*, 2005, **21**, 9023–9031.
91 A. Makishima and T. Tani, *J. Am. Ceram. Soc.*, 1986, **69**, C72–C74.
92 C. Sanchez, B. Lebeau, F. Chaput and J. P. Boilot, *Adv. Mater.*, 2003, **15**, 1969–1994.
93 P. Innocenzi and B. Lebeau, *J. Mater. Chem.*, 2005, **15**, 3821–3831.
94 C. Sanchez, B. Lebeau, F. Chaput and J. P. Boilot, in *Functional Hybrid Materials*, ed. P. Gomez-Romero and C. Sanchez, Wiley-VCH, Weinheim, 2004, ch. 5, p. 122–171.

95 M. Zayat, P. García-Parejo and D. Levy, *Chem. Soc. Rev.*, 2007, **36**, 1270–1281.
96 M. Ogawa and K. Kuroda, *Chem. Rev.*, 1995, **95**, 399–438.
97 M. Ogawa, in *Handbook of Layered Materials*, ed. S. M. Auerbach, K. A. Carrado and P. K. Dutta, Marcell Dekker, New York, NY, 2004, ch. 5, pp. 191–259.
98 M. Ogawa and J. Photochem. Photobiol. C, *J. Photochem. Photobiol., C*, 2002, **3**, 129–146.
99 W. S. Han, H. Y. Lee, S. H. Jung, S. J. Lee and J. H. Jung, *Chem. Soc. Rev.*, 2009, **38**, 1904–1915.
100 H. J. Kim, S. J. Lee, J. H. Jung and J. S. Kim, *Adv. Mater.*, 2008, **20**, 3229–3234.
101 T. Tani, *Photographic Sensitivity*, Oxford University Press, New York, 1995.
102 M. Ogawa, R. Kawai and K. Kuroda, *J. Phys. Chem.*, 1996, **100**, 16218.
103 F. López-Arbeloa, V. Martınez-Martnez, T. Arbeloa and I. López-Arbeloa, *J. Photochem. Photobiol., C*, 2007, **8**, 85–108.
104 W. Xu and D. L. Akins, *J. Phys. Chem. B*, 2002, **106**, 1991–1994.
105 S. Takagi, T. Shimada, T. Yui and H. Inoue, *Chem. Lett.*, 2001, 128–129.
106 P. Wlodarczyk, S. Komarneni, R. Roy and W. B. White, *J. Mater. Chem.*, 1996, **6**, 1967–1969.
107 R. Sasai, T. Itoh, W. Ohmori, H. Itoh and M. Kusunoki, *J. Phys. Chem. C*, 2009, **113**, 415–421.
108 J. L. Colon, C. Y. Yang, A. Clearfield and C. R. Martin, *J. Phys. Chem.*, 1988, **92**, 5777–5781.
109 M. Ogawa, M. T. Nakamura, J. Mori and K. Kuroda, *J. Phys. Chem. B*, 2000, **104**, 8554–8556.
110 M. Ogawa, K. Kuroda and T. Nakamura, *Chem. Lett.*, 2002, 632–633.
111 M. Sohmiya, Y. Sugahara and M. Ogawa, *J. Phys. Chem. B*, 2007, **111**, 8836–8841.
112 M. Ogawa, M. Tsujimura and K. Kuroda, *Langmuir*, 2000, **16**, 4202–4206.
113 N. Kakegawa and M. Ogawa, *Langmuir*, 2004, **20**, 7004–7009.
114 A. J. Aznar and E. Ruiz-Hitzky, *Mol. Cryst. Liq. Cryst.*, 1988, **161**, 459–469.
115 M. H. Lim, C. F. Blanford and A. Stein, *Chem. Mater.*, 1998, **10**, 467–470.
116 I. Diaz, F. Mohino, T. Blasco, E. Sastre. and J. Pérez-Pariente, *Microporous Mesoporous Mater.*, 2005, **80**, 33–42.
117 D. Dubé, M. Rat, F. Béland and S. Kaliaguine, *Microporous Mesoporous Mater.*, 2008, **111**, 596–603.
118 X. Feng, G. E. Fryxell, L. Q. Wang, A. Y. Kim, J. Liu and K. M. Kemner, *Science*, 1997, **276**, 923–926.
119 F. de Juan and Ruiz-Hitzky, *Adv. Mater.*, 2000, **12**, 430–432.
120 E. Gutierrez, A. J. Aznar and E. Ruiz-Hitzky, in *Heterogeneous Catalysis and Fine Chemicals II*, ed. M. Guisnet, J. Barrault, C. Bouchoule, D. Duprez, G. Pérot, R. Maurel and C. Montassier, Elsevier, Amsterdam, 1991, pp. 539–547.
121 A. J. Aznar, J. Sanz and E. Ruiz-Hitzky, *Colloid Polym. Sci.*, 1992, **270**, 165–176.
122 Y. Ide, G. Ozaki and M. Ogawa, *Langmuir*, 2009, **25**, 5276–5281.
123 R. Gupta, S. Paul. and R. Gupta, *J. Mol. Catal. A: Chem.*, 2007, **266**, 50–54.
124 P. F. Siril, A. D. Davison, J. K. Randhawa and D. R. Brown, *J. Mol. Catal. A: Chem.*, 2007, **267**, 72–78.
125 E. Ruiz-Hitzky and J. M. Rojo, *Nature*, 1980, **287**, 28–30.
126 A. Gómez-Avilés, M. Darder, P. Aranda and E. Ruiz-Hitzky, *Angew. Chem., Int. Ed.*, 2007, **46**, 923–925.
127 H. C. Kolb, M. G. Finn and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2001, **40**, 2004–2021.
128 F. Santoyo-Gonzalez and F. Hernandez-Mateo, *Chem. Soc. Rev.*, 2009, **38**, 3449–3462.
129 E. Ruiz-Hitzky and A. Van Meerbeek, in *Handbook of Clay Science*, ed. F. Bergaya, B. K. G. Theng and G. Lagaly, Elsevier, Amsterdam, 2006, vol. 1, ch. 10.3, pp. 583–621.
130 E. Ruiz-Hitzky and P. Aranda, *Adv. Mater.*, 1990, **2**, 545–547.
131 P. Aranda and E. Ruiz-Hitzky, *Chem. Mater.*, 1992, **4**, 1395–1403.
132 P. Aranda and E. Ruiz-Hitzky, *Acta Polym.*, 1994, **45**, 59–67.
133 P. Aranda and E. Ruiz-Hitzky, *Appl. Clay Sci.*, 1999, **15**, 119–135.
134 P. Aranda, Y. Mosqueda, E. Perez-Cappe and E. Ruiz-Hitzky, *J. Polym. Sci., Part B: Polym. Phys.*, 2003, **41**, 3249–3263.
135 P. Aranda, in *Clay-Based Polymer Nanocomposites*, CMS Workshop Lectures Series, ed. K. A. Carrado and F. Bergaya, The Clay Minerals Society, Chantilly, VA, 2007, vol. 15, ch. 6, pp. 171–196.
136 R. A. Vaia, S. Vasudevan, W. Krawiec, L. G. Scanlon and E. P. Giannelis, *Adv. Mater.*, 1995, **7**, 154–156.
137 P. Aranda, M. Darder, R. Fernández-Saavedra, M. López-Blanco and E. Ruiz-Hitzky, *Thin Solid Films*, 2006, **495**, 104–112, and references therein.
138 P. Aranda, in *Conference Proceedings NanoAfrica 2009*, ed. S. Sinha Ray, Pretoria, 2009, paper 40.
139 L. J. Michot, O. Barrds, E. L. Hegg and T. J. Pinnavaia, *Langmuir*, 1993, **9**, 1794–1800.
140 E. Montarges, L. J. Michot, F. Lhote, T. Fablen and F. Villieras, *Clays Clay Miner.*, 1995, **43**, 417–426.
141 N. L. McFarlane, N. J. Wagner, E. W. Kaler and M. L. Lynch, *Langmuir*, 2010, **26**, 6262–6267.
142 A. A. Zaman, M. Bjelopavlic and B. M. Moudgil, *J. Colloid Interface Sci.*, 2000, **226**, 290–298.
143 F. Lafuma, K. Wong and B. Cabane, *J. Colloid Interface Sci.*, 1991, **143**, 9–21.
144 X. L. Wang, A. Mei, M. Li, Y. H. Lin and C. W. Nan, *J. Appl. Phys.*, 2007, **102**, Art. Numb. 054907.
145 Y. Liu, J. Y. Lee and L. Hong, *J. Power Sources*, 2004, **129**, 303–311.
146 M. Templin, A. Franck, A. Du Chesne, H. Leist, Y. Zhang, R. Ulrich, V. Schadler and U. Wiesner, *Science*, 1997, **278**, 1795–1798.
147 D. Y. Zhao, J. L. Feng, Q. S. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka and G. D. Stucky, *Science*, 1998, **279**, 548–552.
148 L. M. Bronstein, R. L. Karlinsey, Z. Yi, J. Carini, U. Werner-Zwanziger, P. V. Konarev, D. I. Svergun, A. Sanchez and S. Khan, *Chem. Mater.*, 2007, **19**, 6258–6265.
149 S. Kohjiya, K. Ochiai and S. Yamashita, *J. Non-Cryst. Solids*, 1990, **119**, 132–135.
150 K. Dahmouche, M. Atik, N. C. Mello, T. J. Bonagamba, H. Panepucci, P. Judeinstein and M. A. Aegerter, *Sol. Energy Mater. Sol. Cells*, 1998, **54**, 1–8.
151 I. Honma, S. Nomura and H. Nakajima, *J. Membr. Sci.*, 2001, **185**, 83–94.
152 M. Laridjani, E. Lafontaine, J. P. Bayle and P. Judeinstein, *J. Mater. Sci.*, 1999, **34**, 5945–5953.
153 R. A. Zoppi and M. C. Gonçalves, *Solid State Ionics*, 2002, **147**, 157–170.
154 L. M. Bronstein, R. L. Karlinsey, B. Stein and J. W. Zwanziger, *Solid State Ionics*, 2005, **176**, 559–570.
155 W. H. Binder and R. Sachsenhofer, *Macromol. Rapid Commun.*, 2008, **29**, 1097–1103.
156 T. H. Anderson, Y. Min, K. L. Weirich, H. Zeng, D. Fygenson and J. N. Israelachvili, *Langmuir*, 2009, **25**, 6997–7005, and references therein.
157 Y. Steinberg, A. Schroeder, Y. Talmon, J. Schmidt, R. L. Khalfin, Y. Cohen, J. M. Devoisselle, S. Begu and D. Avnir, *Langmuir*, 2007, **23**, 12024–12031.
158 D. R. Dunphy, T. M. Alam, M. P. Tate, H. W. Hillhouse, B. Smarsly, A. D. Collord, E. Carnes, H. K. Baca, R. Köhn, M. Sprung, J. Wang and C. J. Brinker, *Langmuir*, 2009, **25**, 9500–9509.
159 A. Galarneau, G. Renard, M. Mureseanu, A. Tourrette, C. Biolley, M. Choi, R. Ryoo, F. Di Renzo and F. Fajula, *Microporous Mesoporous Mater.*, 2007, **104**, 103–114.
160 K. Katagiri, K. Ariga and J. Kikuchi, *Chem. Lett.*, 1999, 661–662.
161 K. Katagiri, M. Hashizume, K. Ariga, T. Terashima and J. Kikuch, *Chem.–Eur. J.*, 2007, **13**, 5272–5281.
162 K. Katagiri, R. Hamasaki, K. Ariga and J. Kikuchi, *Langmuir*, 2002, **18**, 6709–6711.
163 K. Katagiri, R. Hamasaki, K. Ariga and J. Kikuchi, *J. Am. Chem. Soc.*, 2002, **124**, 7892–7893.
164 S. Ahmed and S. L. Wunder, *Langmuir*, 2009, **25**, 3682–3691.
165 T. Sanchez-Verdejo, T. Undabeytia, S. Nir, C. Maqueda and E. Morillo, *Environ. Sci. Technol.*, 2008, **42**, 5779–5784.
166 T. Sanchez-Verdejo, T. Undabeytia, S. Nir, J. Villaverde, C. Maqueda and E. Morillo, *J. Agric. Food Chem.*, 2008, **56**, 10192–10199.

167 T. Undabeytia, F. Sopena, T. Sanchez-Verdejo, J. Villaverde, S. Nir, E. Morillo and C. Maqueda, *Soil Sci. Soc. Am. J.*, 2010, **74**, 898–905.
168 B. Wicklein, M. Darder, P. Aranda and E. Ruiz-Hitzky, *Macla*, 2008, (9), 257–258.
169 S. Sinha Ray and M. Bousmina, *Prog. Mater. Sci.*, 2005, **50**, 962–1079.
170 F. Chivrac, E. Pollet and L. Avérous, *Mater. Sci. Eng., R*, 2009, **67**, 1–17.
171 T. Coradin, J. Allouche, M. Boissière and J. Livage, *Curr. Nanosci.*, 2006, **2**, 219–230.
172 Y. A. Shchipunov, A. Kojima and T. Imae, *J. Colloid Interface Sci.*, 2005, **285**, 574–580.
173 H. Maeda, M. Nakajima, T. Hagiwara, T. Sawaguchi and S. Yano, *J. Mater. Sci.*, 2006, **41**, 5646–5656.
174 B. Leng, X. Chen, Z. Shao and W. Ming, *Small*, 2008, **4**, 755–758.
175 M. Darder and E. Ruiz-Hitzky, in *Clay-Based Polymer Nanocomposite*, Workshop Lectures Series, ed. K. A. Carrado and F. Bergaya, The Clay Minerals Society, Chantilly, VA, 2007, vol. 15, ch. 8, pp. 233–257.
176 T. Coradin, J. Allouche, M. Boissière and J. Livage, *Curr. Nanosci.*, 2006, **2**, 219–230.
177 S. Sh. Rashidova, D. Sh. Shakarova, O. N. Ruzimuradov, D. T. Satubaldieva, S. V. Zalyalieva, O. A. Shpigun, V. P. Varlamov and B. D. Kabulov, *J. Chromatogr., B: Anal. Technol. Biomed. Life Sci.*, 2004, **800**, 49–53.
178 J. W. Rhim and P. K. W. Ng, *Crit. Rev. Food Sci. Nutr.*, 2007, **47**, 411–433.
179 A. Khare and S. Deshmukh, *J. Plastic Film Sheeting*, 2006, **22**, 193–211.
180 A. Sorrentino, G. Gorrasi and V. Vittoria, *Trends Food Sci. Technol.*, 2007, **18**, 84–95.
181 F. Chivrac, O. Gueguen, E. Pollet, S. Ahzi, A. Makradi and L. Averous, *Acta Biomater.*, 2008, **4**, 1707–1714.
182 H.-M. Wilhelm, M.-R. Sierakowski, G. P. Souza and F. Wypych, *Polym. Int.*, 2003, **52**, 1035–1044.
183 S. D. Bhat and T. M. Aminabhavi, *Sep. Purif. Technol.*, 2006, **51**, 85–94.
184 S. D. Bhat, B. V. K. Naidu, G. Shanbhag, S. B. Halligudi, M. Sairam and T. M. Aminabhavi, *Sep. Purif. Technol.*, 2006, **49**, 56–63.
185 Y. L. Liu, C. Y. Hsu, Y. H. Su and J. Y. Lai, *Biomacromolecules*, 2005, **6**, 368–373.
186 V. Singh, S. Pandey, S. K. Singh and R. Sanghi, *J. Sol-Gel Sci. Technol.*, 2008, **47**, 58–67.
187 J. H. An and S. Dultz, *Clays Clay Miner.*, 2008, **56**, 549–557.
188 J. H. An and S. Dultz, *Appl. Clay Sci.*, 2007, **36**, 256–264.
189 M. Boissière, P. J. Meadows, R. Brayner, C. Hélary, J. Livage and T. Coradin, *J. Mater. Chem.*, 2006, **16**, 1178–1182.
190 A. W. Pan, B. B. Wu and J. M. Wu, *Chin. Chem. Lett.*, 2009, **20**, 79–83.
191 D. Depan, L. Saikia and R. P. Singh, *Macromol. Symp.*, 2010, **287**, 80–88.
192 C. Viseras, P. Cerezo, R. Sanchez, I. Salcedo and C. Aguzzi, *Appl. Clay Sci.*, 2010, **48**, 291–295.
193 X. Y. Wang, Y. M. Du and J. W. Luo, *Nanotechnology*, 2008, **19**, Art. 065707.
194 X. Y. Wang, X. F. Pei, Y. M. Du and Y. Li, *Nanotechnology*, 2008, **19**, Art. 375102.
195 V. Thomas, D. R. Dean and Y. K. Vohra, *Curr. Nanosci.*, 2006, **2**, 155–177.
196 M. Okamoto, in *Bio-inorganic Hybrid Nanomaterials: Strategies, Synthesis, Characterization and Application*, ed. E. Ruiz-Hitzky, K. Ariga and Y. Lvov, Wiley-VCH, Weinheim, Germany 2008, ch. 9, pp. 271–312.
197 M. S. Widmer and A. G. Mikos, in *Frontiers in Tissue Engineering*, ed. C. W. Patrick Jr., A. G. Mikos and L. V. McIntire, Elsevier Science Ltd, Oxford, 1998, ch. II.5, pp. 106–120.
198 K. S. Katti, D. R. Katti and R. Dash, *Biomed. Mater.*, 2008, **3**, 034122, Art. 034122.
199 D. Depan, A. P. Kumar and R. P. Singh, *Acta Biomater.*, 2009, **5**, 93–100.
200 M. V. Cabañas, J. Peña, J. Román and M. Vallet-Regí, *J. Biomed. Mater. Res., Part A*, 2006, **78A**, 508–514.
201 E.-J. Lee, D.-S. Shin, H.-E. Kim, H.-W. Kim, Y.-H. Koh and J.-H. Jang, *Biomaterials*, 2009, **30**, 743–750.
202 M. Darder, M. Colilla and E. Ruiz-Hitzky, *Chem. Mater.*, 2003, **15**, 3774–3780.
203 M. Darder, M. Colilla and E. Ruiz-Hitzky, *Appl. Clay Sci.*, 2005, **28**, 199–208.
204 M. Darder, M. López-Blanco, P. Aranda, A. J. Aznar, J. Bravo and E. Ruiz-Hitzky, *Chem. Mater.*, 2006, **18**, 1602–1610.
205 X. Hun and Z. J. Zhang, *Sens. Actuators, B*, 2008, **131**, 403–410.
206 G. H. Wang and L. M. Zhang, *J. Phys. Chem. B*, 2006, **110**, 24864–24868.
207 M. Schuleit and P. L. Luisi, *Biotechnol. Bioeng.*, 2001, **72**, 249–253.
208 S. W. Xu, Z. Y. Jiang, Y. Lu, H. Wu and W. K. Yuan, *Ind. Eng. Chem. Res.*, 2006, **45**, 511–517.
209 M. Kato, H. Saruwatari, K. Sakai-Kato and T. Toyo'oka, *J. Chromatogr., A*, 2004, **1044**, 267–270.
210 Q. F. Shi, Q. B. Li, D. Shan, Q. Fan and H. G. Xue, *Mater. Sci. Eng. C: Biomim. Supramol. Syst.*, 2008, **28**, 1372–1375.
211 X. J. Zhao, Z. B. Mai, X. H. Kang and X. Y. Zou, *Biosens. Bioelectron.*, 2008, **23**, 1032–1038.
212 K. Sangeetha and T. E. Abraham, *J. Appl. Polym. Sci.*, 2008, **107**, 2899–2908.
213 A. Tampieri, G. Celotti and E. Landi, *Anal. Bioanal. Chem.*, 2005, **381**, 568–576.
214 R. Murugan and S. Ramakrishna, *Compos. Sci. Technol.*, 2005, **65**, 2385–2406.
215 F. M. Fernandes, M. Darder, A. I. Ruiz, P. Aranda and E. Ruiz-Hitzky, in *Nanocomposites with Degradable Properties: Synthesis, Properties and Future Perspectives*, ed. V. Mittal, Oxford University Press, USA, 2011, ch. 9.
216 T. Coradin, J. Allouche, M. Boissiere and J. Livage, *Curr. Nanosci.*, 2006, **2**, 219–230.
217 R. Wetherbee, *Science*, 2002, **298**, 547–547; M. Sumper and E. Brunner, *Adv. Funct. Mater.*, 2006, **16**, 17–26.
218 C. W. P. Foo, S. V. Patwardhan, D. J. Belton, B. Kitchel, D. Anastasiades, J. Huang, R. R. Naik, C. C. Perry and D. L. Kaplan, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 9428–9433.
219 P. J. López, C. Gautier, J. Livage and T. Coradin, *Curr. Nanosci.*, 2005, **1**, 73–83.
220 S. V. Patwardhan, N. Mukherjee, M. Steinitz-Kannan and S. J. Clarson, *Chem. Commun.*, 2003, 1122–1123.
221 S. Smitha, P. Mukundan, P. K. Pillai and K. G. K. Warrier, *Mater. Chem. Phys.*, 2007, **103**, 318–322.
222 O. Talibudeen, *Nature*, 1950, **166**, 236–236; O. Talibudeen, *Trans. Faraday Soc.*, 1955, **51**, 582–590.
223 F. M. Fernandes, I. Manjubala and E. Ruiz-Hitzky, *Phys. Chem. Chem. Phys.*, DOI: 10.1039/c0cp00882f.
224 M. F. Desimone, C. Hélary, G. Mosser, M.-M. Giraud-Guille, J. Livage and T. Coradin, *J. Mater. Chem.*, 2010, **20**, 666–668.
225 D. Eglin, S. Maalheem, J. Livage and T. Coradin, *J. Mater. Sci.: Mater. Med.*, 2006, **17**, 161–167.
226 H. L. Zhu, J. Y. Shen, X. X. Feng, H. P. Zhang, Y. H. Guo and J. Y. Chen, *Mater. Sci. Eng., C*, 2010, **30**, 132–140.
227 J. P. Zheng, C. Z. Wang, X. X. Wang, H. Y. Wang, H. Zhuang and K. D. Yao, *React. Funct. Polym.*, 2007, **67**, 780–788.
228 H. Zhuang, J. P. Zheng, H. Gao and K. D. Yao, *J. Mater. Sci.: Mater. Med.*, 2007, **18**, 951–957.
229 A. A. Haroun, A. Gamal-Eldeen and D. R. K. Harding, *J. Mater. Sci.: Mater. Med.*, 2009, **20**, 2527–2540.
230 N. Olmo, M. A. Lizarbe and J. G. Gavilanes, *Biomaterials*, 1987, **8**, 67–69.
231 L. F. Drummy, H. Koerner, D. M. Phillips, J. C. McAuliffe, M. Kumar, B. L. Farmer, R. A. Vaia and R. R. Naik, *Mater. Sci. Eng. C: Biomimetic Supramol. Syst.*, 2009, **29**, 1266–1272.
232 L. Ren, K. Tsuru, S. Hayakawa and A. Osaka, *Biomaterials*, 2002, **23**, 4765–4773.
233 K. Tsuru, S. Hayakawa and A. Osaka, *J. Sol–Gel Sci. Technol.*, 2004, **32**, 201–205.
234 P. Li, J. P. Zheng, Y. L. Ma and K. D. Yao, *J. Appl. Polym. Sci.*, 2003, **88**, 322–326.
235 H. J. Bae, H. J. Park, S. I. Hong, Y. J. Byun, D. O. Darby, R. M. Kimmel and W. S. Whiteside, *LWT–Food Sci. Technol.*, 2009, **42**, 1179–1186.

236 S. Smitha, P. Shajesh, P. Mukundan and K. G. K. Warrier, *J. Sol–Gel Sci. Technol*., 2007, **42**, 157–163.
237 S. Smitha, P. Shajesh, P. Mukundan, T. D. R. Nair and K. G. K. Warrier, *Colloids Surf., B*, 2007, **55**, 38–43.
238 J. Allouche, M. Boissière, C. Hélary, J. Livage and T. Coradin, *J. Mater. Chem*., 2006, **16**, 3120–3125.
239 Z. Y. Wang, Y. Zhao, L. Ren, L. H. Jin, L. P. Sun, P. Yin, Y. F. Zhang and Q. Q. Zhang, *Nanotechnology*, 2008, **19**, Art. 445103.
240 D. Avnir, S. Braun, O. Lev and M. Ottolenghi, *Chem. Mater*., 1994, **6**, 1605–1614.
241 J. Livage, T. Coradin and C. Roux, in *Functional Hybrid Materials*, ed. P. Gómez-Romero and C. Sanchez, Wiley-VCH, Weinheim, Germany, 2004, ch. 11, p. 387–404.
242 D. Avnir, T. Coradin, O. Lev and J. Livage, *J. Mater. Chem*., 2006, **16**, 1013–1030.
243 V. B. Kandimalla, V. S. Tripathi and H. Ju, *Crit. Rev. Anal. Chem*., 2006, **36**, 73–106.
244 W. Jin and J. D. Brennan, *Anal. Chim. Acta*, 2002, **461**, 1–36.
245 L. M. Ellerby, C. R. Nishida, F. Nishida, S. A. Yamanaka, B. Dunn, J. S. Valentine and J. I. Zink, *Science*, 1992, **255**, 1113–1115.
246 I. Gill and A. Ballesteros, *Trends Biotechnol*., 2000, **18**, 282–296.
247 R. Gupta and N. K. Chaudhury, *Biosens. Bioelectron*., 2007, **22**, 2387–2399.
248 H. Frenkel-Mullerad and D. Avnir, *J. Am. Chem. Soc*., 2005, **127**, 8077–8081.
249 K. K. Flora and J. D. Brennan, *Chem. Mater*., 2001, **13**, 4170–4179.
250 R. B. Bathia and C. J. Brinker, *Chem. Mater*., 2000, **12**, 2434–2441.
251 M. L. Ferrer, F. del Monte and D. Levy, *Chem. Mater*., 2002, **14**, 3619–3621.
252 I. Gill and A. Ballesteros, *J. Am. Chem. Soc*., 1998, **120**, 8587–8598.
253 Y. A. Shchipunov, in *Bio-inorganic Hybrid Nanomaterials*, ed. E. Ruiz-Hitzky, K. Ariga and Y. Lvov, Wiley-VCH, Weinheim, 2008, ch. 3, pp. 75–112.
254 Y. Yi, R. Neufeld and S. Kermasha, *J. Sol–Gel Sci. Technol*., 2007, **43**, 161–170.
255 M. Kato, K. Sakai-Kato, N. Matsumoto and T. Toyo'oka, *Anal. Chem*., 2002, **74**, 1915–1921.
256 A. Llobera, V. J. Cadarso, M. Darder, C. Domínguez and C. Fernández-Sánchez, *Lab Chip*, 2008, **8**, 1185–1190.
257 M. Schuleit and P. L. Luisi, *Biotechnol. Bioeng*., 2001, **72**, 249–253.
258 M. Portaccio, M. Lepore, B. Della Ventura, O. Stoilova, N. Manolova, I. Rashkov and D. G. Mita, *J. Sol–Gel Sci. Technol*., 2009, **50**, 437–448.
259 A. Vinu, N. Gokulakrishnan, T. Mori and K. Ariga, in *Bio-inorganic Hybrid Nanomaterials*, ed. E. Ruiz-Hitzky, K. Ariga and Y. Lvov, Wiley-VCH, Weinheim, Germany 2008, ch. 4, pp. 113–157.
260 S. Hudson, E. Magner and J. Cooney, *Angew. Chem., Int. Ed*., 2008, **47**, 8582–8594.
261 M. Tortajada, D. Ramón, D. Beltrán and P. Amorós, *J. Mater. Chem*., 2005, **15**, 3859–3868.
262 M. Hartmann, *Chem. Mater*., 2005, **17**, 4577–4593.
263 Y. Han, S. S. Lee and J. Y. Ying, *Chem. Mater*., 2006, **18**, 643–649.
264 A. Vinu, V. Murugesan and M. Hartmann, *J. Phys. Chem. B*, 2004, **108**, 7323–7330.
265 Y. Han, S. S. Lee and J. Y. Ying, *Chem. Mater*., 2006, **18**, 643–649.
266 I. I. Slowing, B. G. Trewyn and V. S.-Y. Lin, *J. Am. Chem. Soc*., 2007, **129**, 8845–8849.
267 F. Schwochow and L. Puppe, *Angew. Chem., Int. Ed. Engl*., 1975, **14**, 620–628.
268 F. N. Serralha, J. M. Lopes, F. Lemos, D. M. F. Prazeres, M. R. Aires-Barros, J. M. S. Cabral and F. Ramôa-Ribeiro, *J. Mol. Catal. B: Enzym*., 1998, **4**, 303–311.
269 P. Tavolaro, A. Tavolaro and G. Martino, *Colloids Surf., B*, 2009, **70**, 98–107.
270 A. Corma, V. Fornes and F. Rey, *Adv. Mater*., 2002, **14**, 71–74.
271 M. Ergezinger, M. Bohnet, S. Berensmeier and K. Bucholz, *Eng. Life Sci*., 2006, **6**, 481–487.
272 Y. Zhang, Y. Liu, J. Kong, P. Yang, Y. Tang and B. Liu, *Small*, 2006, **2**, 1170–1173.
273 C. Mousty, *Anal. Bioanal. Chem*., 2009, **396**, 315–325.
274 L. E. Ensmiger and J. E. Gieseking, *Soil Sci*., 1939, **48**, 467–474.
275 A. D. McLaren and G. H. Peterson, *Nature*, 1961, **192**, 960–961.
276 I. Lozzi, L. Calamai, P. Fusi, M. Bosetto and G. Stotzky, *Soil Biol. Biochem*., 2001, **33**, 1021–1028.
277 S. Peng, Q. Gao, Q. Wang and J. Shi, *Chem. Mater*., 2004, **16**, 2675–2684.
278 C. Mousty, S. Cosnier, M. Sanchez-Paniagua Lopez, E. Lopez-Cabarcos and B. Lopez-Ruiz, *Electroanalysis*, 2007, **19**, 253–258.
279 E. Lojou, M. T. Giudici-Orticoni and P. Bianco, *J. Electroanal. Chem*., 2005, **579**, 199–213.
280 S. Cosnier, C. Mousty, C. Gondran and A. Lepellec, *Mater. Sci. Eng., C*, 2006, **26**, 442–447.
281 A. A. Safari Sinegani, G. Emtiazi and H. Shariatmadari, *J. Colloid Interface Sci*., 2005, **290**, 39–44.
282 G. J. Chen, M. C. Yen, J. M. Wang, J. J. Lin and H. C. Chiu, *Bioconjugate Chem*., 2008, **19**, 138–144.
283 A. J. Patil and S. Mann, *J. Mater. Chem*., 2008, **18**, 4605–4615.
284 A. J. Patil, E. Muthusamy and S. Mann, *J. Mater. Chem*., 2005, **15**, 3838–3843.
285 V. Caballero, F. M. Bautista, J. M. Campelo, D. Luna, J. M. Marinas, A. A. Romero, J. M. Hidalgo, R. Luque, A. Macario and G. Giordano, *Process Biochem*., 2009, **44**, 334–342.
286 M. E. Sedaghat, M. Ghiaci, H. Aghaei and S. Soleimanian-Zad, *Appl. Clay Sci*., 2009, **46**, 131–135.
287 G. Sanjay and S. Sugunan, *J. Porous Mater*., 2007, **15**, 359–367.
288 D. Knopp, D. P. Tang and R. Niessner, *Anal. Chim. Acta*, 2009, **647**, 14–30.
289 L. M. F. Lopes, A. R. Garcia, A. Fidalgo and L. M. Ilharco, *Langmuir*, 2009, **25**, 10243–10250.
290 A. Pierre, J. Bonnet, A. Vekris and J. Portier, *J. Mater. Sci.: Mater. Med*., 2001, **12**, 51–55.
291 S. Satoh, B. Fugetsu, M. Nomizu and N. Nishi, *Polym. J*., 2005, **37**, 94–101.
292 M. Yamada and A. Hamai, *Anal. Chim. Acta*, 2009, **647**, 249–254.
293 M. Yamada and H. Aono, *Polymer*, 2008, **49**, 4658–4665.
294 F. Gao, P. Botella, A. Corma, J. Blesa and L. Dong, *J. Phys. Chem. B*, 2009, **113**, 1796–1804.
295 P. Cai, Q. Huang, M. Li and W. Liang, *Colloids Surf., B*, 2008, **62**, 299–306.
296 P. Cai, Q.-Y. Huang and X.-W. Wezhan, *Environ. Sci. Technol*., 2006, **40**, 2971–2976.
297 M. H. Shamsi and K. E. Geckeler, *Nanotechnology*, 2008, **19**, 075604, Art. 075604.
298 A. J. Patil, M. Li, E. Dujardin and S. Mann, *Nano Lett*., 2007, **7**, 2660–2665.
299 F.-H. Lin, C.-H. Chen, W. T. K. Cheng and T.-F. Kuo, *Biomaterials*, 2006, **27**, 3333–3338.
300 M. Kawase, Y. Hayashi, F. Kinoshita, E. Yamato, J. Miyazaki, J. Yamakawa, T. Ishida, M. Tamura and K. Yagi, *Biol. Pharm. Bull*., 2004, **27**, 2049–2051.
301 G.-Y. Xu, J.-S. Fan and K. Jiao, *Appl. Clay Sci*., 2008, **40**, 119–123.
302 H. O'Neill and E. Greenbaum, *Chem. Mater*., 2005, **17**, 2654–2661.
303 C. F. Meunier, P. Van Cutsem, Y.-U. Kwon and B.-L. Su, *J. Mater. Chem*., 2009, **19**, 1535–1542.
304 K.-O. Kim, S. Y. Lim, G.-H. Hahn, S. H. Lee, C. B. Park and D.-M. Kim, *Biotechnol. Bioeng*., 2009, **102**, 303–307.
305 C. F. Meunier, P. Van Cutsem, Y.-U. Kwon and B.-L. Su, *J. Mater. Chem*., 2009, **19**, 1535–1542.
306 H. Furukawa, N. Inoue, T. Watanabe and K. Kuroda, *Langmuir*, 2005, **21**, 3992–3997.
307 S. Murata, H. Hata, T. Kimura, Y. Sugahara and K. Kuroda, *Langmuir*, 2000, **16**, 7106–7108.
308 T. Itoh, K. Yano, Y. Inada and Y. Fukushima, *J. Am. Chem. Soc*., 2002, **124**, 13437–13441.
309 T. Itoh, K. Yano, T. Kajino, S. Itoh, Y. Shibata, H. Mino, R. Miyamoto, Y. Inada, S. Iwai and Y. Fukushima, *J. Phys. Chem. B*, 2004, **108**, 13683–13687.
310 H. Takahashi, B. Li, T. Sasaki, C. Miyazaki, T. Kajino and S. Inagaki, *Chem. Mater*., 2000, **12**, 3301–3305.
311 I. Oda, K. Hirata, S. Watanabe, Y. Shibata, T. Kajino, Y. Fukushima, S. Iwai and S. Itoh, *J. Phys. Chem. B*, 2006, **110**, 1114–1120.

312 I. Oda, M. Iwaki, D. Fujita, Y. Tsutsui, S. Ishizaka, M. Dewa, M. Nango, T. Kajino, Y. Fukushima and S. Itoh, *Langmuir*, 2010, **26**, 13399–13406.
313 M. Sasaki and T. Fukuhara, *Photochem. Photobiol.*, 1997, **66**, 716–718.
314 J. Livage, T. Coradin and C. Roux, in *Functional Hybrid Materials*, ed. P. Gómez-Romero and C. Sanchez, Wiley-VCH, Weinheim, 2004, ch. 11, pp. 387–404.
315 H. Bağ, M. Lale and A. R. Türker, *Talanta*, 1998, **47**, 689–696.
316 R. Donat and S. Aytas, *J. Radioanal. Nucl. Chem.*, 2005, **265**, 107–114.
317 M. Darder, M. Colilla, N. Lara and E. Ruiz-Hitzky, *J. Mater. Chem.*, 2002, **12**, 3660–3664.
318 M. Darder, P. Aranda, L. Burgos-Asperilla, A. Llobera, V. J. Cadarso, C. Fernández-Sánchez and E. Ruiz-Hitzky, *J. Mater. Chem.*, 2010, **20**, 9362–9369.
319 N. Nassif, C. Roux, T. Coradin, O. M. M. Bouvet and J. Livage, *J. Mater. Chem.*, 2004, **14**, 2264–2268.
320 D. Fiedler, U. Hager, H. Franke, U. Soltmann and H. Böttcher, *J. Mater. Chem.*, 2007, **17**, 261–266.
321 S. Weiß, M. Tauber, W. Somitsch, R. Meincke, H. Müller, G. Berg and G. M. Guebitz, *Water Res.*, 2010, **44**, 1970–1980.
322 E. J. A. Pope, K. Braun and C. M. Peterson, *J. Sol–Gel Sci. Technol.*, 1997, **8**, 635–639.
323 G. Carturan, R. Dal Toso, S. Boninsegna and R. Dal Monte, *J. Mater. Chem.*, 2004, **14**, 2087–2098.
324 E. Ruiz-Hitzky, M. Darder, P. Aranda, M. A. Martín del Burgo and G. del Real, *Adv. Mater.*, 2009, **21**, 4167–4171.
325 C. F. Meunier, P. Dandoy and B.-L. Su, *J. Colloid Interface Sci.*, 2010, **342**, 211–224.
326 M. L. Ferrer, L. Yuste, F. Rojo and F. del Monte, *Chem. Mater.*, 2003, **15**, 3614–3618.
327 N. Nassif, O. Bouvet, M. N. Rager, C. Roux, T. Coradin and J. Livage, *Nat. Mater.*, 2002, **1**, 42–44.
328 N. Nassif, C. Roux, T. Coradin, M. N. Rager, O. M. M. Bouvet and J. Livage, *J. Mater. Chem.*, 2003, **13**, 203–208.
329 H. K. Baca, C. Ashley, E. Carnes, D. Lopez, J. Flemming, D. Dunphy, S. Singh, Z. Chen, N. Liu, H. Fan, G. P. López, S. M. Brozik, M. Werner-Washburne and C. J. Brinker, *Science*, 2006, **313**, 337–341.
330 M. L. Ferrer, Z. Y. Garcia-Carvajal, L. Yuste, F. Rojo and F. del Monte, *Chem. Mater.*, 2006, **18**, 1458–1463.
331 H. Nguyen-Ngoc and C. Tran-Minh, *Mater. Sci. Eng., C*, 2007, **27**, 607–611.
332 T. Coradin and J. Livage, *Acc. Chem. Res.*, 2007, **40**, 819–826.
333 J. C. Rooke, A. Léonard and B.-L. Su, *J. Mater. Chem.*, 2008, **18**, 1333–1341.
334 U. Soltmann, H. Böttcher, D. Koch and G. Grathwohl, *Mater. Lett.*, 2003, **57**, 2861–2865.
335 M. Darder, P. Aranda, L. Burgos-Asperilla, A. Llobera, V. J. Cadarso, C. Fernández-Sánchez and E. Ruiz-Hitzky, unpublished results.
336 E. Courvoisier and S. Dukan, *Appl. Clay Sci.*, 2009, **44**, 67–70.
337 R. Donat and S. Aytas, *J. Radioanal. Nucl. Chem.*, 2005, **265**, 107–114.
338 H. Bağ, M. Lale and A. R. Türker, *Talanta*, 1998, **47**, 689–696.
339 S. Weiß, M. Tauber, W. Somitsch, R. Meincke, H. Müller, G. Berg and G. M. Guebitz, *Water Res.*, 2010, **44**, 1970–1980.
340 Y. Lvov, K. Ariga, I. Ichinose and T. Kunitake, *Thin Solid Films*, 1996, **284–285**, 797–801.
341 E. Ruiz-Hitzky, *J. Mater. Chem.*, 2001, **11**, 86–91.

